Monoclinic
$P2_1/n$
$a = 11.667\,(3)$ Å
$b = 7.292\,(2)$ Å
$c = 15.275\,(3)$ Å
$\beta = 97.02\,(2)°$
$V = 1289.8\,(5)$ Å^3
$Z = 4$
$D_x = 1.299$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 18–25°$
$\mu = 0.094$ mm^{-1}
$T = 200\,(1)$ K
Block, cut from a large needle
0.45 × 0.38 × 0.30 mm
Colorless

Data collection

Rigaku AFC-6*S* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
2395 measured reflections
2279 independent reflections
1662 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.046$
$\theta_{\rm max} = 25.0°$
$h = 0 \rightarrow 13$
$k = 0 \rightarrow 8$
$l = -18 \rightarrow 18$
3 standard reflections every 200 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.037$
$wR(F^2) = 0.107$
$S = 1.171$
2273 reflections
165 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 0.65P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.222$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.235$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

H atoms were included at geometrically idealized positions, with a C—H distance of 0.95 Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control 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*93 (Sheldrick, 1993). Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1408). Services for accessing these data are described at the back of the journal.

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14-*O*-Benzoyl-8-ethoxybikhaconine and 14-*O*-Benzoyl-8-methoxybikhaconine

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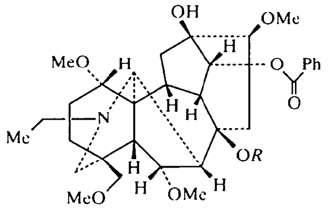
Abstract

The molecular structures of two new C_{19} norditerpenoid alkaloids, 14-*O*-benzoyl-8-methoxybikhaconine [(1α,6α,14α,16β)-20-ethyl-13-hydroxy-1,6,8,16-tetramethoxy-4-methoxymethylaconitan-14-yl benzoate, $C_{33}H_{47}NO_8$, (1)] and 14-*O*-benzoyl-8-ethoxybikhaconine [(1α,6α,14α,16β)-8-ethoxy-20-ethyl-13-hydroxy-1,6,16-trimethoxy-4-methoxymethylaconitan-14-yl benzoate, $C_{34}H_{49}NO_8$, (2)], isolated for the first time from the roots of *Aconitum chasmanthum* Stapf ex Holmes of Pakistani origin, have been determined. The two alkaloids differ by one CH_2 moiety in a side chain (8-methoxy *versus* 8-ethoxy), co-crystallize in a 65 (2):35 (2) ratio, *i.e.* $0.65C_{33}H_{47}NO_8.0.35C_{34}H_{49}NO_8$, and are inseparable by thin-layer and column chromatography. The conformations of the rings in the two alkaloids are: *A* and *E*, chairs; *D*, half-chair; *C* and *F*, envelopes; and *B*, boat. The molecular dimensions are normal; the mean bond distances are C_{sp^3}—N 1.463 (6), C_{sp^3}—C_{sp^3} 1.54 (2), C_{sp^3}—O 1.41 (2), C_{sp^2}—O 1.342 (3) and C=O 1.204 (4) Å. There is a short intramolecular

hydrogen bond with O···O and H···O distances of 2.556 (3) and 2.01 Å, respectively.

Comment

As a continuation of our studies on the C_{19} norditerpenoid alkaloids from the roots of *Aconitum chasmanthum* Stapf ex Holmes of Pakistani origin (Parvez, Gul & Anwar, 1998; Parvez, Gul, Anwar *et al.*, 1998), we have isolated the title compounds as a crystalline mixture which could not be separated by chromatographic techniques, although from NMR spectral data, it was evident that the sample was composed of two distinct compounds, namely, 14-*O*-benzoyl-8-methoxybikhaconine, (1), and 14-*O*-benzoyl-8-ethoxybikhaconine, (2).



(1) $R=CH_3$ (65%)
(2) $R=C_2H_5$ (35%)

The crystal structure contains discrete molecules of (1) and (2) occupying the same site in the crystal; an *ORTEP*II (Johnson, 1976) drawing of (2) is given in Fig. 1. The ethoxy substituent at C8 showed only partial occupancy of C24, with (2) being a 35% fraction of the crystal structure and the major portion (65%) being alkaloid (1). The absolute structures could not be determined in this analysis. The absolute configuration chosen is the same as that reported for chasmanine 14-α-benzoate hydrochloride (De Camp & Pelletier, 1977). The molecular dimensions are within expected values for the corresponding bond lengths and angles; mean bond distances are C_{sp^3}—N 1.463 (6), C_{sp^3}—C_{sp^3} 1.54 (2), C—$C_{aromatic}$ 1.372 (19) and C_{sp^3}—O 1.41 (2) Å, while the C_{sp^2}—C_{sp^2}, C_{sp^2}—O and C═O distances are 1.490 (4), 1.342 (3) and 1.204 (4) Å, respectively.

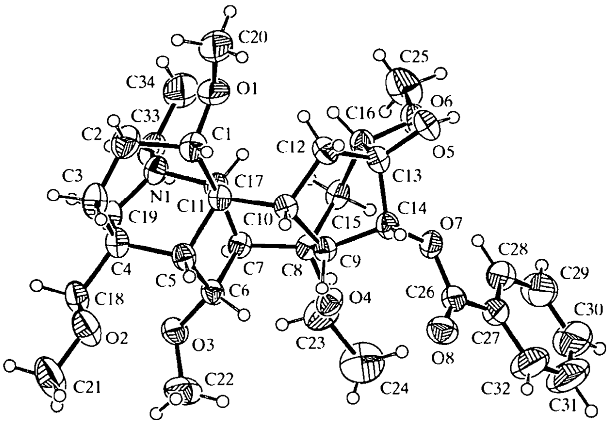


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (2) with the atomic numbering scheme. Displacement ellipsoids are plotted at the 30% probability level and H atoms have been assigned arbitrary radii. The C8 atom in alkaloid (1) has a methoxy substituent instead of the ethoxy group shown above.

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 chasmaconitine (Parvez, Gul, Anwar *et al.*, 1998), chasmanthinine (Parvez, Gul & Anwar, 1998), a chasmanine intermediate (Przybylska & Ahmed, 1980) and aconitine (Codding, 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 atom C14 0.917 (3) Å out of the plane of the remaining ring atoms. The seven-membered ring *B* (C5–C11) adopts a boat conformation, and five-membered rings *C* (C9, C10, C12–C14) and *F* (C5–C7, C11, C17) display C14- and C17-envelope conformations, respectively. The C14 atom of ring *C* is 0.718 (3) Å out of the plane of the remaining four atoms which are essentially planar [maximum deviation 0.042 (1) Å]. Atom C17 of ring *F* is 0.730 (3) Å out of the plane formed by the remainder of the atoms. The benzoate moiety attached to C14 is almost planar, with atom O7 lying 0.191 (5) Å above and atom O8 0.138 (5) Å below the plane composed of atoms C26–C32.

There is an intramolecular O5—H5···O6 hydrogen bond [O5···O6 2.556 (3), H5···O6 2.01 Å and O5—H5···O6 114°]; similar hydrogen bonds have been reported in related alkaloids, *e.g.* chasmaconitine (Parvez, Gul, Anwar *et al.*, 1998) and chasmanthinine (Parvez, Gul & Anwar, 1998). There are no intermolecular interactions between adjacent molecules other than normal van der Waals contacts.

Experimental

The title compounds, (1) and (2), were isolated from the roots of *A. chasmanthum* according to Parvez, Gul, Anwar *et al.* (1998) and crystals of X-ray quality were grown from methanol at room temperature by slow evaporation.

Crystal data

$0.65C_{33}H_{47}NO_8.0.35C_{34}H_{49}NO_8$
$M_r = 590.63$
Monoclinic
$P2_1$
$a = 9.938 (4)$ Å
$b = 11.876 (5)$ Å
$c = 13.611 (5)$ Å
$\beta = 91.960 (10)°$
$V = 1605.4 (11)$ Å^3
$Z = 2$
$D_x = 1.222$ Mg m^{-3}
D_m not measured

Cu $K\alpha$ radiation
$\lambda = 1.54178$ Å
Cell parameters from 25 reflections
$\theta = 20–30°$
$\mu = 0.702$ mm^{-1}
$T = 293 (1)$ K
Prism
0.40 × 0.37 × 0.28 mm
Colorless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: none
6403 measured reflections
5766 independent reflections (including Friedel pairs)
5468 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.023$
$\theta_{\rm max} = 68.0°$
$h = 0 \rightarrow 11$
$k = -14 \rightarrow 14$
$l = -16 \rightarrow 16$
3 standard reflections every 200 reflections intensity decay: none

Refinement

Refinement on F^2
$R(F) = 0.062$
$wR(F^2) = 0.161$
$S = 0.990$
5745 reflections
391 parameters
H atoms riding
$w = 1/[\sigma^2(F_o^2) + (0.136P)^2 + 0.142P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.005$
$\Delta\rho_{\rm max} = 0.284$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.270$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.0 (2)

The methyl C24 atom of the ethoxy group attached to C8 of (2) had only partial site occupancy which refined to a value of 0.35 (2). The H atoms were included at geometrically idealized positions, with C—H and O—H distances of 0.95 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*93 (Sheldrick, 1993). Molecular graphics: *TEXSAN*. Software used to prepare material for publication: *SHELXL*93.

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Hydrogen-Bonding Patterns in a Centrosymmetric Structure with $Z' = 2$: α,α',α''-Trimethyl-1,3,5-benzenetrimethanol

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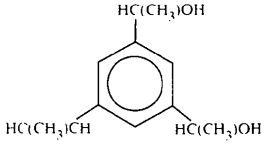
Abstract

The title molecule, $C_{12}H_{18}O_3$, crystallized in the centrosymmetric space group $P2_1/c$ with two molecules in the asymmetric unit. Each molecule donates three, and accepts three, hydrogen bonds. The $O_d\cdots O_a$ distances in these bonds range from 2.687 (3) to 2.787 (2) Å. The hydroxyl H atoms are ordered. A three-dimensional network of hydrogen-bond chains is formed which is 'decorated' with sets of cyclic hydrogen bonds and numerous finite hydrogen-bond patterns. This structure shows both similarities and differences with respect to the structures of the related molecules benzene-1,3,5-triacetic acid and benzene-1,3,5-trimethanol.

Comment

This report on α,α',α''-trimethyl-1,3,5-benzenetrimethanol, (I), is one of a series on hydrogen bonding in aromatic organic solids and follows a study of the related substance benzene-1,3,5-triacetic acid (hereafter BTA) which was shown to have extensive interwoven hydrogen-bonding networks (Fitzgerald & Gerkin, 1997). Structural comparisons with the closely related substance benzene-1,3,5-trimethanol (hereafter BTM) (Bell *et al.*, 1996) are of particular interest.



(I)