

3-( $\alpha$ -Hydroxy-2-methoxybenzylidene)-1-isopropylpyrrolidine-2,4-dione

You-Quan Zhu, Hai-Bin Song, Chang-Sheng Yao, Ying Gao, Fang-Zhong Hu, Xiao-Mao Zou and Hua-Zheng Yang\*

State Key Laboratory and Institute of Elemento-Organic Chemistry, Nankai University, Tianjin 300071, People's Republic of China

Correspondence e-mail: youquan\_zhu@mail.nankai.edu.cn

## Key indicators

Single-crystal X-ray study

$T = 293\text{ K}$

Mean  $\sigma(\text{C}-\text{C}) = 0.004\text{ \AA}$

$R$  factor = 0.038

$wR$  factor = 0.091

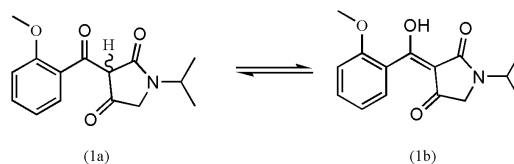
Data-to-parameter ratio = 9.2

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

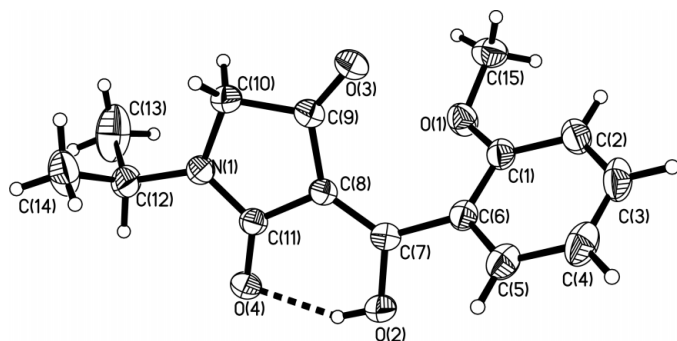
The title compound,  $\text{C}_{15}\text{H}_{17}\text{NO}_4$ , is a potent new herbicide containing the pyrrolidine-2,4-dione ring system. In the crystalline state, the molecular skeleton contains one enol grouping, which is intramolecularly hydrogen bonded to a neighboring keto O atom.

## Comment

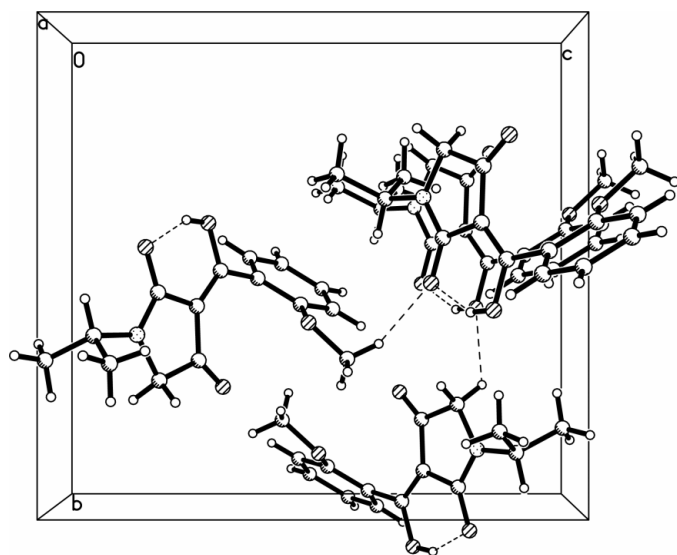
Many compounds containing the 3-acylpyrrolidine-2,4-dione moiety are novel heterocyclic compounds with antibiotic activity; these include tenuazonic acid (Stickings, 1959), streptolydigin (Rinehart *et al.*, 1963), tirandamycin (Rinehart *et al.*, 1971), malonomycin (Bann *et al.*, 1978),  $\alpha$ -cyclopiazonic acid (Stickings, 1959; van Rooyen, 1992) and  $\beta$ -cyclopiazonic acid (Holzapfel *et al.*, 1970). All these compounds possess a 3-acyltetramic acid grouping as a tricarbonylmethane fragment, and the hydrogen chemical shift of the enol hydroxy group is  $\sim 11$  p.p.m. (Wu *et al.*, 2002). Most of the excellent inhibitors of *p*-hydroxyphenylpyruvate dioxygenase also possess similar characteristics, which are crucial for their two kinds of bioactivity (Zhu *et al.*, 2004). Hitherto, we have synthesized a series of 3-(un)substituted benzoyl-1-alkylpyrrolidine-2,4-dione compounds, some of which have high herbicidal activity. The structure reported here, (1b), helps us to investigate the relationship between structure and herbicidal activity.



The analysis of crystals grown from a solution of 3-(2-methoxybenzoyl)-1-isopropylpyrrolidine-2,4-dione, (1a), showed that we had obtained crystals of the related tautomeric form, *viz.* 1-iso-propyl-3-( $\alpha$ -hydroxy-2-methoxybenzylidene)-pyrrolidine-2,4-dione, (1b). The molecular structure of (1b) is shown in Fig. 1. Atom H2, involved in intramolecular hydrogen bonding between O2 and O4, was assigned to O2 rather than to O4, on the basis of the bond lengths. The C11—O4 distance is 1.252 (3) Å, which is longer than the normal carbonyl bond length (C9=O3) of 1.210 (5) Å. In contrast, the C7—O2 distance, 1.331 (3) Å, is intermediate between the normal carbonyl C=O bond and the C—O single bond length (Allen *et al.*, 1987). A similar situation has been reported for 3-(1-hydroxyethylidene)-1-phenylpyrrolidine-2,4-dione (Ellis & Spek, 2001). The crystal structure of (1b) also involves two weak C—H $\cdots$ O hydrogen-bonding interactions (Fig. 2 and Table 2).



**Figure 1**  
A view of the title compound, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 40% probability level. The intramolecular hydrogen bond is indicated by a dashed line.



**Figure 2**  
A packing diagram, showing the intra- and intermolecular hydrogen bonds as dashed lines.

## Experimental

The title compound was obtained according to a reported procedure (Matsuo *et al.*, 1980). Colorless single crystals were obtained by recrystallization of 1-isopropyl-3-( $\alpha$ -hydroxy-2-methoxybenzylidene)pyrrolidine-2,4-dione from petroleum ether and ethyl acetate.

### Crystal data

$C_{15}H_{17}NO_4$   
 $M_r = 275.30$   
Orthorhombic,  $P2_12_12_1$   
 $a = 6.981$  (2) Å  
 $b = 13.720$  (4) Å  
 $c = 14.863$  (5) Å  
 $V = 1423.5$  (8) Å<sup>3</sup>  
 $Z = 4$   
 $D_x = 1.285$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
Cell parameters from 939 reflections  
 $\theta = 2.7$ – $23.7^\circ$   
 $\mu = 0.09$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
Prism, colorless  
 $0.22 \times 0.20 \times 0.16$  mm

### Data collection

Bruker SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)  
 $T_{\min} = 0.965$ ,  $T_{\max} = 0.985$   
8260 measured reflections

1701 independent reflections  
1300 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.031$   
 $\theta_{\text{max}} = 26.4^\circ$   
 $h = -8 \rightarrow 8$   
 $k = -17 \rightarrow 14$   
 $l = -18 \rightarrow 16$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.038$   
 $wR(F^2) = 0.091$   
 $S = 1.07$   
1701 reflections  
185 parameters  
H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0464P)^2 + 0.0951P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.11$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.14$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

O1—C1	1.356 (3)	N1—C12	1.460 (3)
O1—C15	1.429 (3)	C6—C7	1.472 (3)
O2—C7	1.331 (3)	C7—C8	1.363 (3)
O3—C9	1.210 (3)	C8—C9	1.453 (3)
O4—C11	1.252 (3)	C8—C11	1.454 (3)
N1—C11	1.331 (3)	C9—C10	1.522 (4)
N1—C10	1.455 (3)		
C1—O1—C15	118.1 (2)	O3—C9—C8	130.9 (2)
C11—N1—C10	111.63 (18)	O3—C9—C10	123.4 (2)
C11—N1—C12	124.8 (2)	C8—C9—C10	105.7 (2)
C10—N1—C12	123.5 (2)	N1—C10—C9	104.78 (19)
O2—C7—C8	119.5 (2)	O4—C11—N1	125.3 (2)
O2—C7—C6	113.0 (2)	O4—C11—C8	124.4 (2)
C8—C7—C6	127.5 (2)	N1—C11—C8	110.28 (18)
C7—C8—C9	131.4 (2)	N1—C12—C13	111.2 (2)
C7—C8—C11	120.8 (2)	N1—C12—C14	111.5 (2)
C9—C8—C11	107.6 (2)	C13—C12—C14	111.1 (3)
C5—C6—C7—O2	−50.5 (3)	O2—C7—C8—C11	−1.9 (3)
C1—C6—C7—O2	127.5 (2)	C11—C8—C9—O3	177.5 (3)
C5—C6—C7—C8	127.4 (3)	C7—C8—C9—C10	−175.7 (2)
C1—C6—C7—C8	−54.6 (3)	C12—N1—C10—C9	178.3 (2)
O2—C7—C8—C9	172.5 (3)	O3—C9—C10—N1	−178.5 (2)
C6—C7—C8—C9	−5.3 (4)		

**Table 2**

Hydrogen-bonding geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O2—H2 $\cdots$ O4	0.82	1.81	2.555 (3)	150
C15—H15C $\cdots$ O4 <sup>i</sup>	0.96	2.50	3.192 (3)	129
C10—H10A $\cdots$ O2 <sup>ii</sup>	0.97	2.56	3.271 (3)	130

Symmetry codes: (i)  $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$ ; (ii)  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ .

All H atoms were placed in calculated positions, with C—H = 0.93–0.98 Å and O—H = 0.82 Å, and included in the final cycles of refinement using a riding model, with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$  or  $1.5U_{\text{eq}}(\text{O})$ . In the absence of significant anomalous dispersion effects, Friedel pairs were averaged, and the absolute configuration cannot be determined from the crystallographic experiment.

Data collection: SMART (Bruker, 1999); cell refinement: SMART; data reduction: SAINT (Bruker, 1999); program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: SHELXTL (Bruker, 1999); software used to prepare material for publication: SHELXTL.

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