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Crystal structure of 3-oxo-2-(4-hydroxybenzylidene)-butyric acid ethyl ester

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3-Oxo-2-(4-hydroxybenzylidene)-butyric acid ethyl ester (compound **I**), was synthesized and its structure was investigated by X-ray crystallography, IR, ^{1}H-NMR and mass-spectroscopic analyses. The title compound, $C_{13}H_{14}O_4$, crystallizes in the triclinic crystal system in the space group $P\bar{1}$ with cell parameters: $a = 8.7340(14)$ Å, $b = 9.1602(13)$ Å, $c = 9.1640(30)$ Å, $\alpha = 114.964(15)°$, $\beta = 100.197(18)°$, $\gamma = 108.173(11)°$, and $V = 589.5(3)$ Å^3 ($Z = 2$). The molecules are hydrogen-bonded to chains, running parallel to [110]. Additional short contacts stabilize the three dimensional packing in the structure.

Key words: 3-oxo-2-(4-hydroxybenzylidene)-butyric acid ethyl ester, crystal structure.

INTRODUCTION

The investigations on the interaction between 1,3-dicarbonylic compounds (ethyl acetoacetate or 2,4-pentandione) and aldehydes or ketones began at the end of XIX century and they are continuing until now [1, 2]. It was accepted that one of the factors for obtaining large diversity of condensation products is the molar ratio of the reactants, the temperature and the catalyst. Recently we started a systematical investigation of the synthetic products of aromatic aldehydes and ethyl acetoacetate in the presence of piperidine as a catalyst. Here we present crystal structure of 3-oxo-2-(4-hydroxybenzylidene)-butyric acid ethyl ester (**I**), $C_{13}H_{14}O_4$ – a side product obtained in the studied system.

EXPERIMENTAL

Synthesis and characterization

The title compound (**I**) was obtained according to the reaction scheme

The used materials were 4-Hydroxybenzaldehyde (3.66 g, 0.03 mol), acetoacetic ester (6.5 g, 0.05 mol), piperidine (2.6 g, 0.03 mol), glacial acetic acid (2.4 g, 0.04 mol), and 100 mL distilled water. Yellow rectangular crystals suitable for X-ray diffraction analysis have been obtained after slow evaporation from isopropyl alcohol at room temperature.

Elemental analyses: $C_{13}H_{14}O_4$, (234), (C, H) (calculated/measured): % C 66.66 / 66.50, % H 6.02 / 5.94. UV-VIS spectra: λmax = 206, 224, 286 nm (ethanol);

FTIR (nujol): 3325.7, 1732.3, 1641.6, 1597.3, 1205.7, 819.8 cm^{-1};

^{1}H NMR (acetone-d$_6$, 200 MHz): δ = 1.3 (t, J = 7.1 Hz, 3H) (methyl), 2.3 (s, 3H)(methyl), 4.3 (q, J = 7.1 Hz, 2H) (methylene), 6.91–6.85 (m, 2H) (aromatic), 7.44–7.38 (m, 2H) (aromatic), 7.46–7.44 (m, 1H) (methine), 10.5 (s, 1H)(hydroxyl);

^{13}C NMR (acetone-d$_6$, 67 MHz): δ = 15, 30, 55, 110, 116, 130, 135, 140, 142, 160, 166, 190, 196;

EIMS: m/z (%) = 234 (100, M$^+$), 233 (57), 220 (10), 219 (69), 217 (17), 205 (15), 191 (25.4), 189 (38.25), 187 (11.3), 175 (8.7), 163 (11.3), 161 (11.3), 160 (28.7), 151 (28.7), 147 (68.7), 146 (11.3), 145 (37.4), 131 (7), 123 (30.4), 120 (9.6), 119 (20), 118

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(19.1), 115 (2.6), 107 (6), 91 (20), 89 (19.1), 77 (7), 65 (11.3), 63 (12.1), 53 (5), 45 (0.9).

X-ray single crystal analyses

A crystal of the title compound having approximate dimension 0.22×0.20×0.20 mm was placed on a glass fiber and mounted on an Enraf-Nonius CAD-4 diffractometer. X-ray data collection was carried out at 290 K with graphite monochromatized Mo-Kα radiation (λ = 0.71073 Å). The unit cell parameters were determined using 15 reflections and refined employing 22 higher-angle reflections, $18 < \theta < 20°$. The ω/2θ technique was used for data collection using Nonius Diffractometer Control Software [3]. Lorentz and polarization corrections were applied to intensity data using WinGX [4]. The structure was solved by direct methods using SHELXS-97 [5] and refined by full-matrix least-squares procedure on F^2 with SHELXL-97 [5]. The hydrogen atoms were placed in idealized positions and refined as riding on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}$(C or O).

RESULTS AND DISCUSSION

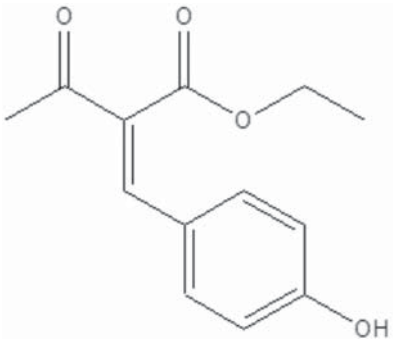
The chemical diagram of the studied compound (**I**) is illustrated in Scheme 1 and experimental conditions, crystal data and refinement parameters are summarized in Table 1. Selected

Table 1. Data collection parameters, crystal data and refinement parameters

Data collection parameters	
Enraf Nonius CAD4 diffractometer	R_{int} = 0.0502
Radiation source: sealed tube	θ_{max} = 29.96°
Monochromator: graphite	θ_{min} = 2.63°
T = 290(2) K	h = –12 12
non–profiled ω/2θ scans	k = –12 12
Absorption correction: none	l = –12 12
6790 measured reflections	3 standard reflections
2436 independent reflections	every 120 min
1933 reflections with $I > 2\sigma(I)$	intensity decay: –1%
Crystal data	
C13 H14 O4	F_{000} = 248
M_r = 234.24	D_x = 1.32 Mg m^{-3}
Triclinic, *P–1*	Melting point: not measured
Hall symbol: –P 1	Mo *K*α radiation
λ = 0.71073 Å	
a = 8.734 (2) Å	Cell parameters from 22 reflections
b = 9.160 (3) Å	θ = 18.0–28.8°
c = 9.163 (6) Å	μ = 0.11 mm^{-1}
α = 114.96 (3)°	T = 290 (2) K
β = 100.20 (3)°	Prism, colorless
γ = 108.17(1)°	Crystal size:
V = 589.5(5) Å^3	0.22 × 0.20 × 0.20 mm
Z = 2	
Refinement parameters	
Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0719P)^2 + 0.0263P]$
where $P = (F_o^2 + 2F_c^2)/3$	
$R[F^2 > 2\sigma(F^2)]$ = 0.052	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2)$ = 0.106	$\Delta\rho_{max}$ = 0.20 e Å^{-3}
S = 0.99	$\Delta\rho_{min}$ = –0.18 e Å^{-3}
3435 reflections	Extinction correction: none
154 parameters	

bond distances and bond angles are listed in Table 2. Hydrogen bonding geometry is presented in Table 3. A diagram of the molecular structure with 50% probability and the atom numbering scheme is shown in Fig. 1. The data for publication were prepared with WinGX [3], ORTEP [6], and Mercury [7] program packages.

In the asymmetric unit of **I** two symmetrically equivalent molecules are present. The structural parameters of the title compound are comparable with those reported earlier [8, 9] The phenyl ring system is essentially planar with r.m.s. deviations of 0.021(4) Å. In the three-dimensional arrangement of the molecules of **I** only one classical hydrogen bond could be described (Fig. 2). Additional C-H…O week interactions stabilize the molecular arrangement.



Scheme 1. Chemical diagram of the studied compound

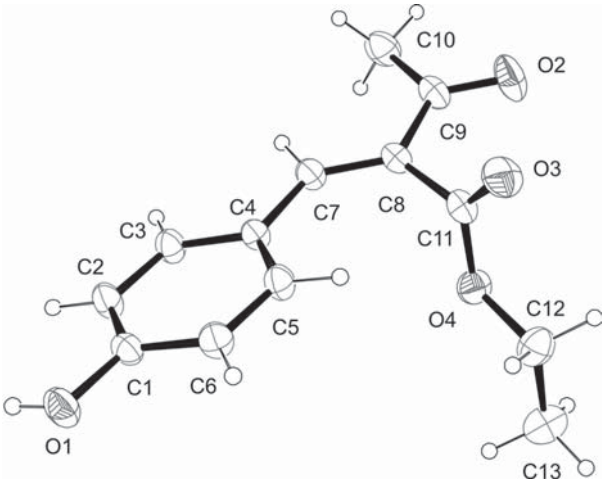


Fig. 1. View of molecule with an atom-numbering scheme. Displacement ellipsoids for the non-H atoms are drawn at the 50% probability level. The H atoms are presented with spheres with arbitrary radii.

Table 2. Selected geometrical parameters for I (Å, °)

O3 – C11	1.335(2)	C6 – C5	1.399(2)
O3 – C12	1.457(2)	C1 – C2	1.376(2)
O1 – C3	1.362(2)	C11 – O4	1.198(2)
C7 – C8	1.347(2)	C11 – C8	1.501(3)
C7 – C6	1.455(2)	C8 – C9	1.476(2)
C6 – C1	1.399(2)	C3 – C2	1.380(3)
C11 – O3 – C12	115.89(15)	C9 – C8 – C11	114.45(15)
C8 – C7 – C6	131.11(17)	O1 – C3 – C2	122.67(15)
C1 – C6 – C5	117.25(15)	O1 – C3 – C4	117.31(16)
C1 – C6 – C7	117.32(15)	C2 – C3 – C4	120.00(15)
C5 – C6 – C7	125.36(15)	C4 – C5 – C6	121.13(15)
C2 – C1 – C6	121.87(16)	C1 – C2 – C3	119.59(16)
O4 – C11 – O3	124.16(17)	C5 – C4 – C3	120.13(16)
O4 – C11 – C8	125.35(17)	O2 – C9 – C8	119.14(18)
O3 – C11 – C8	110.48(15)	O2 – C9 – C10	119.66(18)
C7 – C8 – C9	122.02(17)	C8 – C9 – C10	121.18(16)
C7 – C8 – C11	123.53(16)	O3 – C12 – C13	107.46(17)

Table 3. Hydrogen bond for I (Å, °)

D-H···A	D(D-H)	d(H···A)	d(D···A)	<(DHA)
O(1)-H(1)···O(2)^{i}	0.820	1.940	2.754(3)	169.2

Symmetry codes: (i) *1–x, 1–y, z*

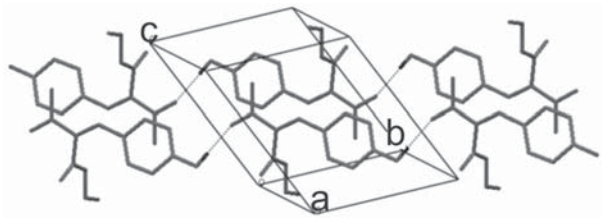


Fig. 2. Three-dimensional packing of the molecules. Only the hydrogen atoms involved in hydrogen bonding are shown.

SUPPLEMENTARY MATERIALS

CCDC 805277 contains the supplementary crystallographic data for this paper. This data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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КРИСТАЛНА СТРУКТУРА НА 3-OXO-2-(4-HYDROXYBENZYLIDENE)-BUTYRIC ACID ETHYL ESTER

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(Резюме)

3-Oxo-2-(4-hydroxybenzylidene)-butyric acid ethyl ester бе синтезирано и изследвано чрез монокристален рентгеноструктурен, ИЧ, ^{1}H-ЯМР и мас спектроскопски анализи. Съединението, $C_{13}H_{14}O_4$, кристализира в триклинна кристална система и пространствена група $\bar{P}1$ с параметри на елементарна клетка a = 8.7340(14) Å, b = 9.1602(13) Å, c = 9.1640(30) Å, α = 114.964(15)°, β = 100.197(18)°, γ = 108.173(11)° и V = 589.5(3) Å^3 (Z = 2). Молекулите са свързани с водородни връзки и образуват верижки паралелни на [110]. Тримерната структура е допълнително стабилизирана от слаби електростатични взаимодействия.