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## Key indicators

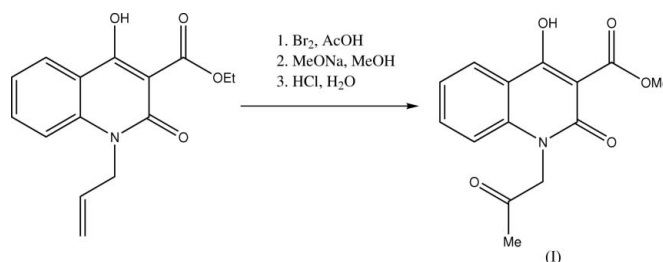
Single-crystal X-ray study  
 $T = 293\text{ K}$   
Mean  $\sigma(\text{C}-\text{C}) = 0.006\text{ \AA}$   
 $R$  factor = 0.049  
 $wR$  factor = 0.138  
Data-to-parameter ratio = 12.1For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

## Methyl 1-acetonyl-4-hydroxy-2-oxo-1,2-dihydroquinoline-3-carboxylate

The title compound,  $\text{C}_{14}\text{H}_{13}\text{NO}_5$ , exhibits a resonance-assisted hydrogen bond  $\text{O}-\text{H}\cdots\text{O}=\text{C}$  [2.505 (4) Å], which leads to a lengthening of the carbonyl  $\text{C}=\text{O}$  bond, a shortening of the  $\text{C}-\text{OH}$  bond and delocalization of the electron density within the dihydropyridine ring.

## Comment

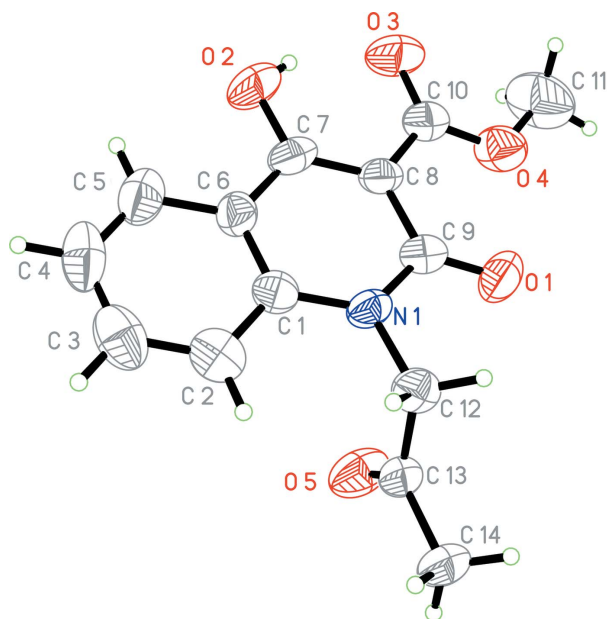
Ethyl esters of 1-alkyl (or aryl) 4-hydroxy-2-oxo-1,2-dihydroquinoline-3-carboxylic acids give different products during bromination in acetic acid. In the presence of water this reaction leads to the corresponding 3-bromo-3-ethoxycarbonyl-2,4-dioxo-1,2,3,4-tetrahydroquinolines (Ukrainets *et al.*, 1995). Dehydration of the solvent and reagents results in the formation of 6-bromo-substituted derivatives (Ukrainets *et al.*, 2004).



Recently it was found (Ukrainets *et al.*, 2005) that the ethyl ester of 1-allyl-4-hydroxy-2-oxo-1,2-dihydroquinoline-3-carboxylic acid shows different behaviour under some reaction conditions. This bromination reaction is accompanied by the reaction of interesterification, but more important changes occur on the *N*-allyl substituent. We can assume that the bromination of the reactant leads to the *N*-2,3-dibromopropyl derivative. It is known that such vicinal dibromides undergo easy dehydrobromination in the presence of strong bases. The resulting acetylenes, with a terminal triple bond, give the corresponding ketones in the acid medium. The bromination product of the reactant was treated with sodium methoxide in methanol. The 2-oxoquinoline, (I), was isolated after delution of the reaction mixture with water and acidification with hydrochloric acid. In the present paper, we report the crystal structure of the title compound, (I).

All non-H atoms of the molecule, except atoms C13, C14, O5, C11, O4 and O3, are coplanar within 0.04 Å. The formation of the  $\text{O2}-\text{H2O}\cdots\text{O3}$  intramolecular hydrogen bond (Tables 1 and 2) affects bond lengths in the hydroxy and ester groups as observed for resonance-assisted hydrogen bonds (Gilli & Bertolasi, 1990; Jeffrey, 1997): the  $\text{O3}-\text{C10}$  bond is longer than the standard value for the  $\text{C}=\text{O}$  bond (1.210 Å;

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**Figure 1**  
View of the title compound. The non-H atoms are shown with displacement ellipsoids drawn at the 50% probability level.

Bürgi & Dunitz, 1994) and the O2—C7 bond is shorter than the standard value for the  $Csp^2$ —O bond length (1.362 Å). The presence of the hydrogen bond results in the delocalization of the electron density within the dihydropyridine ring; the C7=C8 bond is longer and the C6—C7 bond is shorter than standard values for C=C (1.334 Å) and  $Csp^2$ — $Csp^2$  (1.455 Å) bond lengths, respectively (Bürgi & Dunitz, 1994). The substituent at atom C8 is slightly displaced with respect to the plane of the bicyclic fragment; the C7—C8—C10—O4 torsion angle is 170.9 (3)°. The repulsion between the substituent at atom N1 and the carbonyl group and the H atom in the *peri*-position of the benzene ring results in shortened intramolecular contacts: O1···H12A = 2.24 Å [van der Waals radii sum is 2.46 Å (Zefirov & Zorky, 1995)], H2···C12 = 2.52 Å (van der Waals sum 2.87 Å), H12B···C2 = 2.59 Å (van der Waals sum 2.87 Å), H12B···H2 = 2.08 Å (van der Waals sum 2.34 Å), C13···C2 = 3.34 Å (van der Waals sum 3.42 Å) and C13···H2 = 2.84 Å (van der Waals sum 2.87 Å). The planar substituent at atom N1 is oriented almost orthogonal to the plane of the pyridine ring; the C1—N1—C12—C13 torsion angle is 82.2 (4)°. In the crystal structure, molecules are stacked along [001] with an intermolecular contact C10···C4( $x, 1 + \frac{1}{2} - y, \frac{1}{2} + z$ ) = 3.39 Å (van der Waals radii sum 3.42 Å).

## Experimental

To a stirred solution of ethyl 1-allyl-4-hydroxy-2-oxo-1,2-dihydroquinoline-3-carboxylate monohydrate (2.91 g, 10.0 mmol) in acetic acid (50 ml) was added bromine (0.52 ml, 10.0 mmol) (the solution became colourless). The mixture was diluted with water. The precipitate formed was filtered off, washed with cold water and dried. The product obtained was added to a solution of sodium (1.15 g, 50.0 mmol) in methanol (50 ml), and the mixture was refluxed for 1 h. After cooling, the reaction mixture was diluted with water and

acidified with HCl to pH 4. The isolated ester (I) was filtered off, washed with water and dried. Yield 2.06 g (76%). M.p. 450–452 K (from ethanol).

## Crystal data

$C_{14}H_{13}NO_5$   
 $M_r = 275.25$   
Monoclinic,  $P2_1/c$   
 $a = 11.084$  (4) Å  
 $b = 15.120$  (5) Å  
 $c = 8.133$  (3) Å  
 $\beta = 109.77$  (3)°  
 $V = 1282.7$  (8) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.425$  Mg m<sup>-3</sup>  
Mo  $K\alpha$  radiation  
Cell parameters from 12 reflections  
 $\theta = 2$ –25°  
 $\mu = 0.11$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
Block, colourless  
0.40 × 0.20 × 0.20 mm

## Data collection

Siemens P3/PC diffractometer  
 $\omega$ – $2\theta$  scans  
Absorption correction: none  
2406 measured reflections  
2238 independent reflections  
857 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.069$

$\theta_{max} = 25.1^\circ$   
 $h = -13 \rightarrow 12$   
 $k = -18 \rightarrow 0$   
 $l = 0 \rightarrow 9$   
2 standard reflections  
every 98 reflections  
intensity decay: 5%

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.049$   
 $wR(F^2) = 0.138$   
 $S = 0.88$   
2238 reflections  
185 parameters  
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0631P)^2]$   
where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{max} < 0.001$   
 $\Delta\rho_{max} = 0.17$  e Å<sup>-3</sup>  
 $\Delta\rho_{min} = -0.17$  e Å<sup>-3</sup>  
Extinction correction: *SHELXL97*  
Extinction coefficient: 0.0044 (13)

**Table 1**

Selected bond lengths (Å).

N1—C1	1.385 (4)	O4—C10	1.315 (4)
N1—C9	1.402 (4)	C6—C7	1.422 (5)
O1—C9	1.216 (4)	C7—C8	1.384 (5)
O2—C7	1.324 (4)	C8—C10	1.447 (5)
O3—C10	1.234 (4)		

**Table 2**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2O···O3	0.82	1.77	2.505 (4)	148

All H atoms, except the H atom of the hydroxy group, were placed in calculated positions and included in the refinement in the riding-model approximation, with  $U_{iso}$  constrained to be 1.2 times  $U_{eq}$  of the carrier atom (C—H = 0.93–0.97 Å). The H atom of the hydroxy group was located in an electron density difference map and then treated as riding [ $U_{iso}(H) = 1.5U_{eq}(O)$ ].

Data collection: *P3* (Siemens, 1989); cell refinement: *P3*; data reduction: *XDISK* (Siemens, 1991); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1991); software used to prepare material for publication: *SHELXL97*.

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