

A new polymorph of atranorin, a lichen paradespide

Yen-Hsiang Liu,[†] Steven L. Robbs, Frank R. Fronczek,* Steven F. Watkins and Nikolaus H. Fischer[‡]

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803-1804, USA

[†] Current address: Institute of Chemistry, Academia Sinica, Taipei 115, Taiwan

[‡] Current address: Department of Pharmacognosy, Research Institute of Pharmaceutical Sciences, School of Pharmacy, University of Mississippi, University, MS 38677, USA

Correspondence e-mail: ffronz@lsu.edu

Key indicators

Single-crystal X-ray study

$T = 120\text{ K}$

Mean $\sigma(\text{C}-\text{C}) = 0.002\text{ \AA}$

R factor = 0.050

wR factor = 0.137

Data-to-parameter ratio = 22.3

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the title compound, methyl 4-(3-formyl-2,4-dihydroxy-6-methyl-benzoyloxy)-2-hydroxy-3,6-dimethylbenzoate, $\text{C}_{19}\text{H}_{18}\text{O}_8$, there are three intramolecular $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds, with lengths 2.5515 (14), 2.5711 (15), and 2.5437 (13) \AA . The two aromatic rings form a dihedral angle of $60.38(3)^\circ$, differing from that in the previously reported *Pbca* polymorph, *viz.* $84(1)^\circ$.

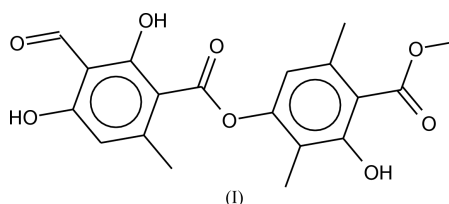
Received 27 June 2002

Accepted 4 July 2002

Online 19 July 2002

Comment

The title compound, (I), was isolated from the lichen *Cladonia prostrata*, which was being studied for allelopathic activity in the Florida Scrub (Robbs, 1997). Atranorin has been reported to show phytotoxic activity against watercress and to stimulate growth of oats (Huneck & Schreber, 1972), and also to stimulate the growth of *Rudbeckia* (Robbs, 1997). The crystal structure has been reported in space group *Pbca* (Brassy *et al.*, 1982), but recrystallization from ethyl acetate yielded a monoclinic polymorph, the structure of which is reported here.



The conformation of the molecule is described by the five torsion angles in Table 1, and is such that the two aromatic rings form a dihedral angle of $60.38(3)^\circ$. This conformation differs from that observed in the *Pbca* polymorph, mainly in the torsion angle $\text{C11}-\text{O4}-\text{C1}-\text{C2}$, which has a value of $89(1)^\circ$, causing the dihedral angle between the aromatic rings to be much more nearly orthogonal, $84(1)^\circ$. Smaller differences in torsion angles also exist between the two polymorphs about $\text{C4}-\text{C9}$, $10(1)^\circ$, and $\text{C11}-\text{C12}$, $8(1)^\circ$.

The molecule in the reported polymorph exhibits three intramolecular hydrogen bonds (Table 2), one of which is bifurcated, having an intermolecular component which forms dimers about an inversion center (Fig. 2). The hydrogen bonding in the *Pbca* polymorph is similar. In that structure, the three intramolecular hydrogen bonds also exist, and atom O7 also has an intermolecular component. However, it does not form dimers as does the present structure, but instead forms chains, with the intermolecular acceptor being O3.

The cell dimensions at 293 K are $a = 10.922(2)$, $b = 11.257(2)$, and $c = 14.875(3)$ \AA , and $\beta = 109.60(2)^\circ$.

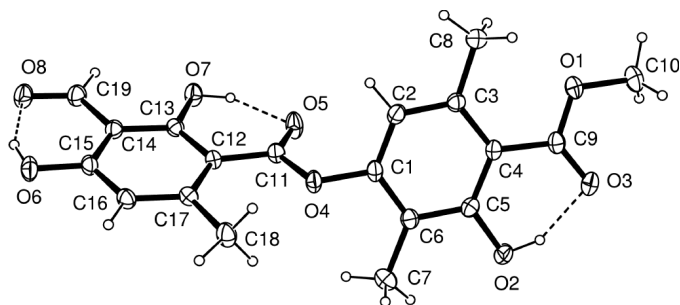


Figure 1
The atom-numbering scheme for (I), with ellipsoids at the 50% probability level, showing the intramolecular hydrogen bonds.

Experimental

The title compound was isolated from the CH_2Cl_2 extract of a sample of the lichen *Cladonia prostrata*, collected in Sebring, Florida. Crystals were grown from ethyl acetate.

Crystal data

$\text{C}_{19}\text{H}_{18}\text{O}_8$
 $M_r = 374.33$
Monoclinic, $P2_1/n$
 $a = 10.929$ (3) Å
 $b = 10.976$ (3) Å
 $c = 14.843$ (3) Å
 $\beta = 109.745$ (12)°
 $V = 1675.7$ (7) Å³
 $Z = 4$

$D_x = 1.484$ Mg m⁻³
Mo $K\alpha$ radiation
Cell parameters from 5466 reflections
 $\theta = 2.5\text{--}32.0^\circ$
 $\mu = 0.12$ mm⁻¹
 $T = 120$ K
Prism, colorless
 $0.40 \times 0.30 \times 0.15$ mm

Data collection

KappaCCD diffractometer with an Oxford Cryosystems Cryostream cooler
 ω scans with κ offsets
Absorption correction: none
21781 measured reflections
5796 independent reflections

4257 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.025$
 $\theta_{\text{max}} = 32.0^\circ$
 $h = -16 \rightarrow 16$
 $k = -16 \rightarrow 15$
 $l = -22 \rightarrow 22$

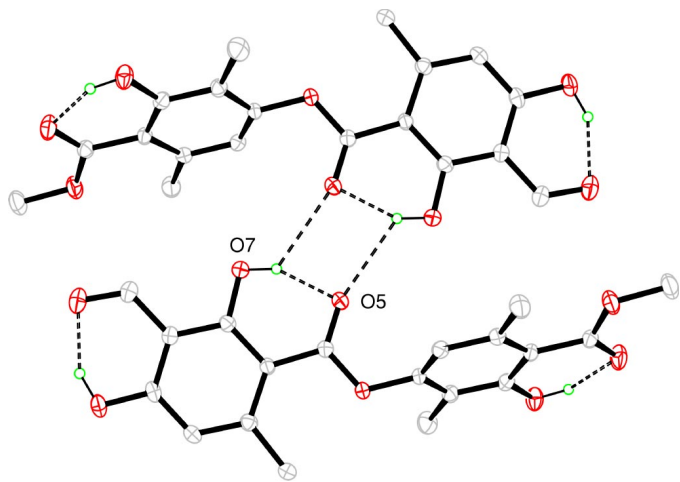


Figure 2
The hydrogen-bonded dimer about the the center at (1/2, 0, 1/2). Only the hydroxy H atoms are shown.

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.050$
 $wR(F^2) = 0.137$
 $S = 1.06$
5796 reflections
260 parameters
H atoms treated by a mixture of independent and constrained refinement

$$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2 + 0.7055P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\text{max}} < 0.001$$

$$\Delta\rho_{\text{max}} = 0.43 \text{ e \AA}^{-3}$$

$$\Delta\rho_{\text{min}} = -0.29 \text{ e \AA}^{-3}$$

Table 1

Selected geometric parameters (Å, °).

C11—O4—C1—C2	63.23 (15)	O5—C11—C12—C13	−4.84 (19)
C3—C4—C9—O1	−10.13 (18)	C15—C14—C19—O8	−2.3 (2)
C1—O4—C11—C12	−172.30 (11)		

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O2—H2O \cdots O3	0.89 (2)	1.72 (2)	2.5515 (14)	152.5 (18)
O6—H6O \cdots O8	0.90 (2)	1.74 (2)	2.5711 (15)	151.1 (18)
O7—H7O \cdots O5	0.87 (2)	1.74 (2)	2.5437 (13)	151.9 (18)
O7—H7O \cdots O5 ⁱ	0.87 (2)	2.437 (19)	3.0251 (14)	125.1 (16)

Symmetry code: (i) $1 - x, -y, 1 - z$.

H atoms on C atoms were placed in calculated positions, with C—H distances in the range 0.95–1.00 Å and thereafter treated as riding. A torsional parameter was refined for each methyl group. Hydroxy H atoms were placed from difference maps, and their coordinates were refined. $U_{\text{iso}} = 1.2U_{\text{eq}}$ of the attached atom ($1.5U_{\text{eq}}$ for methyl and OH groups).

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* for Windows (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

The purchase of the diffractometer was made possible by grant No. LEQSF(1999-2000)-ESH-TR-13, administered by the Louisiana Board of Regents.

References

- Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
- Brassy, C., Bachet, B., Bodo, B. & Molho, D. (1982). *Acta Cryst.* **B38**, 3126–3128.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Huneck, S. & Schreiber, K. (1972). *Phytochemistry*, **11**, 2429–2434.
- Nonius (1999). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
- Robbs, S. L. (1997). PhD dissertation, Louisiana State University, USA.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.