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Dibromophakellin methanol hemisolvate

Shi-Hai Xu,[a]* Xiao-Jian Liao,[a] Xiang-Chao Zeng,[a] Kai Yang,[a] Dong-Hong He[a] and Kai-Bei Yu[b]

[a]Department of Chemistry, Jinan University, Guangzhou, Guangdong, 510632, People's Republic of China, and [b]Chengdu Branch, The Chinese Academy of Sciences, Chengdu 610041, People's Republic of China

Correspondence e-mail: txush@jnu.edu.cn

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Key indicators

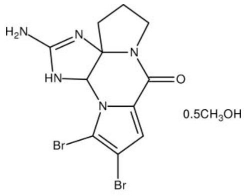
Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.012 Å
Disorder in solvent or counterion
R factor = 0.037
wR factor = 0.067
Data-to-parameter ratio = 15.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The title compound, $C_{11}H_{11}Br_2N_5O\cdot0.5CH_3OH$, was isolated from algae (*Laurencia majuscula Lucas*) collected from the South China Sea and its crystal structure was determined. It exhibits mild antibacterial and antineoplastic activity. The crystal structure has supramolecular layers with N—H···O and N—H···N hydrogen bonds. The methanol solvent molecule is threefold disordered.

Comment

Dibromophakellin (m.p. 515 K), (I), a brominated pyrrole alkaloid, was first isolated by Sharma & Burkholder (1971) from the marine Phakellia flabellate off the coast of the Great Barrier Reef in Australia. It has also been prepared by a biomimetic synthesis (Foley & Büchi, 1982). Its structure has been confirmed by X-ray analysis of its acetate (Fedoreyev *et al.*, 1986). Despite the presence of both aminoacetal and diaminoketal functionalities dibromophakellin exhibits considerable stability toward hydrolytic reagents.



(I)

X-ray diffraction analysis reveals that the title compound, (I), as its methanol hemisolvate, has a compact tetracyclic core that includes a pyrrole and a guanidine unit in a five-membered ring. There are two essentially identical molecules in the asymmetric unit, together with a molecule of methanol disordered over three orientations. Supramolecular layers are stabilized by N—H···O and N—H···N hydrogen bonds (Table 1 and Fig. 2).

Experimental

The chopped algae were extracted with ethanol at room temperature. The extract was subjected to silica-gel column chromatography, eluting with petroleum ether containing an increasing amount of ethyl acetate and then chloroform containing an increasing amount of methanol. The fraction eluted with chloroform–methanol (3:97) gave the title compound after evaporation of the solvent.

Crystal data

$C_{11}H_{11}Br_2N_5O\cdot0.5CH_4O$
M_r = 405.09
Monoclinic, $P2_1$
a = 7.646 (1) Å
b = 28.050 (6) Å
c = 7.670 (1) Å
β = 118.65 (1)°
V = 1443.5 (5) Å^3
Z = 4
D_x = 1.864 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 38 reflections
θ = 3.0–15.3°
μ = 5.62 mm^{-1}
T = 296 (2) K
Irregular, colourless
0.48 × 0.30 × 0.22 mm

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: multi-scan (*SHELXTL*; Siemens, 1994)
$T_{\min} = 0.104$, $T_{\max} = 0.290$
6923 measured reflections
5939 independent reflections
3078 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.037$
$\theta_{\max} = 26.5°$
$h = -9 \rightarrow 9$
$k = -35 \rightarrow 35$
$l = -9 \rightarrow 8$
3 standard reflections every 97 reflections intensity decay: 7.6%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.037$
$wR(F^2) = 0.067$
$S = 0.80$
5939 reflections
393 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.023P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.29$ e Å^{-3}
$\Delta\rho_{\min} = -0.43$ e Å^{-3}
Absolute structure: Flack (1983); 2877 Friedel pairs
Flack parameter = 0.000 (11)

Table 1
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N3—H3N$\cdots$O1$^{\rm i}$	0.856 (10)	2.14 (3)	2.921 (7)	151 (4)
N5—H5*B*N$\cdots$O1$^{\rm i}$	0.86	2.36	3.096 (7)	143
N5—H5*A*N$\cdots$N4$'^{\rm ii}$	0.86	2.13	2.981 (8)	171
N3′—H3N′$\cdots$O1$'^{\rm iii}$	0.855 (10)	2.13 (3)	2.833 (7)	139 (5)
N5′—H5′*D*$\cdots$O1$'^{\rm iii}$	0.86	2.34	3.062 (7)	142
N5′—H5′*C*$\cdots$N4$^{\rm iv}$	0.86	2.12	2.961 (7)	167

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

The methanol solvent molecule is disordered over three orientations on approximately the same site. These orientations were refined with a C—O bond-length restraint of 1.480 (4) Å and riding H atoms (C—H = 0.96 Å and O—H = 0.82 Å). In the molecule of dibromophakellin, H atoms were positioned geometrically and refined as riding, with C—H = 0.93–0.98 Å and N—H = 0.86 Å, except that the H atoms attached to ring N atoms were refined freely. For all constrained H atoms, $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(parent atom).

Data collection: *XSCANS* (Siemens, 1994); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1994); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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References

Fedoreyev, S. A., Utkina, N. K., Ilyin, S. G., Reshetnyak, M. V. & Maximov, O. B. (1986). *Tetrahedron Lett.* **27**, 3177–3180.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Foley, L. H. & Büchi, G. (1982). *J. Am. Chem. Soc.* **104**, 1776–1777.

Sharma, G. M. & Burkholder, P. R. (1971). *J. Chem. Soc. C*, pp. 151–152.

Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.

Siemens (1994). *XSCANS* and *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

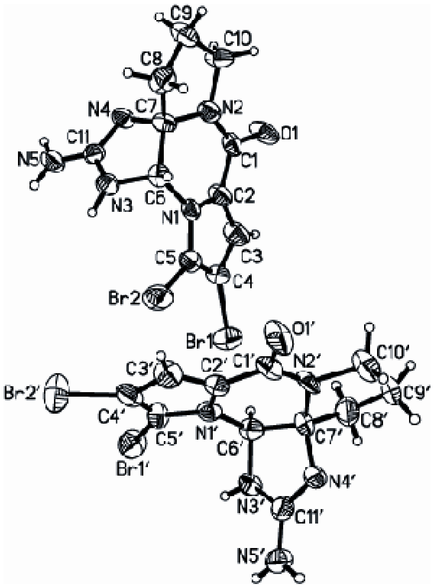

Figure 1
The two molecules in the asymmetric unit of the title compound, shown with 50% probability ellipsoids. The disordered solvent molecule is not shown.

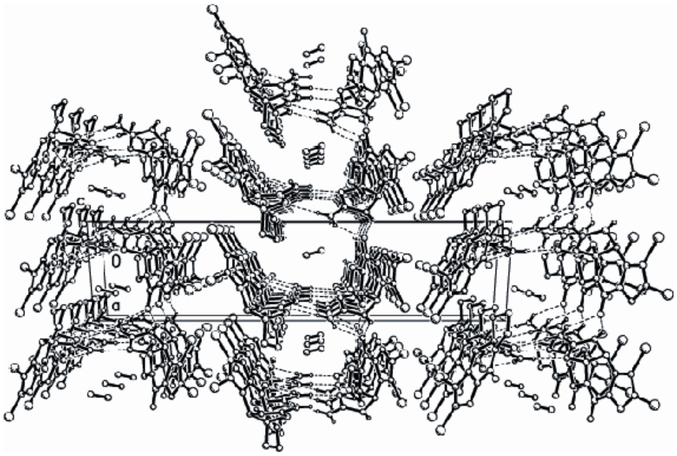

Figure 2
The packing of the title compound, with hydrogen bonds shown as dashed lines. H atoms of the disordered solvent molecule have been omitted, and only one methanol orientation is shown on each site.

Acta Cryst. (2004). E**60**, o782–o783 Xu *et al.* • $C_{11}H_{11}Br_2N_5O\cdot0.5CH_4O$ **o783**