Cohen, M. D., Schmidt, G. M. J. & Flavian, S. (1964). *J. Chem. Soc.* pp. 2041–2051.
Elerman, Y., Elmali, A., Atakol, O. & Svoboda, I. (1995). *Acta Cryst.* C**51**, 2344–2346.
Elerman, Y., Elmali, A., Kabak, M., Aydin, M. & Peder, M. (1994). *J. Chem. Cryst.* **24**, 603–606.
Elerman, Y., Elmali, A., Kendi, E., Özbey, S. & Ertüzün, V. (1997). *Acta Cryst.* C**53**, 1158–1160.
Elerman, Y., Kabak, M., Elmali, A. & Svoboda, I. (1998). *Acta Cryst.* C**54**, 128–130.
Elerman, Y., Paulus, H., Svoboda, I. & Fuess, H. (1992). *Z. Kristallogr.* **198**, 135–136.
Elerman, Y., Svoboda, I. & Fuess, H. (1991). *Z. Kristallogr.* **196**, 309–311.
Elmali, A. & Elerman, Y. (1997). *Acta Cryst.* C**53**, 791–793.
Elmali, A. & Elerman, Y. (1998). *J. Mol. Struct.* **442**, 31–37.
Elmali, A., Elerman, Y. & Zeyrek, C. T. (1998). *J. Mol. Struct.* **443**, 123–130.
Elmali, A., Özbey, S., Kendi, E., Kabak, M. & Elerman, Y. (1995). *Acta Cryst.* C**51**, 1878–1880.
Enraf–Nonius (1994). *CAD-4 EXPRESS*. Version 5.1/1.2. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Frenz, B. A. (1985). *Enraf–Nonius SDP-Plus Structure Determination Package*. Version 3.0. Enraf–Nonius, Delft, The Netherlands.
Garnovskii, A. D., Nivorozhkin, A. L. & Minkin, V. I. (1993). *Coord. Chem. Rev.* **126**, 1–69.
Gavranić, M., Kaitner, B. & Meštrović, E. (1996). *J. Chem. Cryst.* **26**, 23–28, and references therein.
Hadjoudis, E., Vitterakis, M. & Moustakali-Mavridis, I. (1987). *Tetrahedron*, **43**, 1345–1360.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kaitner, B. & Pavlović, G. (1996). *Acta Cryst.* C**52**, 2573–2575.
Kevran, S., Elmali, A. & Elerman, Y. (1996). *Acta Cryst.* C**52**, 3256–3258.
Moustakali, I., Moustakali-Mavridis, I. & Hadjoudis, E. (1978). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1998). C**54**, 1139–1141

3α-Bikhaconine Acetone Solvate

MASOOD PARVEZ,[a] WASEEM GUL[a] AND SAEED ANWAR[b]

[a]*Department of Chemistry, The University of Calgary, 2500 University Drive NW, Calgary, Alberta, Canada T2N 1N4, and* [b]*Department of Chemistry, Gomal University, Dera Ismail Khan, NWFP, Pakistan. E-mail: parvez@acs.ucalgary.ca*

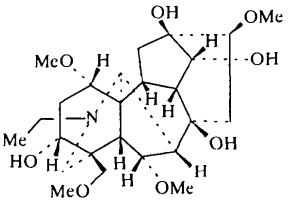
(Received 13 January 1998; accepted 11 February 1998)

Abstract

The crystal structure of 3α-bikhaconine acetone solvate [1α,6α,16β-trimethoxy-4β-(methoxymethyl)aconitane-3α,8β,13β,14α-tetrol acetone solvate, $C_{25}H_{41}NO_8.C_3H_6O$], a C_{19} norditerpenoid alkaloid which has been partially synthesized from indaconitine, contains discrete molecules separated by normal van der Waals distances. The molecular dimensions are normal; the mean bond distances are C_{sp^3}—N 1.471 (9), C_{sp^3}—C_{sp^3} 1.54 (2) and C_{sp^3}—O 1.425 (14) Å. The fused-ring system contains two chair, one half-chair, two envelope and one boat conformation. There are both inter- and intramolecular hydrogen bonds, with O···O separations in the range 2.655 (3)–3.048 (3) Å and H···O interactions in the range 1.92–2.38 Å. There are no interactions between the alkaloid and the solvate molecules.

Comment

Continuing our crystallographic studies of C_{19} norditerpenoid alkaloids (Parvez, Gul, Anwar *et al.*, 1998; Parvez, Gul & Anwar, 1998*a*,*b*), we now report the crystal structure of 3α-bikhaconine, (1), as its acetone solvate. The alkaloid was originally isolated from the roots of *Aconitum chasmanthum* Stapf ex Holmes of Pakistani origin, but its quantity was insufficient to grow crystals for X-ray diffraction studies. It was subsequently synthesized from indaconitine, which was isolated from the same plant.



(1)

The crystal structure contains independent molecules of 3α-bikhaconine (Fig. 1) and acetone solvate separated by normal van der Waals distances. The absolute structure could not be established in this analysis and the absolute structure reported in this article is the same as that known for chasmanine 14α-benzoate hydrochloride (De Camp & Pelletier, 1977). The molecular dimensions in (1) are normal and lie within expected values for the corresponding bond distances and angles, with mean bond distances C_{sp^3}—N 1.471 (9), C_{sp^3}—C_{sp^3} 1.54 (2) and C_{sp^3}—O 1.425 (14) Å.

The six-membered rings *A* (C1–C5, C11) and *E* (C4, C5, C11, C17, N1, C19) adopt chair conformations. Ring *A* is slightly flattened at C1 due to the methoxy substituent attached to C1, as observed in the structures of a chasmanine intermediate (Przybylska & Ahmed, 1980), aconitine (Codding, 1982), chasmaconitine methanol solvate (Parvez, Gul, Anwar *et al.*, 1998) and chasmanthinine (Parvez, Gul & Anwar, 1998*a*). Ring *E* is also slightly flattened at C19 due to the presence of an ethyl-substituted N atom in the ring. The six-membered ring *D* (C8, C9, C13–C16) has a half-

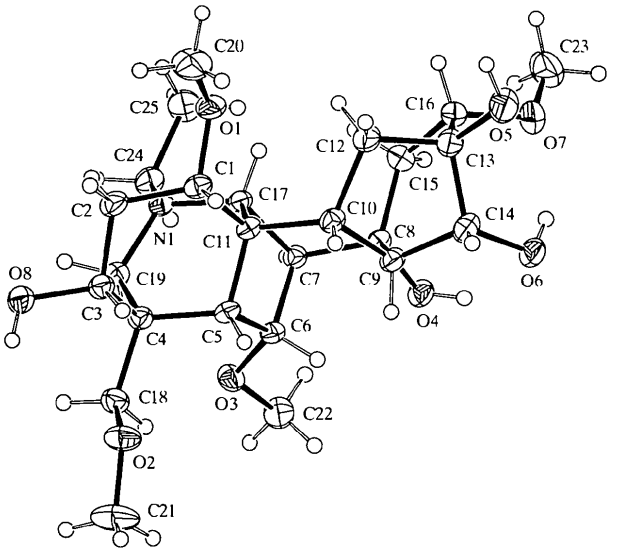


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (1) with the atomic numbering scheme. Displacement ellipsoids are plotted at the 30% probability level and H atoms have been assigned arbitrary radii.

chair conformation, with C14 0.781 (3) Å out of the plane of the remaining ring atoms. The seven-membered ring *B* (C5–C11) adopts a boat conformation. The five-membered rings *C* (C9, C10, C12–C14) and *F* (C5–C7, C11, C17) display C14- and C17-envelope conformations, respectively. The C14 atom is 0.692 (4) Å out of the plane of the remaining four atoms of ring *C*, which are almost planar [maximum deviation 0.078 (2) Å]. The C17 atom is 0.781 (3) Å out of the plane formed by the rest of the atoms of ring *F*.

A network of hydrogen bonds comprised of intra- and intermolecular interactions provides stability to the crystal lattice; details of the hydrogen-bonding geometry are given in Table 1.

Experimental

3α-Bikhaconine was isolated from a methanolic extract of the roots of *Aconitum chasmanthum*, using 200–300 mesh alumina and silica gel for column chromatography, and silica gel GF_{254} as adsorbent for PTLC, employing *n*-hexane/chloroform/diethylamine as the solvent system for column chromatography and chloroform/methanol/ammonia as the solvent system for PTLC. The alkaloid was characterized by ^1H and ^{13}C NMR spectroscopy. The title compound was partially synthesized from indaconitine, which was also isolated from the roots of *Aconitum chasmanthum*. Indaconitine (50 mg) in ethanol (10.0 ml) was mixed with 10% NaOH (2.0 ml) and the mixture was kept at room temperature for 3 d, extracted with chloroform and subjected to vacuum rotavapourization. The product was identical (PTLC) to 3α-bikhaconine isolated from the same plant and was confirmed by spectroscopic techniques. Crystals of X-ray quality were grown from acetone at room temperature.

Crystal data

$C_{25}H_{41}NO_8.C_3H_6O$	Cu $K\alpha$ radiation
M_r = 541.67	λ = 1.54178 Å
Orthorhombic	Cell parameters from 25 reflections
$P2_12_12_1$	θ = 20–30°
a = 11.8320 (10) Å	μ = 0.779 mm^{-1}
b = 14.216 (2) Å	T = 293 (1) K
c = 16.649 (3) Å	Prismatic
V = 2800.4 (7) $Å^3$	0.47 × 0.42 × 0.31 mm
Z = 4	Pale
D_x = 1.285 Mg m^{-3}	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer	R_{int} = 0.033
$\omega/2\theta$ scans	θ_{max} = 68.0°
Absorption correction: none	$h = 0 \rightarrow 14$
5424 measured reflections	$k = 0 \rightarrow 17$
5004 independent reflections	$l = -17 \rightarrow 20$
4806 reflections with $I > 2\sigma(I)$	3 standard reflections every 200 reflections
	intensity decay: none

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max}$ = 0.001
$R[F^2 > 2\sigma(F^2)]$ = 0.057	$\Delta\rho_{max}$ = 0.288 e $Å^{-3}$
$wR(F^2)$ = 0.149	$\Delta\rho_{min}$ = −0.267 e $Å^{-3}$
S = 1.064	Extinction correction: none
5004 reflections	Scattering factors from *International Tables for Crystallography* (Vol. C)
348 parameters	
H atoms riding	Absolute structure: Flack (1983)
$w = 1/[\sigma^2(F_o^2) + (0.106P)^2 + 0.619P]$ where $P = (F_o^2 + 2F_c^2)/3$	Flack parameter = 0.2 (2)

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

D—H···A	H···A	D···A	D—H···A
O4—H4···O6	2.33	2.969 (3)	136
O6—H6···O7	1.92	2.655 (3)	149
O4—H4···O2^i	2.38	3.048 (3)	140
O5—H5···O8^{ii}	1.97	2.760 (3)	162
O8—H8···O6^{iii}	2.06	2.863 (3)	164

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

Based on the systematic absences, the space group was uniquely determined to be $P2_12_12_1$ (No. 19). Friedel pairs were collected and were not merged. The H atoms were included at geometrically idealized positions with distances C—H 0.95 and O—H 0.82 Å.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1994). Program(s) used to solve structure: *SAPI*91 (Fan, 1991). Program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997). Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *SHELXL*97.

The authors thank Professor M. H. Benn, Chemistry Department, University of Calgary, Canada, for laboratory space, supervision in the isolation and partial syntheses of alkaloids and financial assistance (to WG),

Professor Shafiq-ur-Rehman, Taxonomist, Department of Botany, University of Azad Jammu and Kashmir, Pakistan, for help in plant collection and identification, and the University of Calgary for financial support.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1439). Services for accessing these data are described at the back of the journal.

References

Codding, P. W. (1982). *Acta Cryst.* B**38**, 2519–2522.
De Camp, W. H. & Pelletier, S. W. (1977). *Acta Cryst.* B**33**, 722–727.
Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Fan, H.-F. (1991). *SAPI91. Structure Analysis Program with Intelligent Control*. Rigaku Corporation, Tokyo, Japan.
Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Molecular Structure Corporation (1994). *TEXSAN. Single Crystal Structure Analysis Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
Parvez, M., Gul, W. & Anwar, S. (1998*a*). *Acta Cryst.* C**54**, 125–126.
Parvez, M., Gul, W. & Anwar, S. (1998*b*). *Acta Cryst.* C**54**, 790–792.
Parvez, M., Gul, W., Anwar, S., Miana, G. A., Atta-ur-Rahman & Choudhary, M. I. (1998). *Acta Cryst.* C**54**, 236–238.
Przybylska, M. & Ahmed, F. R. (1980). *Acta Cryst.* B**36**, 494–497.
Sheldrick, G. M. (1997). *SHELXL97. Program for the Refinement of Crystal Structures*. University of Göttingen, Germany.

Acta Cryst. (1998). C**54**, 1141–1143

(1′*S*,5′*S*,6′*R*,8′*S*)-1-[(6′-Acetoxy-8′-hydroxy-2′-oxabicyclo[3.2.1]oct-5′-yl)oxymethyl]-N^4-benzoylcytosine†

CARL EPPLE,[a] CHRISTIAN LEUMANN[a] AND HELEN STOECKLI-EVANS[b]

[a]*Department für Chemie und Biochemie, Universität Bern, Freiestrasse 3, CH-3012 Bern, Switzerland, and* [b]*Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland. E-mail: helen.stoeckli-evans@ich.unine.ch*

(*Received 13 January 1998; accepted 29 January 1998*)

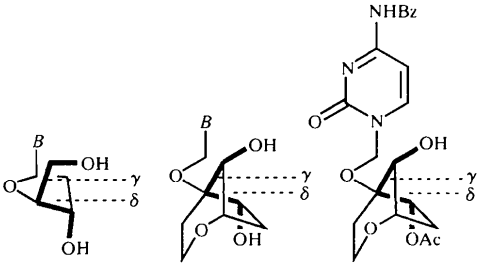
Abstract

The structure of the title compound, $C_{21}H_{23}N_3O_7$, has been determined at 193 K. The equivalent DNA-backbone torsion angles δ (O6′—C6′—C5′—C8′) and γ (C6′—C5′—C8′—O8′) are 157.3 (4) and 67.5 (5)°, respectively. An intramolecular hydrogen bond involving the hydroxy O8′ and carbonyl O2 atoms helps fix the molecule in an extended arrangement with the torsion angle between the bicyclo and pyrimidinyl moieties (C5′—O1—C1—N1) being 159.9 (4)°.

† Systematic name: (1*S*,5*S*,6*R*,8*S*)-5-[(4-benzamido-1,2-dihydro-2-oxopyrimidin-1-yl)methyloxy]-8-hydroxy-2-oxabicyclo[3.2.1]oct-6-yl acetate.

Comment

In our research programme on the synthesis and evaluation of the pairing properties of nucleic acid analogues, we became interested in oligonucleotides built from the bicyclo[3.2.1] nucleoside (1). In this class of nucleoside analogues, the natural deoxyribofuranose unit is replaced by a synthetic bicyclic sugar surrogate to which the nucleobases are attached *via* a flexible linker. Extrapolated to the oligomeric level, these structural changes bring about a locked conformation around the DNA-backbone torsion angles δ and γ in a geometry which conforms with that observed in DNA duplexes of the *B* type, while at the same time the structural preorganization imposed by the (cyclic) furanose unit in natural DNA is missing. In order to have access to precise geometrical data associated with the torsion angles δ and γ, as well as with the flexible base-linker unit of this class of nucleoside analogues, we synthesized (2) and studied its crystal structure.



Deoxyribonucleosides (1) (2)

The DNA-backbone torsion angles of interest are δ [O6′—C6′—C5′—C8′ 157.3 (4)°] and γ [C6′—C5′—C8′—O8′ 67.5 (5)°]. They compare well with the respective torsion angles found for natural DNA duplexes of the *B* type, with values of δ 122±30° and γ 57±10° (Saenger, 1984). The planes of the aromatic rings of the benzoyl protecting group and the cytosine core unit are slightly twisted at the C7—C8 bond [torsion angle C9—C8—C7—N4 is −16.1 (7)°]. The molecule is folded about the O1—C1 bond with a torsion angle C5′—O1—C1—N1 of 159.9 (4)°. An intramolecular hydrogen bond involving the hydroxy O8′ and carbonyl O2 atoms helps fix the molecule in an extended arrangement (see Table 1). The bond distances and angles in the molecule are normal within experimental error. The absolute configuration of the molecule was assigned with