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Similar environments for the ClO_4^-, HSO_4^- and $H_2PO_4^-$ anions offered by strychnine self-assemblies

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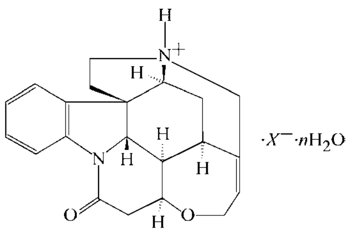
In strychninium chlorate(VII) monohydrate, $C_{21}H_{23}N_2O_2^+\cdot ClO_4^-\cdot H_2O$, strychninium hydrogensulfate(VI) dihydrate, $C_{21}H_{23}N_2O_2^+\cdot HSO_4^-\cdot 2H_2O$, and strychninium dihydrogenphosphate(V) dihydrate, $C_{21}H_{23}N_2O_2^+\cdot H_2PO_4^-\cdot 2H_2O$, the strychninium cations form bilayer sheets separated by water–anion sheets. The strychnine bilayer sheets in the three compounds are similar to one another. In all three structures, the surfaces of the cation and water–anion sheets exhibit donor–acceptor matching.

Comment

The recently described racemic resolution of alanine derivatives by strychnine (and brucine) has revealed that enantiomeric recognition of the *N*-protected alanine (Gould & Walkinshaw, 1984; Bialonska & Ciunik, 2004) is dependent on the type of alkaloid self-assembly, which is determined by the donor/acceptor properties of the resolved substrate. Co-crystallization of strychnine with chloric(VII), sulfuric(VI) or phosphoric(V) acid provides an opportunity to control, *via* the number of donor/acceptor sites, the molecular recognition.



(I) X=ClO_4, n=1
(II) X=HSO_4, n=2
(III) X=H_2PO_4, n=2

Views of the molecules of $C_{21}H_{23}N_2O_2^+\cdot ClO_4^-\cdot H_2O$, (I), $C_{21}H_{23}N_2O_2^+\cdot HSO_4^-\cdot 2H_2O$, (II), and $C_{21}H_{23}N_2O_2^+\cdot H_2PO_4^-\cdot 2H_2O$, (III), with the atom-numbering schemes, are presented in Fig. 1. The strychnine molecules in (I), (II) and (III) form [in a similar way to many other crystals (NO_3^-, SO_4^{2-}, Cl^-, Br^- and I^-; Mostad, 1985; Bokhoven *et al.*, 1951; Ghosh *et al.*, 1989;

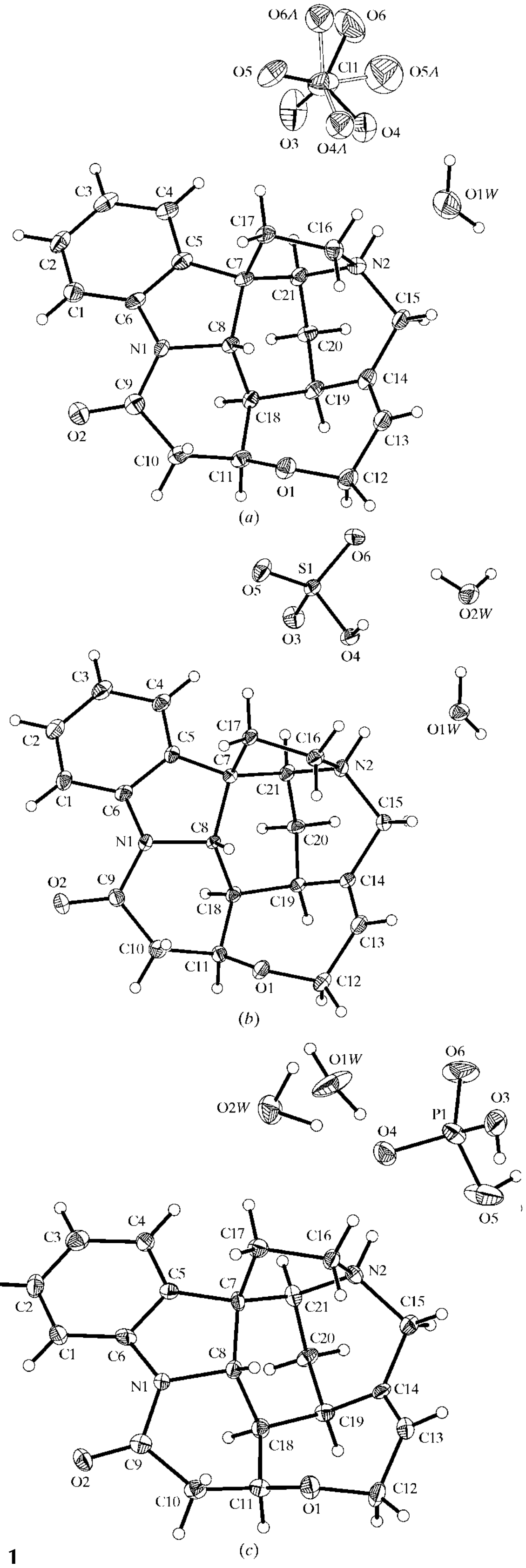


Figure 1
The independent components in (*a*) compound (I), (*b*) compound (II) and (*c*) compound (III), with the atom-numbering schemes. Displacement ellipsoids are shown at the 50% probability level. The anion in (I) is disordered over two sets of sites, with occupancies of 0.673 (7) and 0.327 (7).

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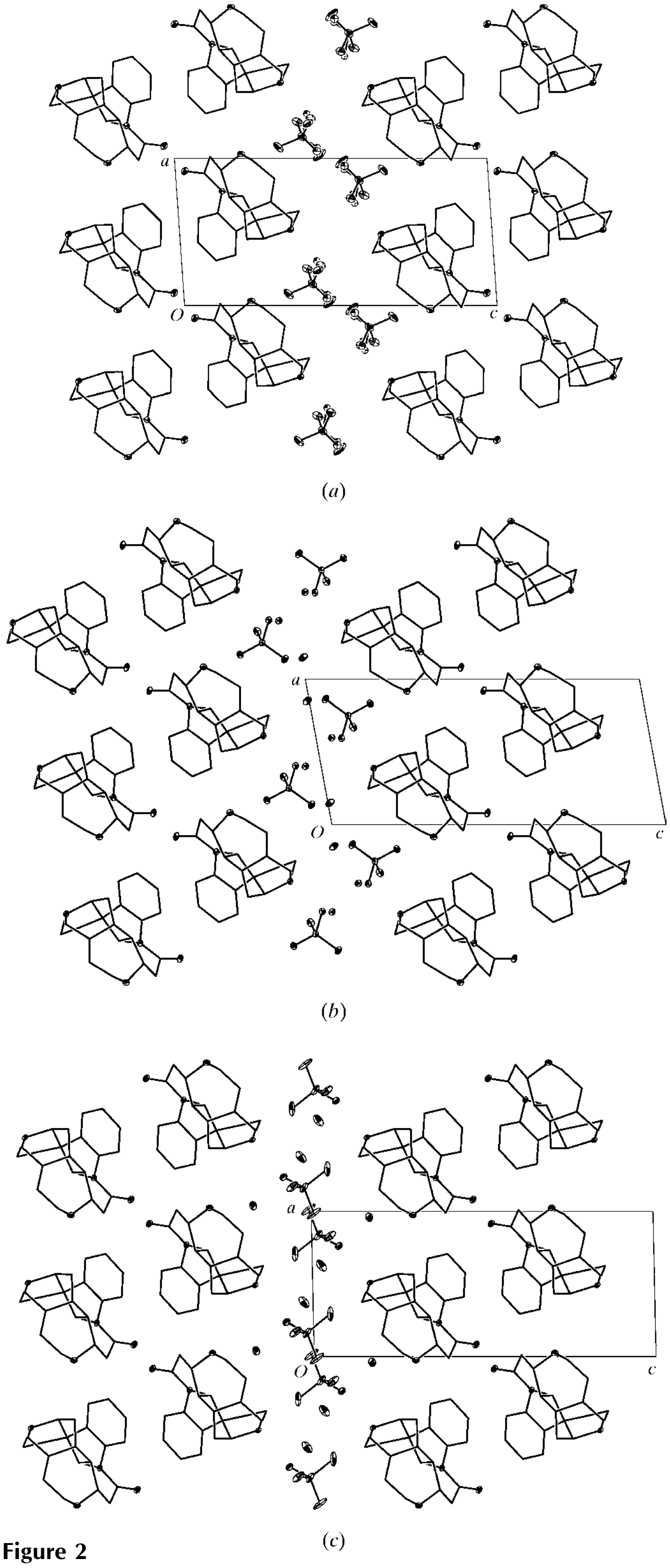

Figure 2
The molecular packing of (*a*) compound (I), (*b*) compound (II) and (*c*) compound (III), showing the similarity of the strychnine bilayers and the variety of their water/anion environments. For clarity, H atoms have been omitted.

Robertson & Beevers, 1951; Yuan *et al.*, 1994)] herring-bone bilayer sheets separated by anions and water molecules (Fig. 2). The carbonyl O atom and arene ring of the strychnine molecule are directed inwards in the bilayer sheet. This configuration, coupled with protonation of the tertiary amine N atom, enables the surface of the strychnine bilayer sheet to provide hydrogen-bond donors.

In the crystal structure of (I), the chlorate(VII) anion adopts two arrangements (in a 2:1 ratio) around the Cl1—O3 bond. Atom O3 of the anion is directed towards a flat hole at the surface of the strychnine layer (see Fig. 2*a*). As shown in Fig. 3(*a*), protonated amine atom N2 of the strychnine molecule acts as a donor in a bifurcated hydrogen bond, in which water molecule O1*W* and atom O4 (or O4*A*) of the disordered anion act as acceptors. The anion and the water molecule are also directly linked by one branch [O1*W*—H11*W*···O4 (or O5*A*)] of another bifurcated hydrogen bond; atom O6 (or O6*A*) of the anion at $(-x, y + \frac{1}{2}, -z + 1)$ is the other acceptor. The O1*W*—H12*W*···O5$(x, y+1, z)$ [or O6*A*$(x, y+1, z)$] interaction completes the hydrogen-bonded network, resulting in anion/water tapes along the [010] direction (Table 1).

In contrast, in the crystal structure of (II), two water molecules and a hydrogensulfate(VI) anion form, through symmetry operations, a hydrogen-bonded sheet. However, the chlorate(VII) anion/water tapes in (I) and the hydrogensulfate(VI) anion/water layers in (II) exhibit similar hydrogen-bonding patterns. This similarity results from (i) a similar occupancy of the holes on the surface of the strychnine sheet by the anion (see Fig. 2*b*) and (ii) the similar environment of the protonated tertiary amine atom, N2, of the strychnine molecule, which in (II) is again the donor in a bifurcated hydrogen bond to the anion and a water molecule (Fig. 3*b*). However, whereas two anions and a water molecule are connected by the bifurcated hydrogen bond in (I), the equivalent interaction in (II) involves an additional water molecule (O2*W*). The formation of the layer results from the fact that, besides participating in the N2—H22···O4 hydrogen bond, atom O4 of the hydrogensulfate(VI) anion also acts as a donor in a hydrogen bond to water molecule O1*W* at $(-x + 1, y - \frac{1}{2}, -z + 2)$ (Table 2).

The holes at the surface of the strychnine bilayer sheet in (III) are occupied by water molecules O2*W* (Fig. 2*c*), and atom N2 of the strychnine molecule acts as a donor in a hydrogen bond of which atom O4 of the dihydrogenphosphate(V) anion is the only acceptor (Fig. 3*c*). The anion/water layer that results from the hydrogen-bond network formed by the dihydrogenphosphate(V) anions and water molecules is quite different from the layers in (II). In (III), each O atom of the anion participates in short hydrogen bonds (Table 3). Atoms O3 and O5 of the anion act as hydrogen-bond donors to water molecule O1*W* and atom O6 in the adjacent anion at $(-x, y + \frac{1}{2}, -z + 2)$, respectively. Each of the two remaining O atoms (O4 and O6) acts as an acceptor of three hydrogen bonds; besides one of the above-mentioned interactions with either atom O5 or atom N2 as donor, water molecules O1*W* and O2*W*, as bridges, are the donors of the other two bonds.

In summary, the chlorate(VII), hydrogensulfate(VI) and dihydrogenphosphate(V) anions are recognized by similar strychnine self-assembled bilayers in (I), (II) and (III), respectively. However, the molecular recognition of the anions, resulting from the control of their donor/acceptor sites,

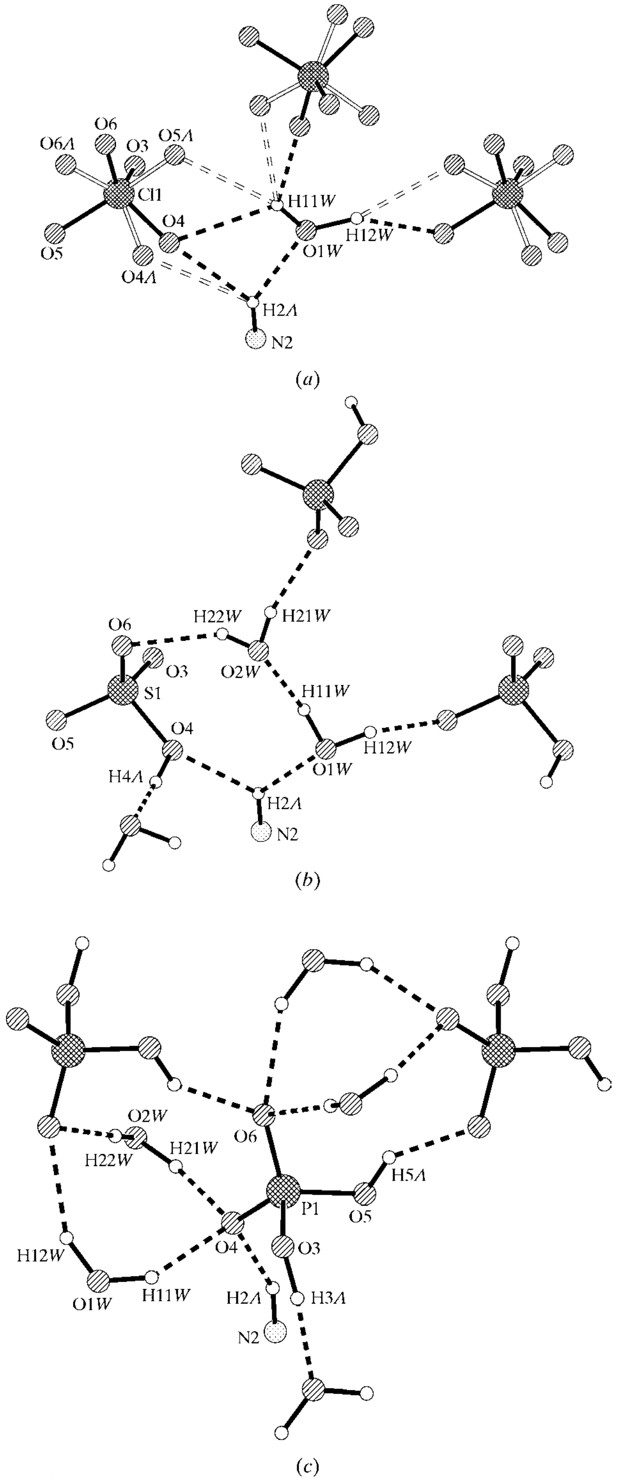

Figure 3
The hydrogen bonds of (*a*) the anion/water tape in the structure of (I), and the anion/water layers in the crystal structures of (*b*) (II) (*c*) and (III). Bonds to the two alternative positions of the anion in (I) are distinguished by solid and open dashed lines.

shows a great diversity of non-covalent interactions inside the water/anion sheet. The various hydrogen-bonding patterns in the anion/water sheet are determined by the different numbers of water molecules and especially by the different occupancy of the holes on the surface of the strychnine bilayer, by the anion in (I) and (II), and by a water molecule in (III). Furthermore, the formation of bifurcated hydrogen bonds or participation of one acceptor in several intermolecular interactions causes the surfaces of both the water/anion and the strychnine sheets to fit well in accordance with their donor/acceptor properties.

Experimental

Strychnine (POCh, Poland) and the appropriate acid were dissolved in water in a 1:1 molar ratio. Crystals of (I), (II) and (III) grew after slow evaporation of the solvent.

Compound (I)

Crystal data

$C_{21}H_{23}N_2O_2^+ \cdot ClO_4^- \cdot H_2O$
$M_r = 452.88$
Monoclinic, $P2_1$
$a = 7.8016$ (8) Å
$b = 7.6538$ (9) Å
$c = 16.5597$ (17) Å
$\beta = 93.966$ (9)°
$V = 986.44$ (18) Å^3
$Z = 2$
$D_x = 1.525$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2062 reflections
$\theta = 3.5$–29.0°
$\mu = 0.24$ mm^{-1}
$T = 100$ (2) K
Plate, colourless
0.10 × 0.10 × 0.05 mm

Data collection

Kuma KM-4 CCD diffractometer
ω scans
13 754 measured reflections
4042 independent reflections
3083 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.084$
$\theta_{\rm max} = 29.0°$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 8$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.055$
$wR(F^2) = 0.140$
$S = 1.01$
4042 reflections
293 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0818P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.91$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.87$ e Å^{-3}
Absolute structure: from known structure (Robertson & Beevers, 1951); Flack (1983), 1269 Friedel pairs
Flack parameter: 0.09 (10)

Table 1
Hydrogen-bond geometry (Å, °) for (I).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H22···O1*W*	0.93	1.95	2.758 (4)	145
N2—H22···O4	0.93	2.27	3.004 (5)	135
N2—H22···O4*A*	0.93	2.50	3.073 (10)	120
O1*W*—H11*W*···O6$^{\rm i}$	0.86	1.97	2.709 (5)	143
O1*W*—H11*W*···O6*A*$^{\rm i}$	0.86	2.43	3.238 (12)	158
O1*W*—H12*W*···O5$^{\rm ii}$	0.86	1.98	2.791 (5)	156
O1*W*—H12*W*···O6*A*$^{\rm ii}$	0.86	2.42	3.244 (12)	159

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

Compound (II)

Crystal data

$C_{21}H_{23}N_2O_2^+ \cdot HSO_4^- \cdot 2H_2O$
$M_r = 468.51$
Monoclinic, $P2_1$
$a = 7.7884$ (8) Å
$b = 7.6686$ (8) Å
$c = 17.5780$ (18) Å
$\beta = 100.388$ (7)°
$V = 1032.66$ (18) Å^3
$Z = 2$
$D_x = 1.507$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1886 reflections
$\theta = 3.5$–27.5°
$\mu = 0.21$ mm^{-1}
$T = 100$ (2) K
Needle, colourless
0.35 × 0.25 × 0.15 mm

Data collection

Kuma KM-4 CCD diffractometer
ω scans
6972 measured reflections
4009 independent reflections
3552 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.076$
$\theta_{\rm max} = 27.5°$
$h = -10 \rightarrow 9$
$k = -9 \rightarrow 9$
$l = -18 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.047$
$wR(F^2) = 0.126$
$S = 1.05$
4009 reflections
289 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0753P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.33$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.55$ e Å^{-3}
Absolute structure: from known structure (Robertson & Beevers, 1951); Flack (1983), 1493 Friedel pairs
Flack parameter: −0.14 (9)

Table 2
Hydrogen-bond geometry (Å, °) for (II).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H22⋯O4	0.93	2.17	2.900 (3)	134
N2—H22⋯O1W	0.93	2.26	3.017 (3)	138
O1W—H11W⋯O2W	0.86	1.82	2.673 (3)	170
O1W—H12W⋯O5$^{\rm ii}$	0.86	1.86	2.694 (3)	162
O2W—H21W⋯O6$^{\rm iii}$	0.86	1.89	2.749 (3)	173
O2W—H22W⋯O6	0.86	2.01	2.845 (3)	164
O4—H4A⋯O1$W^{\rm iv}$	0.84	1.71	2.551 (3)	174

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

Compound (III)

Crystal data

$C_{21}H_{23}N_2O_2^+ \cdot H_2PO_4^- \cdot 2H_2O$
$M_r = 468.43$
Monoclinic, $P2_1$
$a = 7.6407$ (12) Å
$b = 7.6624$ (9) Å
$c = 17.992$ (2) Å
$\beta = 91.203$ (12)°
$V = 1053.1$ (2) Å^3
$Z = 2$

$D_x = 1.477$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1674 reflections
$\theta = 3.5$–27.0°
$\mu = 0.18$ mm^{-1}
$T = 100$ (2) K
Plate, colourless
0.15 × 0.10 × 0.06 mm

Data collection

Kuma KM-4 CCD diffractometer
ω scans
7082 measured reflections
3353 independent reflections
2421 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.056$
$\theta_{\rm max} = 27.0°$
$h = -9 \rightarrow 9$
$k = -9 \rightarrow 8$
$l = -22 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.083$
$S = 1.00$
3353 reflections
289 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0241P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.23$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.24$ e Å^{-3}
Absolute structure: from known structure (Robertson & Beevers, 1951); Flack (1983), 909 Friedel pairs
Flack parameter: −0.05 (14)

Table 3
Hydrogen-bond geometry (Å, °) for (III).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
N2—H22⋯O4	0.93	1.75	2.648 (3)	163
O1W—H11W⋯O4	0.86	1.93	2.768 (4)	166
O1W—H12W⋯O6$^{\rm vi}$	0.86	2.09	2.919 (4)	161
O2W—H21W⋯O6$^{\rm vi}$	0.86	2.56	3.307 (4)	146
O2W—H22W⋯O4	0.86	1.94	2.797 (3)	172
O3—H3A⋯O1$W^{\rm vi}$	0.84	1.81	2.642 (4)	169
O5—H5A⋯O6$^{\rm iii}$	0.84	1.73	2.510 (4)	154

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

Atoms O4A, O5A and O6A in (I) each have an occupancy of 0.327 (7) and were refined isotropically. All H atoms were located from difference maps and then treated as riding, with C—H distances of 0.95–1.00 Å, N—H distances of 0.93 Å and O—H distances of 0.84–0.86 Å. The absolute structures of (I)–(III) were determined from the known absolute configuration of strychnine (Robertson & Beevers, 1951) and confirmed by the values of the Flack (1983) parameters.

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

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1357). Services for accessing these data are described at the back of the journal.

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