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Taraxerol acetate at 100 K

DAMON R. BILLODEAUX, GLORIA A. BENAVIDES,
NIKOLAUS H. FISCHER AND FRANK R. FRONCZEK

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA. E-mail: fronz@chxray1.chem.lsu.edu

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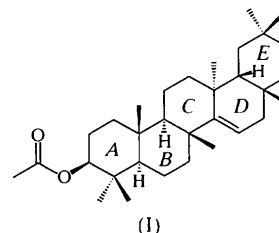
Abstract

The title triterpene, *D*-friedoolean-14-en-3 β -yl acetate, C₃₂H₅₂O₂, was isolated from dichloromethane extracts of the roots of common ragweed *Ambrosia artemisiifolia*. The skeleton contains five fused six-membered rings with an average Csp³—Csp³ bond distance of 1.549 (6) Å and one double bond of length 1.348 (6) Å. The *D* and *E* rings are *cis*-fused. The compound also contains a β -oriented acetate group with a C—O distance 1.461 (5) Å.

Comment

In the course of our search for biologically active natural products, the dichloromethane extract of roots

of common ragweed, *Ambrosia artemisiifolia*, showed activity in a radiorespirometric assay (Franzblau & Collins, 1997) against *Mycobacterium tuberculosis* H₃₇Rv (Cantrell *et al.*, 1998). The crude extract was chromatographed by standard vacuum liquid chromatography procedures (Cantrell *et al.*, 1996) using silica gel with solvent mixtures of increasing polarity. From non-polar fractions, taraxerol acetate, (I), was isolated, but showed no antimycobacterial activity. We determined the crystal structure in order to confirm the identity of the compound and ascertain the ring conformations.



The structure contains five fused six-membered rings with only the *D* and *E* rings *cis*-fused. The average Csp³—Csp³ bond in the rings is 1.549 (6) Å, comparable to the equivalent distance of 1.539 (17) Å recently reported in taraxerone (Parvez *et al.*, 1999), as well as other similar triterpenes in the literature (Chakravarty *et al.*, 1989; Tinant *et al.*, 1982). The solitary Csp²—Csp² bond (C14=C15) has length 1.348 (6) Å, comparable with 1.338 (3) Å reported for taraxerone. The conformations of the rings in the title compound are similar to the reported conformations of taraxerone (Parvez *et al.*, 1999). Rings *A* and *B* adopt chair conformations with puckering parameters $Q = 0.566$ (3) and 0.595 (3) Å, $\varphi = 63.85$ (5) and 347.03 (3)°, and $\theta = 4.4$ (1) and 8.3 (2)° (Cremer & Pople, 1975). Ring *C* has a twist-boat conformation [$Q = 0.709$ (2) Å, $\varphi = 20.83$ (2)°, $\theta = 87.1$ (3)°], while the conformations of rings *D* and *E* resemble twist

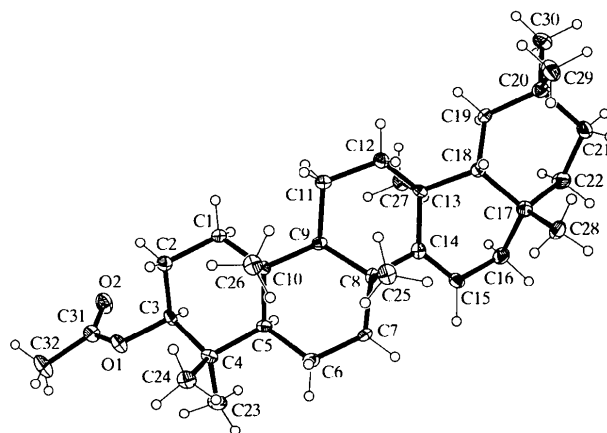


Fig. 1. Numbering scheme and ellipsoids at the 50% level. H atoms are represented by circles of arbitrary radius.

boats [$Q = 0.637(3)$ and $0.726(4)$ Å, $\varphi = 7.88(2)$ and $299.97(3)^\circ$, $\theta = 92.0(2)$ and $89.9(7)^\circ$].

An acetate group is β -oriented at C3 at a bond distance of 1.461(5) Å (C3—O1). The C=O distance within the acetate group is 1.209(6) Å (C31=O2). The C—O distance [1.349(6) Å] and the C=O distance compare well to other reported triterpenes with 3β -oriented acetates [1.338(16) and 1.213(16) Å] (Tinant *et al.*, 1982).

Experimental

The crude dichloromethane extract of *Ambrosia artemisifolia* roots was chromatographed using a standard vacuum liquid technique. The crystals were then grown by evaporation from hexane at room temperature.

Crystal data

C ₃₂ H ₅₂ O ₂	Mo K α radiation
$M_r = 468.74$	$\lambda = 0.71073$ Å
Monoclinic	Cell parameters from 25 reflections
C2	$\theta = 7.6\text{--}10.8^\circ$
$a = 13.513(2)$ Å	$\mu = 0.067$ mm ⁻¹
$b = 6.2880(9)$ Å	$T = 100$ K
$c = 32.903(3)$ Å	Plate
$\beta = 98.22(3)^\circ$	$0.43 \times 0.23 \times 0.05$ mm
$V = 2767.1(10)$ Å ³	Colorless
$Z = 4$	
$D_x = 1.125$ Mg m ⁻³	
D_m not measured	

Data collection

Enraf–Nonius CAD-4 diffractometer (with an Oxford Cryosystems Cryostream cooler)	$R_{\text{int}} = 0.040$
ω – 2θ scans	$\theta_{\text{max}} = 30.0^\circ$
Absorption correction: none	$h = -18 \rightarrow 10$
5316 measured reflections	$k = 0 \rightarrow 8$
4308 independent reflections	$l = -45 \rightarrow 46$
2623 reflections with $I > 2\sigma(I)$	3 standard reflections frequency: 60 min intensity decay: 1.2%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.063$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.249$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 0.813$	$\Delta\rho_{\text{max}} = 0.35$ e Å ⁻³
4308 reflections	$\Delta\rho_{\text{min}} = -0.31$ e Å ⁻³
320 parameters	Extinction correction: none
H atoms treated by a mixture of independent and constrained refinement	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)

Table 1. Selected geometric parameters (Å, °)

C3—O1	1.461(5)	O2—C31	1.209(6)
C14—C15	1.348(6)	C31—O1	1.349(6)
O1—C3—C2	109.6(3)	O2—C31—O1	124.6(4)
C15—C14—C13	118.7(4)	O2—C31—C32	123.5(5)
C15—C14—C8	121.6(4)	O1—C31—C32	111.9(4)

C13—C14—C8	119.7(3)	C31—O1—C3	117.1(4)
C14—C15—C16	120.5(4)		
C1—C2—C3—C4	59.8(5)	C11—C12—C13—C14	-53.4(5)
C2—C3—C4—C5	-54.6(5)	C12—C13—C14—C8	15.2(6)
C3—C4—C5—C10	51.3(5)	C7—C8—C14—C13	156.0(4)
C10—C5—C6—C7	-62.6(5)	C13—C14—C15—C16	5.1(7)
C5—C6—C7—C8	56.6(6)	C14—C15—C16—C17	44.7(6)
C6—C7—C8—C9	-49.5(5)	C15—C16—C17—C18	-48.4(5)
C7—C8—C9—C10	52.2(5)	C14—C13—C18—C17	36.5(5)
C8—C9—C10—C5	-56.9(5)	C16—C17—C18—C13	8.6(6)
C4—C5—C10—C1	-51.5(5)	C17—C18—C19—C20	-53.8(6)
C3—C2—C1—C10	-58.3(5)	C18—C19—C20—C21	53.0(6)
C5—C10—C1—C2	53.3(5)	C29—C20—C21—C22	122.8(5)
C8—C9—C11—C12	23.5(6)	C18—C17—C22—C21	52.9(6)
C9—C11—C12—C13	34.0(6)	C20—C21—C22—C17	-54.3(6)

H atoms were allowed for as riding atoms except for H15 which was refined isotropically [C15—H15 1.04(6) Å].

Refinement of the Flack (1983) parameter yielded a value of -1(3), so the absolute configuration is undetermined, but was assumed to correspond to that of oleanic acid diacetate bromolactone (van Schalkwyk & Kruger, 1974). Friedel pairs were averaged for the final refinement.

Data collection: CAD-4 EXPRESS (Enraf–Nonius, 1995). Cell refinement: CAD-4 EXPRESS. Data reduction: XCAD4 (Harms & Wocadlo, 1996). Program(s) used to solve structure: SHELXS97 (Sheldrick, 1990). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: SHELXTL (Bruker, 1998). Software used to prepare material for publication: SHELXTL.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1098). Services for accessing these data are described at the back of the journal.

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1-Ethynylcyclohexylammonium acetate

THOMAS STEINER,^a ANTOINE M. M. SCHREURS^b AND JAN KROON^b

^a*Institut für Chemie – Kristallographie, Freie Universität Berlin, Takustraße 6, D-14195 Berlin, Germany, and* ^b*Bijvoet Center for Biomolecular Research, Department of Crystal and Structural Chemistry, Utrecht University, Padualaan 8, 3584 CH Utrecht, The Netherlands. E-mail: steiner@chemie.fu-berlin.de*

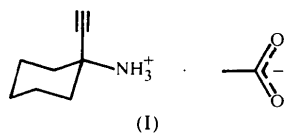
(Received 27 August 1999; accepted 30 September 1999)

Abstract

The title compound, $C_8H_{14}N^+ \cdot CH_3CO_2^-$, contains a short $C\equiv C-H \cdots O$ hydrogen bond to the acetate ion with a $C \cdots O$ distance of 3.139 (2) Å and a normalized $H \cdots O$ distance of 2.11 Å. $N-H \cdots O$ and $C\equiv C-H \cdots O$ hydrogen bonds are linked together to form a ribbon motif.

Comment

Terminal alkynes, $R-C\equiv C-H$, are an interesting model system to study $C-H \cdots X$ hydrogen bonds (Steiner, 1998a). This is because the acetylenic $C-H$ group is relatively acidic, and therefore one of the best hydrogen-bond donors of all $C-H$ groups (Desiraju & Steiner, 1999). The title compound, (I), was prepared and its crystal structure was determined in expectation of finding a short hydrogen bond $C\equiv C-H \cdots O^-$, which is one of the less well investigated kinds of $C-H \cdots O$ interaction.



In the crystal structure of (I), the cyclohexane ring adopts a chair conformation with the ammonium group

in an equatorial and the ethynyl group in an axial position. The chair is almost undistorted with the ethynyl group close to perpendicular to the ring [angles $C3 \cdots C1-C7 = 95.6(1)$, $C5 \cdots C1-C7 = 95.7(1)^\circ$]. The geometry of the ethynyl group is normal with $C7\equiv C8 = 1.188(2)$ Å and $C1-C7\equiv C8 = 179.2(1)^\circ$.

As expected, the primary ammonium group forms three $N^+-H \cdots O^-$ hydrogen bonds to the acetate ion, with geometries as given in Table 1. The ethynyl group donates a hydrogen bond to the acetate ion too, Fig. 1, with a $C \cdots O$ distance of 3.139 (2) Å. If the $C-H$ bond is normalized to 1.08 Å, an $H \cdots O$ distance of 2.11 Å and a $C-H \cdots O$ angle of 159° are obtained. Even for an acetylenic donor, this is a short $C-H \cdots O$ contact. For comparison, the mean distance in 145 $C\equiv C-H \cdots O$ bonds in organic and organometallic structures has been found as $H \cdots O = 2.40(2)$ Å, and $C \cdots O = 3.35(1)$ Å (Steiner, 1998b). However, much shorter $(C)H \cdots O$ distances also occur in crystal structures of terminal alkynes. Examples are the adduct triphenylsilylacetylene–triphenylphosphin oxide, $H \cdots O = 1.99$ Å with a $P=O$ acceptor (for normalized $C-H$; Steiner *et al.*, 1997), 1:2:4 1,4-diethynylbenzene–water–triphenylphosphin oxide, $H \cdots O = 1.96$ Å with an H_2O acceptor (for normalized $C-H$; Kariuki *et al.*, 1997), and 2-ethynyladamantan-2-ol, $H \cdots O = 2.07$ Å with a $C=O-H$ acceptor [neutron diffraction study by Allen *et al.* (1996)]. It is interesting that these three examples are all in uncharged compounds.

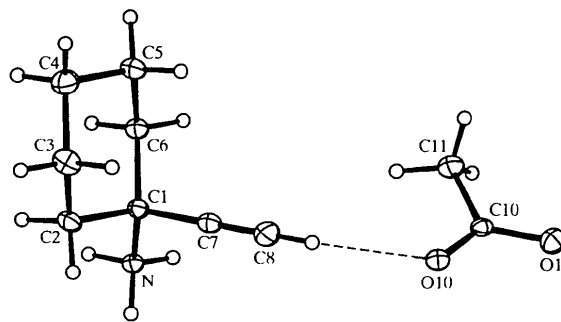


Fig. 1. The molecular structure of (I) showing 50% probability displacement ellipsoids.

The hydrogen-bond interactions of the acetate ion are shown in detail in Fig. 2. All four hydrogen bonds are directed at the oxygen lone-pair regions. It is obvious that the $C\equiv C-H \cdots O$ bond acts as a full member in hydrogen-bond coordination of the ion, not just as a bystander. The covalent bond $O11-C10$ of the acetate ion [1.276 (2) Å] is slightly but significantly longer than $O10-C10$ [1.249 (2) Å]. Because in $X-H \cdots O=C$ bonds, $O=C$ is lengthened, this would indicate that the sum of the hydrogen bonds accepted by $O11$ (two $N^+-H \cdots O^-$ bonds) is significantly stronger than the sum of the bonds accepted by $O10$ (one $N^+-H \cdots O^-$ and one