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Ceratiolin from *Ceratiola ericoides*

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Abstract

The title compound, 3-phenyl-1-(2,4,5-trihydroxy-3,5-dimethyl-6-oxo-1,5-cyclohexadienyl)-1-propanone, was confirmed to be a dihydrochalcone containing a fully substituted cyclohexadienone ring. This ring has a flattened half-chair conformation, with the dione C atom 0.203 (1) Å out of the diene plane and the tetrahedral C atom 0.184 (1) Å to the opposite side of the plane. The hydroxy substituent on the tetrahedral C atom forms an intramolecular hydrogen bond to the carbonyl O atom of the cyclohexadienone, having an O···O distance of 2.658 (1) Å and an angle at H of 116 (2)°. One of the other hydroxy substituents forms an intramolecular hydrogen bond

with the carbonyl O atom of the β-phenylpropionyl group, having an O···O distance of 2.414 (2) Å and an angle at H of 160 (2)°.

Comment

The title compound is an external leaf constituent of false rosemary (*Ceratiola ericoides*, Empetraceae), which is endemic to the Florida scrub. There exists strong evidence that the ecological role of the non-active ceratiolin lies in its photochemical decomposition into β-phenylpropionic acid, which is a potent selective allelopathic agent for native Florida grasses (Fischer, Tanrisever & Williamson, 1988). The structure of ceratiolin was initially inferred from NMR, mass spectral and chemical data (Tanrisever, Fronczek, Fischer & Williamson, 1987). Although its structure was later verified by total synthesis (Obara, Onodera, Yusa, Tsuchiya & Matsuba, 1989), the initial structure elucidation was based partially on biogenetic considerations, which left some structural uncertainties. This fact, together with the presence of the unusual cyclohexadienone moiety in ceratiolin, led us to determine its crystal structure.

The conformation of the β-phenylpropionyl substituent is described by three torsion angles. That about the central C8—C9 bond is *anti*, while the C9—C8—C7—O5 torsion angle is more nearly orthogonal [102.4 (2)°], as is that defining the conformation of the phenyl group relative to the propionyl group, C8—C9—C10—C11 [69.8 (2)°]. The first intramolecular hydrogen bond described in the Abstract, O2—H···O1, is actually bifurcated, the second component being intermolecular, and also with carbonyl O1 (at −x, 1 − y, 1 − z) as acceptor. The O···O distance in this contact is 2.875 (1) Å, and the angle about H is 147 (2)°. Another intermolecular O—H···O hydrogen bond exists, with O3 as donor and hydroxy O2 (at 1 − x, 1 − y, 1 − z) as acceptor. This contact has an O···O distance of 2.677 (1) Å and an angle at H of 151 (2)°. This hydrogen bond may also be considered to be bifurcated, with an intramolecular component, O3···O2 2.719 (1) Å, O—H···O 107 (2)°.
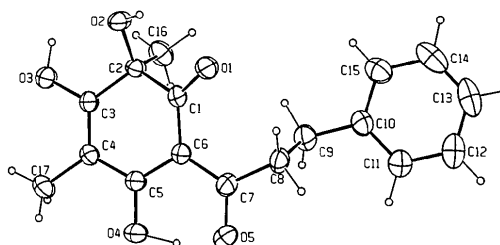

Fig. 1. *ORTEP* (Johnson, 1965) drawing of the title compound, with thermal ellipsoids drawn at the 40% probability level.

A search of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) for the fully substituted cyclohexadienone fragment yielded nine compounds for which crystal structure determinations have been carried out. Those most closely related to ceratiolin are aspersitin-A p-bromobenzoate (Buchi, Francisco, Murray, Kachholz, Demain & Blount, 1983), two isomers of 6-hydroxypentamethylchroman-5(6H)-one (Matsumoto, Matsuo & Iitaka, 1986), and hypercalins A and C (Decosterd, Stoeckli-Evans, Chapuis, Sordat & Hostettmann, 1989).

Experimental

Crystal data

$C_{17}H_{18}O_5$	Cu $K\alpha$ radiation
$M_r = 302.3$	$\lambda = 1.54184$ Å
Triclinic	Cell parameters from 25
$P\bar{1}$	reflections
$a = 7.5972$ (10) Å	$\theta = 25$–$30°$
$b = 8.9585$ (10) Å	$\mu = 0.77$ mm^{-1}
$c = 12.672$ (2) Å	$T = 299$ K
$\alpha = 73.824$ (11)°	Sphenoidal
$\beta = 76.383$ (11)°	$0.25 \times 0.18 \times 0.15$ mm
$\gamma = 67.823$ (1)°	Yellow
$V = 758.8$ (2) Å^3	Crystal source: recrystalliza-
$Z = 2$	tion from CH_2Cl_2
$D_x = 1.323$ Mg m^{-3}	

Data collection

Enraf-Nonius CAD-4 diffractometer	$\theta_{max} = 75°$
ω-2θ scans	$h = 0 \rightarrow 9$
Absorption correction:	$k = -9 \rightarrow 11$
none	$l = -15 \rightarrow 15$
3126 measured reflections	3 standard reflections
3126 independent reflections	frequency: 167 min
2718 observed reflections	intensity variation: <2%
$[I > 2\sigma(I)]$	

Refinement

Refinement on F	$\Delta\rho_{max} = 0.28$ e Å^{-3}
Final $R = 0.042$	$\Delta\rho_{min} = -0.11$ e Å^{-3}
$wR = 0.060$	Extinction correction:
$S = 2.857$	$(I + gI_c)^{-1}$ applied to F_c
2718 reflections	Extinction coefficient:
272 parameters	$g = 4.2$ (6) $\times 10^{-6}$
All H-atom parameters refined	Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

$w = 4F^2[\sigma^2(I) + (0.02F^2)^2]^{-1}$

$(\Delta/\sigma)_{max} = 0.06$

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

$B_{eq} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
O1	-0.0777 (1)	0.5553 (1)	0.61632 (8)	3.70 (2)
O2	0.2906 (1)	0.4837 (1)	0.52812 (7)	3.32 (2)
O3	0.5698 (1)	0.3462 (1)	0.66077 (8)	3.86 (2)
O4	0.1079 (1)	0.3021 (1)	0.96915 (8)	3.91 (2)
O5	-0.2327 (1)	0.4351 (1)	0.96403 (9)	4.36 (3)
C1	0.0339 (2)	0.5101 (2)	0.6841 (1)	2.71 (2)
C2	0.2383 (2)	0.5125 (2)	0.6380 (1)	2.71 (2)
C3	0.3857 (2)	0.3863 (2)	0.7076 (1)	2.76 (3)
C4	0.3423 (2)	0.3198 (2)	0.8155 (1)	2.90 (3)
C5	0.1441 (2)	0.3621 (2)	0.8641 (1)	2.89 (3)
C6	-0.0117 (2)	0.4619 (2)	0.8030 (1)	2.79 (3)
C7	-0.2031 (2)	0.4963 (2)	0.8607 (1)	3.20 (3)
C8	-0.3767 (2)	0.6118 (2)	0.8092 (1)	3.43 (3)
C9	-0.3908 (2)	0.7917 (2)	0.7919 (1)	3.82 (3)
C10	-0.5832 (2)	0.9085 (2)	0.7611 (1)	3.61 (3)
C11	-0.7481 (2)	0.9204 (2)	0.8391 (1)	4.52 (4)
C12	-0.9265 (3)	1.0199 (3)	0.8109 (2)	5.68 (5)
C13	-0.9443 (3)	1.1100 (2)	0.7043 (2)	6.03 (5)
C14	-0.7836 (3)	1.1025 (2)	0.6272 (2)	5.77 (5)
C15	-0.6026 (2)	1.0022 (2)	0.6552 (1)	4.57 (4)
C16	0.2360 (2)	0.6860 (2)	0.6340 (1)	4.01 (3)
C17	0.4953 (2)	0.2057 (2)	0.8849 (1)	4.11 (4)

Table 2. *Geometric parameters* (Å, °)

O1—C1	1.230 (2)	C5—C6	1.431 (2)
O2—C2	1.423 (2)	C6—C7	1.425 (2)
O3—C3	1.336 (1)	C7—C8	1.495 (2)
O4—C5	1.295 (1)	C8—C9	1.530 (2)
O5—C7	1.273 (2)	C9—C10	1.507 (2)
C1—C2	1.531 (2)	C10—C11	1.390 (2)
C1—C6	1.442 (2)	C10—C15	1.378 (2)
C2—C3	1.505 (2)	C11—C12	1.378 (2)
C2—C16	1.535 (2)	C12—C13	1.375 (3)
C3—C4	1.347 (2)	C13—C14	1.364 (3)
C4—C5	1.432 (2)	C14—C15	1.394 (2)
C4—C17	1.501 (2)		
O1—C1—C2	116.6 (1)	C4—C5—C6	123.8 (1)
O1—C1—C6	126.2 (1)	C1—C6—C5	117.5 (1)
C2—C1—C6	117.1 (1)	C1—C6—C7	123.5 (1)
O2—C2—C1	110.1 (1)	C5—C6—C7	118.7 (1)
O2—C2—C3	108.50 (9)	O5—C7—C6	119.9 (1)
O2—C2—C16	108.7 (1)	O5—C7—C8	116.0 (1)
C1—C2—C3	113.04 (9)	C6—C7—C8	123.9 (1)
C1—C2—C16	106.7 (1)	C7—C8—C9	111.4 (1)
C3—C2—C16	109.6 (1)	C8—C9—C10	111.4 (1)
O3—C3—C2	117.6 (1)	C9—C10—C11	120.3 (1)
O3—C3—C4	118.9 (1)	C9—C10—C15	121.6 (1)
C2—C3—C4	123.3 (1)	C11—C10—C15	118.1 (1)
C3—C4—C5	118.3 (1)	C10—C11—C12	121.1 (2)
C3—C4—C17	121.7 (1)	C11—C12—C13	120.2 (2)
C5—C4—C17	120.0 (1)	C12—C13—C14	119.5 (2)
O4—C5—C4	116.7 (1)	C13—C14—C15	120.6 (2)
O4—C5—C6	119.5 (1)	C10—C15—C14	120.5 (1)
H2O—O2—C2—C1	8.4 (13)	C1—C2—C3—C4	-22.0 (2)
H3O—O3—C3—C2	1 (2)	C2—C3—C4—C5	4.8 (2)
H4O—O4—C5—C6	-1.7 (11)	C3—C4—C5—C6	4.5 (2)
O1—C1—C2—O2	-30.2 (2)	O4—C5—C6—C7	1.8 (2)
C6—C1—C2—C3	30.8 (2)	C4—C5—C6—C1	5.5 (2)
C2—C1—C6—C5	-23.6 (2)	C5—C6—C7—O5	-1.7 (2)
O2—C2—C3—O3	39.5 (2)	C7—C8—C9—C10	-169.0 (1)

Programs used include *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), *MolEN* (Fair, 1990) and *ORTEP* (Johnson, 1965).

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Enantioselective Synthesis of Isoquinoline Alkaloids from Simple Sugar. I. Structure of an Oxaziridine Derivative

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Abstract

1-(6,7-Dimethoxy-1,2,3,4-tetrahydro-1,2-epoxyiso-quinolin-1-yl)-1,2,3,4-butanetetrayl tetraacetate is a chiral precursor in the synthesis of some natural products. The three-membered oxaziridine ring is almost perpendicular to the best plane of the two remaining rings. The structure of the acetyl fragment is partly disordered.

Comment

In the course of our study on the enantioselective synthesis of isoquinoline alkaloids from various naturally occurring chiral substrates, we launched a project using a simple sugar, D-ribonolactone (Bhat, Chen & Joullie, 1985, 1989), as a chiral building block. As a result of synthesis *via* several steps, we obtained two isoquinoline alkaloids: (*R*)-calycotomine and (*S*)-xylopinine (Czarnocki, 1992*a,b*). The oxaziridine derivative was obtained as one of many intermediate products. Its chemical reactivity will be the subject of a separate study. The compound was characterized by ^{1}H and ^{13}C NMR and its structure was established with some degree of certainty. However, the relative stereochemistry of the oxaziridine ring could not be established firmly by these methods. For this reason we decided to elucidate the proposed structure *via* an X-ray crystallographic study.
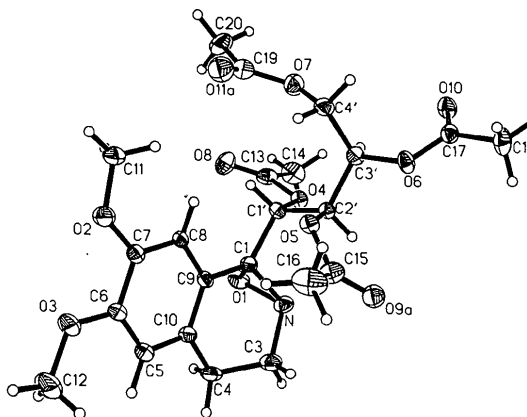

Fig. 1. Molecular geometry of the oxaziridine derivative.

The molecular geometry and numbering scheme are shown in Fig. 1. Only one position for each disordered acetyl O atom, O9 and O11, is shown in the figure for clarity. The refined site occupancies of the O9 atom were 0.48 (1) and 0.52 (1) for the *a* and *b* positions, respectively, whereas those of the O11 atom were 0.49 (2) and 0.51 (2), respectively. All bond lengths and angles are reasonable within experimental error. The aromatic ring (C5–C10) is planar. The C1—C9 and C6—O3 bonds are in the plane of the ring [angles with the normal to the plane are 89.7 (2) and 90.6 (2)°, respectively], whereas the two remaining bonds, C4—C10 and C7—O2, are slightly out of the plane [angles with the normal to the plane are 88.0 (3) and 91.6 (3)°, respectively]. The oxaziridine three-membered ring is almost perpendicular to the best plane defined by atoms of the two other rings [the dihedral angle is 91.8 (2)°]. The relative conformations on the C1 and C1′ atoms, as shown in Fig. 1, were characterized by a series of torsion angles.