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3-Acetoxy-6-hydroxy-2,4-dimethoxyacetophenone†

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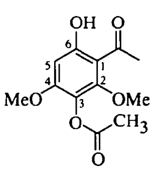
Abstract

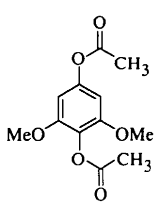
The title compound, $C_{12}H_{14}O_6$, has been isolated from a Fries reaction on 3,6-dihydroxy-2,4-dimethoxyacetophenone. Its molecular structure contains an intramolecular hydrogen-bonded unit involving the $-COCH_3$ and $-OH$ substituents. The best plane through the acetoxy group makes a dihedral angle of 88.74 (5)° with the plane of the aromatic ring.

Comment

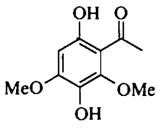
Acetophenones are useful synthons for the preparation of a wide variety of polyphenolic compounds such as chalcones and flavones (Parmar *et al.*, 1996). The synthesis of 3,6-dihydroxy-2,4-dimethoxyacetophenone, (III), was attempted *via* the Fries reaction on compound (II). However, this reaction failed to produce the desired product and instead the partially protected compound (I) (Fig. 1) was obtained as one of the side products; this latter compound has potential in the synthesis of bioactive flavonoids. The X-ray structure of (I) has been determined in order to obtain an unambiguous characterization.



(I)



(II)



(III)

The bond lengths and angles are unexceptional. The variation in C—O bond lengths within the methoxy groups is as expected, *i.e.* $O—C_{sp^3} > O—C_{sp^2}$ (*e.g.* Mukherjee *et al.*, 1996). The methoxy substituent at C4 is almost coplanar with the aromatic ring, but that at C2 is twisted to give a C9—O2—C2—C3 torsion angle of 61.2 (2)°. The acetoxy group is also twisted, making a dihedral angle of 88.7 (1)° with the plane of the aromatic ring. The O1—C7—C1—C6—O6—H6 unit is essentially planar (r.m.s. deviation 0.018 Å) as a result of

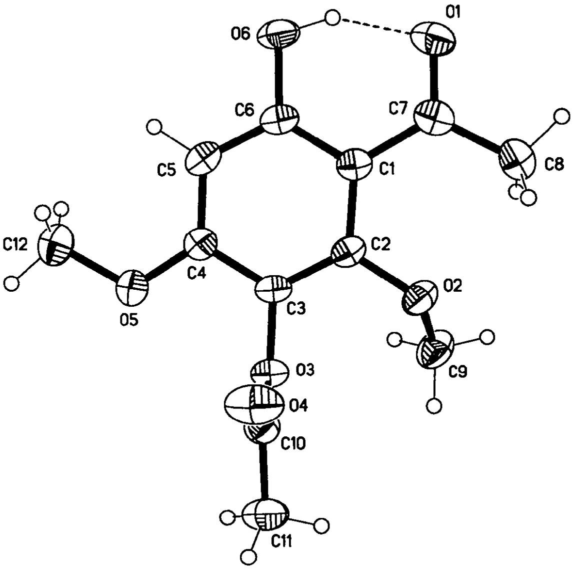


Fig. 1. View of the title molecule showing the atomic numbering. Displacement ellipsoids are drawn at the 50% probability level.

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† Alternative name: 3-acetyl-4-hydroxy-2,6-dimethoxyphenyl ethanoate.

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intramolecular hydrogen bonding; this interaction results in an O6···O1 separation of 2.482 (2) Å (*cf.* sum of van der Waals radii is 3.04 Å). There are no obvious short-range intermolecular interactions.

Experimental

1,4-Diacetoxy-2,6-dimethoxybenzene [(II), 1 g, 3.7 mmol, prepared by the method of Oliverio, Marini-Bettolo & Bargellini (1948)] was mixed with finely powdered anhydrous aluminium chloride (1.57 g, 11.8 mmol) and the reaction mixture was heated at 393 K for 30 min and at 413 K for 2 h on an oil bath. The reaction mixture was cooled to 300 K, ice-cold water (100 ml) was added and the contents heated in a boiling water bath for 30 min after acidification with dilute HCl. The solid that separated was filtered and subjected to column chromatography over silica gel. Compound (I) eluted out with ethyl acetate–petroleum ether (1:20) as a white solid and was recrystallized from an ethyl acetate–petroleum ether mixture as shiny white crystals (100 mg), m.p. 385–386 K [literature m.p. 385 K (Nakazawa, 1968)]. MS (EI, 70 eV), *m/z* (%): 254 (11) (M^+), 212 (100), 197 (78), 179 (8), 151 (10), 69 (18) and 43 (61); ^{1}H NMR (90MHz, $CDCl_3$): δ 2.30 (3H, *s*, $COCH_3$), 2.60 (3H, *s*, $OCOCH_3$), 3.80 and 3.85 (3H each, 2*s*, 2 × OCH_3), 6.30 (1H, *s*, H-5), 13.40 (1H, *s*, C-6 OH).

Crystal data

$C_{12}H_{14}O_6$
$M_r = 254.23$
Orthorhombic
Pbca
$a = 15.9349\ (6)$ Å
$b = 8.0535\ (3)$ Å
$c = 18.6618\ (9)$ Å
$V = 2394.9\ (1)$ Å^3
$Z = 8$
$D_x = 1.410$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 7813 reflections
$\theta = 2.18–28.67°$
$\mu = 0.114$ mm^{-1}
$T = 180\ (2)$ K
Block
0.50 × 0.40 × 0.40 mm
Colourless

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: none
13 508 measured reflections
2913 independent reflections

1803 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.065$
$\theta_{\rm max} = 28.67°$
$h = -21 \rightarrow 16$
$k = -10 \rightarrow 9$
$l = -24 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.042$
$wR(F^2) = 0.105$
$S = 0.885$
2913 reflections
171 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0553P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.195$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.259$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O1—C7	1.2367 (18)	O4—C10	1.1931 (17)
O2—C2	1.3641 (16)	O5—C4	1.3503 (16)
O2—C9	1.4376 (18)	O5—C12	1.4368 (19)
O3—C10	1.3540 (17)	O6—C6	1.3510 (17)
O3—C3	1.4010 (16)		
C9—O2—C2—C3	61.24 (17)	C7—C1—C6—O6	0.4 (2)
C12—O5—C4—C3	178.17 (14)	C2—C1—C7—O1	−176.62 (13)

The temperature of the crystal was controlled using an Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). Data were collected over a hemisphere of reciprocal space, by a combination of three sets of exposures. Each set had a different φ angle for the crystal and each exposure of 10 s covered 0.3° in ω. The crystal to detector distance was 5.01 cm. Coverage of the unique set was over 95% complete to at least 28° in θ. Crystal decay was monitored by repeating the initial frames at the end of the data collection and analysing the duplicate reflections. H atoms were added at calculated positions and refined using a riding model; an exception was the hydroxyl H atom which was located from the electron-density map and allowed to refine freely. Anisotropic displacement parameters were used for all non-H atoms, while the H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the atom to which they are attached.

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1994). Program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

We wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury Laboratory (Fletcher, McMeeking & Parkin, 1996) for access to the Cambridge Structural Database (Allen & Kennard, 1993). SM thanks the University Grants Commission (UGC, New Delhi, India) for the award of a research fellowship.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1189). Services for accessing these data are described at the back of the journal.

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Chasmanthinine†

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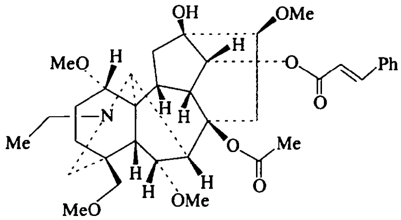
Abstract

The crystal structure of chasmanthinine, $C_{36}H_{49}NO_9$, a C_{19} norditerpenoid alkaloid which has been isolated from the roots of *Aconitum chasmanthum* Stapf ex Holmes, contains independent molecules separated by normal van der Waals distances. The mean bond distances are: N—C_{sp^3} 1.468 (11), C_{sp^3}—C_{sp^3} 1.54 (2), C_{sp^2}—C_{sp^2} 1.471 (2), O—C_{sp^3} 1.428 (18), O—C_{sp^2} 1.338 (2) and C=O 1.205 (4) Å. The fused-ring system contains one boat, one half-chair, two chair and two envelope conformations.

Comment

Continuing our studies on the diterpenoid alkaloids of *Aconitum chasmanathum* Stapf ex Holmes of Pakistani origin (Parvez *et al.*, 1998), we have isolated the title compound, (1). We report here the structure of (1), which contains discrete molecules of chasmanthinine separated by normal van der Waals distances. The absolute configuration (Fig. 1) was not determined by 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 angles, with mean bond distances: N—C_{sp^3} 1.468 (11), C_{sp^3}—C_{sp^3} 1.54 (2), C_{sp^2}—C_{sp^2} 1.471 (2), O—C_{sp^3} 1.428 (18), O—C_{sp^2} 1.338 (2) and C=O 1.205 (4) Å, while the C_{sp^3}—C_{sp^2} and C_{sp^2}=C_{sp^2} distances are 1.482 (5) and 1.318 (5) Å, respectively.



(1)

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 reported in the structures of a chasmanine intermediate (Przybylska & Ahmed, 1980), aconitine (Codding, 1982) and chasmaconitine (Parvez *et al.*, 1998). The six-membered ring *D* (C8, C9, C13–C16) has a half-chair conformation, with C14 0.899 (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) have C14- and C17-envelope conformations, respectively, with C14 0.714 (5) and C17 0.742 (4) Å out of the planes formed by the remaining atoms of their respective rings. The 3-phenyl-2-propenoate moiety attached to C14 is essentially planar, with O8 lying 0.290 (4) Å below and O9 0.189 (5) Å above the plane formed by atoms C26–C34. The conformations of rings *A*–*F* in (1) are identical to the corresponding rings in chasmaconitine (Parvez *et al.*, 1998). There is a short intramolecular O6—H···O7 hydrogen bond [O6···O7 2.588 (4), H···O7 2.02 Å and O6—H···O7 116°]. A diagram of the molecular packing in the unit cell of (1) has been deposited.

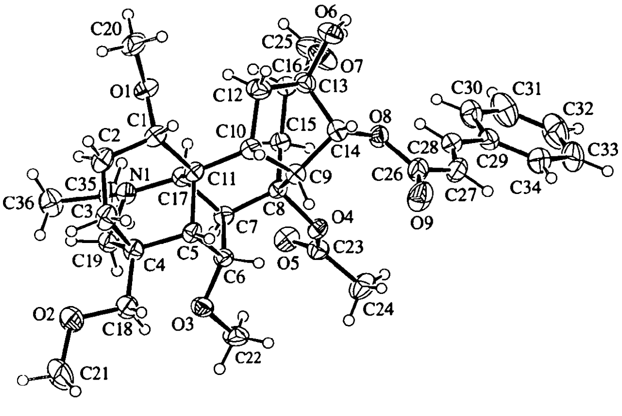


Fig. 1. *ORTEP*II (Johnson, 1976) drawing of (1) with the atomic numbering scheme. Displacement ellipsoids are plotted at the 30% probability level and H atoms are drawn as small circles of arbitrary radii.

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† Alternative name: [1α,6α,14α(*E*),16β]-20-ethyl-13-hydroxy-1,6,16-trimethoxy-4-methoxymethylaconitane-8,14-diyl 8-acetate 14-(3-phenyl-2-propenoate).