Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Rotenone *α*-oxime

Shi-Ping Yang,[a]* Xi-Bin Yu,[a] Ji-Guang Huang[b] and Han-Hong Xu[b]

[a]School of Chemistry, Shanghai Teacher's University, Shanghai 200234, People's Republic of China, and [b]Laboratory of Insect Toxicology, South China Agricultural University, Guangzhou 510642, People's Republic of China
Correspondence e-mail: shipingy@shtu.edu.cn

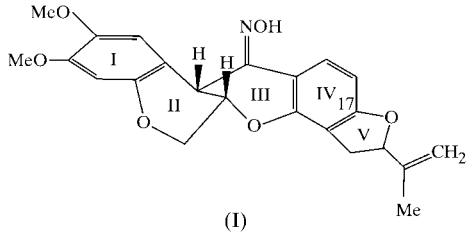
Received 14 March 2003
Accepted 20 May 2003
Online 20 June 2003

The structure determination of the title compound, rotenone *α*-oxime [systematic name: 1,2,12,12a-tetrahydro-8,9-dimethoxy-2-(1-methylethenyl)-[1]benzopyrano[3,4-*b*]furo[2,3-*h*][1]-benzopyran-6(6*H*)-one oxime], $C_{23}H_{23}NO_6$, confirms that the molecule has an approximately V-shaped structure. One of the rings has a typical cyclohexene-like monoplanar conformation and the central ring adopts a 1,2-diplanar conformation.

Comment

Rotenone, a naturally occurring heterocyclic compound with inhibitory effects on oxidative phosphorylation and mitosis, is obtained from the roots of the legumes *Derris elliptical* and *D. malaccensis* in Malaysia, and *D. Uruco* and *Lonchocarpus utilis* in South America (McEwen & Stephenson, 1979; Ware, 1983). Rotenone is a widely used pesticide (Carson, 1962; Haley, 1978; Gosalvez, 1983) and, together with other botanical pesticides (*e.g.* pyrethrum, sabadilla, nicotine and ryania), it is a valuable alternative to the synthetic pesticides in use today, as some insects have developed resistance in response to the heavy use of synthetic pesticides. In contrast, botanical pesticides exert their action through a variety of biochemical lesions and, therefore, can control neurotoxicant-resistant insects. Additionally, as naturally occurring substances, botanical pesticides appear to be metabolized to less toxic derivatives. For rotenone, these are the polar rotenolones and hydroxyrotenone (Fukami *et al.*, 1967). Rotenone photochemically decomposes to form over 20 degradation products, including rotenoids, rotenolones and rotenonone, and their expoxides (Carson, 1962; Brien, 1967; Fukami *et al.*, 1967; Haley, 1978; Engstrom-Heg & Colesante, 1979; Newsome & Scheneider, 1980; Gosalvez, 1983).

Rotenone is biochemically very active, exerting its effects mainly by blocking oxidative phosphorylation and/or mitosis in cells through apparently separate pathways (Loffler & Schneider, 1982). It is important to obtain information on the mode of action and selectivity of rotenone so that it can be used safely and efficiently. The three-dimensional structure of most biologically active molecules plays a role in governing their interactions and activities. In the course of a systematic study of the relation between the structure and bioactivity of rotenone, we have isolated the title compound, (I), and report here its preparation and structure.



(I)

Fig. 1 shows the title molecule with the atom-numbering scheme. Except for the isopropenyl group, the non-H atoms lie close to the plane of aromatic rings I and IV, resulting in an approximately V-shaped molecule with an angle of 78.7 (4)° between the planes of rings I and IV. Some ring torsion angles are given in Table 1. Ring II has a typical cyclohexene-like monoplanar conformation (Bucourt, 1974) and ring III adopts a 1,2-diplanar conformation (Bucourt, 1974). The five-membered ring, V, has an envelope conformation with the isopropenyl group in an equatorial position, as proposed

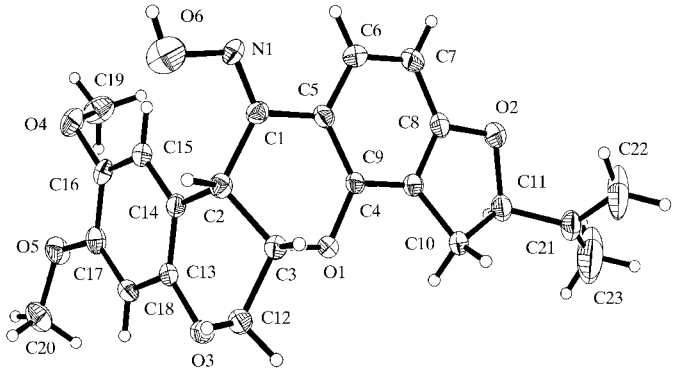


Figure 1
A view of the structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are shown at the 50% probability level.

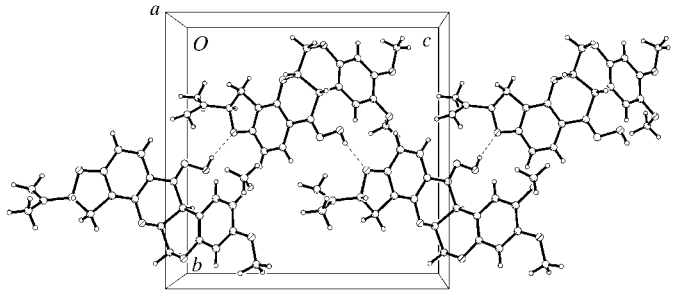


Figure 2
A perspective view of the molecular packing of (I), viewed along the *a* axis.

  DOI: 10.1107/S010827010301117X

previously by Büchi *et al.* (1961) and Carlson *et al.* (1973). The methoxy groups are not coplanar with ring I; the angles between the plane of ring I and planes C20—O5—C17 and C19—O4—C16 are 12.5 (3) and 73.1 (4)°, respectively.

The packing of (I) is shown in Fig. 2. The molecules are able to fit together tightly, maximizing intermolecular interaction through hydrogen bonds between the O6 hydroxy group and the O atom of ring V [O6···O2^{i} = 2.997 (4) Å, O6—H20 = 0.82 Å, H20···O2^{i} = 2.20 Å and O6—H20···O2^{i} = 165°; symmetry code: (i) $-x+\frac{3}{2}, -y+1, z+\frac{1}{2}$].

Experimental

Rotenone (5 g), hydroxylamine hydrochloride (5 g) and sodium acetate (6 g) in ethyl alcohol (200 ml) were refluxed for 10 h, and then water was added until crystallization commenced. The resulting rotenone oxime was crystallized from alcohol, and a single crystal suitable for X-ray analysis was recrystallized from ethyl alcohol after two months.

Crystal data

$C_{23}H_{23}NO_6$
M_r = 409.42
Orthorhombic, $P2_12_12_1$
a = 9.3994 (10) Å
b = 14.4249 (15) Å
c = 14.8129 (15) Å
V = 2008.4 (4) Å^3
Z = 4
D_x = 1.354 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2303 reflections
θ = 5.1–44.2°
μ = 0.10 mm^{-1}
T = 293 (2) K
Block, colourless
0.58 × 0.40 × 0.36 mm

Data collection

Bruker CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Bruker, 1998)
T_{min} = 0.865, T_{max} = 1.000
12 340 measured reflections
4704 independent reflections
2808 reflections with $I > 2\sigma(I)$
R_{int} = 0.058
θ_{max} = 28.3°
$h = -12 \rightarrow 12$
$k = -19 \rightarrow 19$
$l = -10 \rightarrow 19$

Table 1
Selected torsion angles (°).

C5—C1—C2—C3	34.7 (4)	C8—C9—C10—C11	−13.1 (3)
C4—O1—C3—C2	46.4 (3)	C8—O2—C11—C10	−18.7 (3)
C1—C2—C3—O1	−52.6 (3)	C9—C10—C11—O2	18.9 (3)
C14—C2—C3—C12	−46.4 (3)	C13—O3—C12—C3	−36.4 (4)
C3—O1—C4—C5	−20.6 (4)	C2—C3—C12—O3	55.2 (4)
O1—C4—C5—C1	1.4 (5)	C12—O3—C13—C14	10.0 (4)
C2—C1—C5—C4	−9.9 (4)	O3—C13—C14—C2	−4.3 (5)
C11—O2—C8—C9	10.9 (4)	C3—C2—C14—C13	23.2 (4)
O2—C8—C9—C10	1.9 (4)		

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.064
$wR(F^2)$ = 0.176
S = 0.92
4704 reflections
277 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0983P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.006
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.52 e Å^{-3}

The absolute structure of (I) was not determined, and the initial material, rotenone, was used as the basis of the configuration (Rossi *et al.*, 1988). Atoms C22 and C23 of the isopropenyl group were disordered; the occupancy factors for atoms C22 and C23 were accordingly reduced and their secondary positions, C22′ and C23′, were included. The occupancy factors for C22/C23 and C22′/C23′ were 0.667 and 0.333, respectively. H-atom occupancy factors were consistent with those of the corresponding C atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998) and *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXL*97.

We acknowledge the financial support of the NSFC (grant No. 30100118) and the SHTU (science grant No. 870).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1014). Services for accessing these data are described at the back of the journal.

References

Büchi, G., Crombie, L., Godin, P. J., Kaltenbronn, J. S., Siddalingaiah, K. S. & Whiting, D. A. (1961). *J. Chem. Soc.* pp. 2843–2860.
Bucourt, R. (1974). *Top. Stereochem.* **8**, 159–175.
Bruker (1998). *SMART*, *SAINT*, *SHELXTL* (Version 5) and *SADABS* (Version 5). Bruker AXS Inc., Madison, Wisconsin, USA.
Carlson, D. G., Weisleder, D. & Tallent, W. H. (1973). *Tetrahedron*, **29**, 2731–2735.
Carson, R. L. (1962). *Silent Spring*. New York: Fawcett Crest.
Engstrom-Heg, R. & Colesante, R. T. (1979). *N. Y. Fish Game J.* **26**, 22–36.
Fukami, J. I., Yamamoto, I. & Casida, J. (1967). *Science*, **155**, 713–716.
Gosalvez, M. (1983). *Life Sci.* **32**, 809–816.
Haley, T. J. (1978). *J. Environ. Pathol. Toxicol.* **1**, 315–337.
Loffler, M. & Schneider, F. (1982). *Mol. Cell. Biochem.* **48**, 77–90.
McEwen, F. L. & Stephenson, G. R. (1979). In *The Use and Significance of Pesticides in the Environment.* New York: Wiley.
Newsome, W. H. & Scheneider, F. B. (1980). *J. Agric. Food Chem.* **28**, 722–724.
O'Brien, R. D. (1967). In *Insecticide Action and Metabolism.* New York/London: Academic Press.
Rossi, M., Fule, P. Z. & Taylor, M. R. (1988). *Bioorg. Chem.* **16**, 376–387.
Sheldrick, G. M. (1997). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Ware, G. W. (1983). In *Pesticides Theory and Application.* San Franciso: Freeman.