

Table 2. Selected geometric parameters (Å, °) for (3)

O1—C6	1.365 (5)	C5—C7	1.377 (5)
O1—C2	1.443 (5)	C5—C6	1.472 (5)
C2—O3	1.435 (4)	C6—O6	1.207 (5)
O3—C4	1.355 (4)	C7—C8	1.473 (5)
C4—O4	1.223 (4)	C7—S1	1.744 (4)
C4—C5	1.472 (5)	S1—C12	1.817 (5)
C7—C5—C4	123.4 (3)	C5—C7—S1	121.2 (3)
C7—C5—C6	120.8 (3)	C8—C7—S1	116.8 (2)
C4—C5—C6	115.6 (3)	C7—S1—C12	104.1 (2)
C5—C7—C8	122.0 (3)		

The thienyl ring in (3) exhibits twofold rotational disorder about the C7—C8 axis and the two components were restrained during refinement to be geometrically similar. The relative occupancy was refined to 0.681 (5) for the major component. The S atoms in both components were refined with anisotropic displacement parameters; the higher-occupancy C atoms were modelled with independent isotropic displacement parameters, while a common isotropic displacement parameter was refined for the remainder.

For both compounds, data collection: *DIF4* (Stoe & Cie, 1990a); cell refinement: *DIF4*; data reduction: *REDU4* (Stoe & Cie, 1990b). Program(s) used to solve structures: *SIR92* (Altomare *et al.*, 1994) for (2); *SHELXTL* (Sheldrick, 1994) for (3). Program(s) used to refine structures: *CRYSTALS* (Watkin *et al.*, 1996) for (2); *SHELXL96* (Sheldrick, 1996) for (3). For both compounds, molecular graphics: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1192). Services for accessing these data are described at the back of the journal.

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Chasmaconitine 0.5-Methanol Solvate†

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Abstract

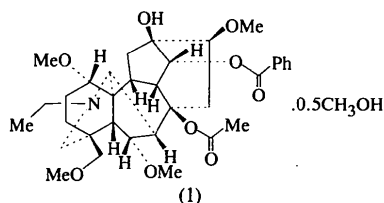
The crystal structure of chasmaconitine hemimethanol solvate, C₃₄H₄₇NO₉·0.5CH₄O, a C₁₉ norditerpenoid alkaloid, isolated from the roots of *Aconitum chasmanthum* Stapf ex Holmes of Pakistani origin, contains discrete molecules separated by normal van der Waals distances. The fused-ring system contains one boat, one half-chair, two envelope and two chair conformations. The molecular dimensions are normal with no interactions between the alkaloid and the disordered solvate molecules; the mean bond distances are C_{sp³}—N 1.467 (14), C_{sp³}—C_{sp³} 1.54 (2), C_{sp³}—O 1.42 (2), C_{sp²}—O 1.337 (5) and C=O 1.197 (5) Å.

Comment

Aconitum chasmanthum Stapf ex Holmes is a small herbaceous shrub which grows wild in Kashmir, Hattian and Rescuta Top. It contains a large number of norditerpenoid alkaloids, e.g. chasmaconitine and chasmanthine (Achmatowicz & Marion, 1964), homochasmanine (Achmatowicz & Marion, 1965), indaconitine (Miana *et al.*, 1971) and chasmanine (Pelletier *et al.*, 1984). The pharmacological properties of the diterpenoid alkaloids which include the control and induction of cardiac arrhythmia, effects on smooth and skeletal muscles, central nervous activity and analgesia, have been reviewed (Benn & Jacyno, 1983; Pelletier & Page, 1986; Amiya

† Alternative name: (1 α ,6 α ,14 α ,16 β)-20-ethyl-13-hydroxy-1.6.16-trimethoxy-4-(methoxyethyl)aconitane-8,14-diyl 8-acetate 14-benzoate 0.5-methanol solvate.

& Bando, 1988). We have determined the molecular structure of chasmaconitine unequivocally by the X-ray crystallographic method and report the crystal structure of its hemimethanol solvate, (1), in this article.



The crystal structure of the title compound contains discrete molecules of chasmaconitine and half a molecule of disordered methanol solvate per asymmetric unit. The absolute configuration (Fig. 1) was not determined in this X-ray analysis but was chosen to be the same as that known for chasmanine 14- α -benzoate hydrochloride (De Camp & Pelletier, 1977). The molecular dimensions in (1) are normal and lie within expected values for the corresponding bond distances and bond angles with mean bond distances $C_{sp^3}-N$ 1.467 (14), $C_{sp^3}-C_{sp^3}$ 1.54 (2), $C_{sp^3}-O$ 1.42 (2), $C_{sp^2}-O$ 1.337 (5), and $C=O$ 1.197 Å, while the $C_{sp^3}-C_{sp^2}$ and $C_{sp^2}-C_{sp^2}$ distances are 1.504 (6) and 1.475 (4) Å, respectively.

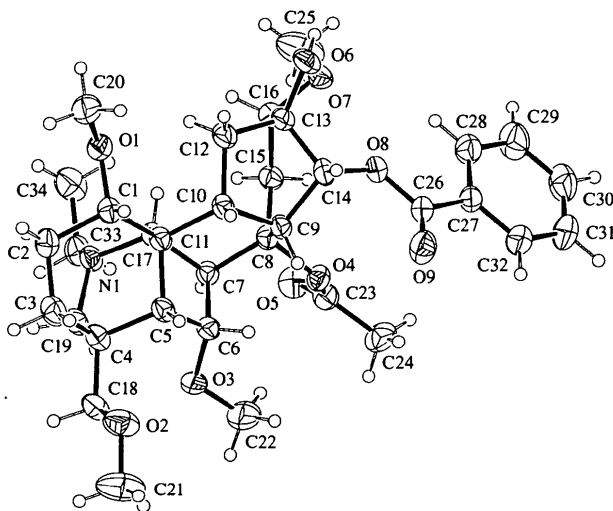


Fig. 1. ORTEPII (Johnson, 1976) drawing of (1) with the atomic numbering scheme. Displacement ellipsoids are plotted at the 30% probability level and H atoms are drawn as small circles of arbitrary radii. One of the disordered methyl sites, C22A, has been omitted.

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) and aconitine (Coddington, 1982). 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-chair conformation, with the C14 atom 0.898 (4) 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 0.708 (5) Å out of the plane of the remaining four atoms of the ring which are essentially planar; maximum deviation 0.022 (2) Å. The C17 atom is 0.734 (4) Å out of the plane formed by the remaining atoms of ring F. The benzoate moiety attached to C14 is almost planar, with O8 lying 0.173 (7) Å below and O9 0.087 (7) Å above the plane of the constrained phenyl ring. There are no short intermolecular interactions involving chasmaconitine and the methanol solvate. However, there is a short intramolecular O—H...O hydrogen bond between the hydroxyl group and carbonyl O7 atom [O6...O7 2.580 (4) Å], resulting in a five-membered ring with dimensions O6—H...O7 116° and H...O7 2.02 Å. A diagram of the molecular packing of the title compound has been deposited.

The crystal structures of an intermediate of chasmanine (Przybylska & Ahmed, 1980), aconitine (Coddington, 1982) and delphinifoline (Kerr & Coddington, 1982), which bear the basic skeleton of (1), have been reported previously.

Experimental

Chasmaconitine was isolated from the roots of *A. chasmanthum* using 200–300 mesh alumina and silica gel for column chromatography and silica gel GF₂₅₄ as adsorbent for TLC using *n*-hexane–chloroform–diethylamine as the solvent system. The pure compound was recrystallized from methanol at room temperature by slow evaporation.

Crystal data

$C_{34}H_{47}NO_9 \cdot 0.5CH_4O$
 $M_r = 629.77$
 Monoclinic
 C2
 $a = 31.919 (5) \text{ \AA}$
 $b = 9.399 (2) \text{ \AA}$
 $c = 11.260 (3) \text{ \AA}$
 $\beta = 93.83 (1)^\circ$
 $V = 3370.5 (13) \text{ \AA}^3$
 $Z = 4$
 $D_x = 1.241 \text{ Mg m}^{-3}$
 D_m not measured

Cu $K\alpha$ radiation
 $\lambda = 1.54178 \text{ \AA}$
 Cell parameters from 25 reflections
 $\theta = 20\text{--}30^\circ$
 $\mu = 0.735 \text{ mm}^{-1}$
 $T = 293 (1) \text{ K}$
 Prismatic
 $0.42 \times 0.25 \times 0.20 \text{ mm}$
 Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: none

$\theta_{\max} = 68.0^\circ$
 $h = 0 \rightarrow 38$
 $k = -10 \rightarrow 10$
 $l = -12 \rightarrow 13$

5206 measured reflections
5164 independent reflections
4646 reflections with
 $I > 2\sigma(I)$
 $R_{\text{int}} = 0.020$

3 standard reflections
every 200 reflections
frequency: 120 min
intensity decay: none

Refinement

Refinement on F^2
 $R(F) = 0.058$
 $wR(F^2) = 0.157$
 $S = 1.054$
5133 reflections
422 parameters
H atoms riding
 $w = 1/[\sigma^2(F_o^2) + (0.115P)^2 + 1.50P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.003$
 $\Delta\rho_{\text{max}} = 0.445 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.222 \text{ e } \text{Å}^{-3}$
Extinction correction: none
Scattering factors from
*International Tables for
Crystallography* (Vol. C)
Absolute structure: Flack
(1983)
Flack parameter = $-0.1(3)$

Based on the systematic absences of hkl , $h + k = 2n + 1$, packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be C2 (No. 5). Friedel pairs (2467) were collected to a θ_{max} of 60° and were not merged. A methoxymethyl group attached to C6 was disordered and its atoms were allowed to refine over two locations, C22 and C22A, with site-occupancy factors of 0.50. The phenyl ring was refined as a regular hexagon. The H atoms were included at geometrically idealized positions with C—H and O—H distances of 0.95 Å. A half molecule of methanol solvate per asymmetric unit was found close to a twofold axis and was disordered; its H atoms were ignored. The non-H atoms of chasmaconitine were given anisotropic displacement parameters, while the methanol C and O atoms were given isotropic displacement parameters.

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: *SAP191* (Fan, 1991). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976) in *TEXSAN*. Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1327). Services for accessing these data are described at the back of the journal. A packing diagram has also been deposited.

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Citraconic Acid

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Abstract

Molecules of the title compound, C₅H₆O₄, form extended tapes via O—H···O interactions. The tapes assemble via C—H···O interactions giving rise to planar sheets.

Comment

Carboxylic acids have been used successfully in the supramolecular design of organic crystalline solids (Pedireddi *et al.*, 1996; Zhao *et al.*, 1990). Their potential to form strong and predictable hydrogen-bonded motifs is particularly useful. Leiserowitz (1976) reported that carboxylic acids predominantly interact via a centrosymmetric cyclic motif.

Molecules of the title compound, (I), assemble via two crystallographically distinct cyclic hydrogen-bond motifs [O1···O2 2.609(3) Å and O1···H2O—O2(1-x, 1-y, 1-z) 175(2)^o; O3···O4 2.714(3) Å and O3···H4O—O4(-x, 1-y, -z) 175(1)^o] giving rise to an extended molecular tape. The C—O bond lengths for the O1—C1—O2 carboxyl group [C=O 1.260(3) and C—O 1.270(3) Å] lie outside the expected ranges