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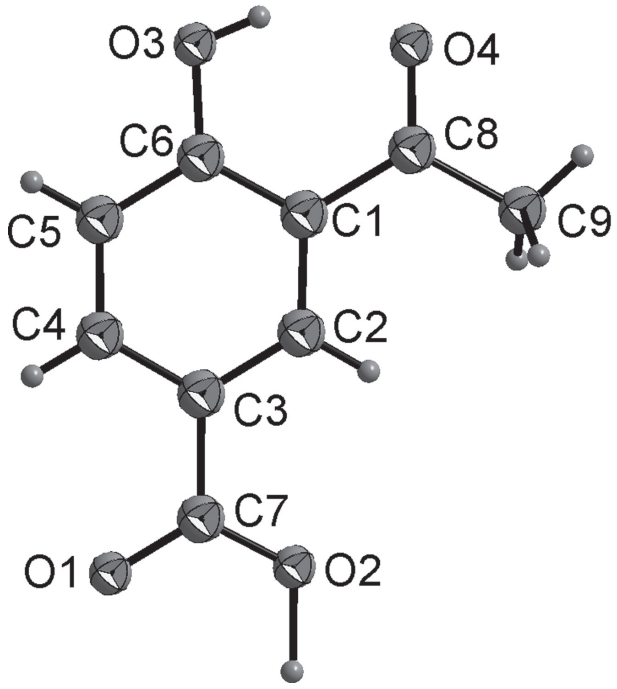
Crystal structure of 3-acetyl-4-hydroxybenzoic acid, $C_{18}H_{16}O_8$



https://doi.org/10.1515/ncrs-2020-0021
Received January 8, 2020; accepted February 28, 2020; available online March 25, 2020

Abstract

$C_{18}H_{16}O_8$, monoclinic, $P2_1/c$ (no. 14), $a = 5.3210(8)$ Å, $b = 5.1825(8)$ Å, $c = 29.598(5)$ Å, $\beta = 93.875(2)°$, $V = 814.3(2)$ Å^3, $Z = 2$, $R_{gt}(F) = 0.0340$, $wR_{ref}(F^2) = 0.1011$, $T = 296(2)$ K.

CCDC no.: 1987036

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Table 1: Data collection and handling.

Crystal:	Colorless block
Size:	0.20 × 0.12 × 0.12 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	0.12 mm^{-1}
Diffractometer, scan mode:	Bruker APEX-II, φ and ω-scans
θ_{max}, completeness:	25.5°, >99%
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	5627, 1503, 0.022
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 1350
$N(param)_{refined}$:	125
Programs:	Bruker programs [1], SHELX [2, 3], DIAMOND [4]

Source of materials

The mixture of methyl 4-acetoxybenzoate (1.94 g, 0.01 mol), $AlCl_3$(8.00 g, 0.06 moL) was reacted at 145 °C. When the sample was put into the pot, a large amount of white smoke was produced. The solid began to melt and continued to react. After the reaction completed (monitored by TLC), dilute hydrochloric acid (5%, 30 ml) was added slowly under ice water cooling and magnetic stirring. The white solid was filtered off and washed with water 3 times respectively. Then the solid was dissolved in sodium hydroxide solution (20%, 40 ml) and stirred at 45 °C for 2 hours. The reaction mixture was cooled to room temperature, pH was adjusted to 2-3 with dilute hydrochloric acid. A white solid was obtained, filtered, and the solid was washed 2-3 times, and finally dried. The title compound was crystallized from ethanol to get a white solid (1.4 g, 0.008 mol). The yield was 77.8%. The crystals were obtained after one week of slow volatilisation at room temperature.

Experimental details

All H atoms were included in calculated positions and refined as riding atoms, with O—H = 0.82 Å with U_{iso} (H) = 1.2 U_{eq} (O), C—H = 0.93–0.98 Å with U_{iso}(H) = 1.2–1.5 U_{eq}(C) [4].

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2).

Atom	*x*	*y*	*z*	U_{iso}*/U_{eq}
O1	0.7052(2)	0.2425(2)	0.49128(4)	0.0612(4)
O2	0.3621(2)	0.1223(2)	0.44956(4)	0.0611(4)
O3	0.7659(2)	1.0062(2)	0.32697(4)	0.0579(3)
H3	0.6685	0.9954	0.3044	0.087*
O4	0.3941(2)	0.8276(2)	0.27683(4)	0.0565(3)
H1	0.337(6)	-0.049(7)	0.4775(11)	0.169(13)*
C1	0.5045(2)	0.6541(3)	0.34885(4)	0.0373(3)
C2	0.4591(3)	0.4734(3)	0.38221(4)	0.0389(3)
H2	0.3248	0.3596	0.3774	0.047*
C3	0.6078(3)	0.4586(3)	0.42216(5)	0.0418(3)
C4	0.8107(3)	0.6293(3)	0.42918(5)	0.0498(4)
H4	0.9137	0.6195	0.4558	0.060*
C5	0.8589(3)	0.8102(3)	0.39732(5)	0.0520(4)
H5	0.9935	0.9232	0.4025	0.062*
C6	0.7076(3)	0.8263(3)	0.35712(5)	0.0427(3)
C7	0.5572(3)	0.2640(3)	0.45662(5)	0.0456(4)
C8	0.3513(3)	0.6630(3)	0.30531(5)	0.0403(3)
C9	0.1485(3)	0.4693(3)	0.29531(5)	0.0485(4)
H9A	0.0545	0.5146	0.2676	0.073*
H9B	0.0379	0.4666	0.3196	0.073*
H9C	0.2223	0.3017	0.2922	0.073*

Comment

Flavonoids, also known as bioflavonoids, are a class of natural compounds with the basic nuclear structure of 2-phenyl chromone flavone [5]. Flavonoids are widely existent in fruits, vegetables, seeds, pollen, bark and medicinal plants [6–9]. Flavonoids have been reported to exhibits a variety of pharmacological activities. Because of their extensive biological activity and strong pharmacological action, the synthesis of flavonoids have attracted much research interest [10–14]. The total synthesis of flavone compounds has two classical methods of the Baker-Venkataraman reaction and the Algar-Flynn-Oyamada reaction [15, 16]. We still focused on the synthesis and antibacterial activities of preservatives. In order to synthesis novel preservatives, we have designed and synthesised a series of flavonoids carboxylate glycosides *via* the chalcone route. Herein we report the synthesis and single crystals of the title compound as an important intermediate for the flavonoid synthesis [17].

There is one molecule in the asymmtric unit. The molecules in the title structure are connected by hydrogen bonds. In the molecule of the title compound bond lengths and angles within 3-acetyl-4-hydroxybenzoic acid are very similar to those given in the literature for methyl 4-acetoxybenzoate and p-hydroxybenzoic acid [18] and those in the structures of related benzoic acids [19, 20]. In the title structure, all the non-hydrogen atoms are almost approximately co-planor. The dihedral angles formed by the C1—C6 plane, the carboxlate group C7—O1—O2 plane and the acetyl group C8—C9—O4 plane are 4.4(1)°, 4.5(1)° and 8.8(1)°, respectively.

Acknowledgements: X-ray data were collected at Instrumental Analysis Center Nanchang Hangkong University, Nanchang, 330063, People's Republic of China. This study was supported by grants from Natural Science Foundation of Education Department of Jiangxi Province (Nos. GJJ160382, 170275), and Natural Science Foundation of Jiangxi Agriculture University (No. 201910410043).

References

1. Bruker: APEX3 , SAINT-Plus, XPREP. Bruker AXS Inc., Madison, WI, USA (2016).
2. Sheldrick, G. M.: SHELXT – Integrated space-group and crystal-structure determination. Acta Crystallogr. **A71** (2015) 3–8.
3. Sheldrick, G. M.: Crystal structure refinement with SHELXL. Acta Crystallogr. **C71** (2015) 3–8.
4. Brandenburg, K.: DIAMOND. Visual Crystal Structure Information System. Ver. 4.0. Crystal Impact, Bonn, Germany (2015).
5. Malikov, V. M.; Yuldashev, M. P.: Phenolic compounds of plants of the Scutellaria L. genus. distribution, structure, and properties. Chem. Nat. Compd. **38** (2002) 358–406.
6. Wang, J. R.; Ma, L.; Li, W. F.; Tang, X. H.; Zhao, G.; Peng, L. X.; Zhao, J. L.: Effect of trace elements on the flavonoids and phenolic acids in tartary buckwheat sprouts. Acta. Agric. Univ. Jiangxiensis. **39** (2017) 55–63.
7. Zeng, Z.; Liu, H. G.; Hong, Y. P.; Wu, G. Q.; Lu, Q.; Xu, X. X.; Hu, J. F.; Wang, X. Y.: A study on purification of total flavonoids from prunus persica by macroporous resin and their antioxidant activity. Acta. Agric. Univ. Jiangxiensis. **39** (2017) 182–189.
8. Liu, W.; Gao, H. Y.; Li, Z. W.; La, P.; Wan, C. P.: Comparison of the Determination Methods for Total Flavonoids in Prunus divaricata Ldb Leaves. Acta. Agric. Univ. Jiangxiensis. **38** (2016) 192–197.
9. Shang-Guan, X. C.; Jiang, Y.; Mi, L. X.; Chen, J. G.; Zhang, Q. F.; Zou, L.: Effects of five macronutrients on the growth and flavonoid accumulation of cyclocarya paliurus callus. Acta. Agric. Univ. Jiangxiensis. **33** (2011) 502–507.
10. Guo, W.; Zhang, R. P.; Li, X. H.; Wang, N.: Flavonoids from Pu-erh Raw Tea. Chem. Nat. Compd. **54** (2018) 570–C571.
11. Mantas, A.; Deretey, E.; Ferretti, F. H.; Estrada, M. R.; Csizmadia, I. G.: Structural analysis of flavonoids with anti-HIV activity. J. Mol. Struct. (THEOHEM) **504** (2000) 171–179.
12. Jeffrey, B. H.; Christine, A. W.: Advances in flavonoid research since 1992. Phytochem. **55** (2000) 481–504.
13. George, W. K.; Arjun, R. M.: Microwave-assisted synthesis of functionalized flavones and chromones. Tetrahedron. Lett. **46** (2005) 6315–6317.
14. Julio, A. S.; Pilar, V. T.; Raquel, C. R.: Solvent-free synthesis of functionalized flavones under microwave irradiation. J. Org. Chem. **70** (2005) 2855–2858.
15. Kondo, T.; Yoshida, K.; Oyama, K. I.: Recent progress in the synthesis of flavonoids: from monomers to supra-complex molecules. Curr. Org. Chem. **15** (2011) 2567–2607.

16. Xu, H. J.; Li, Z. M.; Wu, Y. Q.; Luo, D.; Qiu, L.; Xie, J. Z.; Li, X. H.: Advances on synthesis of flavonoid glycosides. Chin. J. Org. Chem. **39** (2019) 1875–1890.
17. Pessel, F.; Billault, I.; Scherrmann, M.-C.: Total synthesis of triazole-linked C-glycosyl flavonoids in alternative solvents and environmental assessment in terms of reaction, workup and purification. Green Chem. **18** (2016) 5558–5568.
18. Fang, L. M.; Huang, J. P.; Dai, J. C.; Nie, X. L.; Liu, C. X.; Kang, N. Q.; Huang, L.: Crystal structure of methyl 4-acetoxybenzoate, $C_{10}H_{10}O_4$. Kristallogr. NCS **234** (2019) 585–586.
19. Wen, G. J.; Gu, L. S.; Sun, B. W.: Tuning crystal structure and absorption properties of 4-hydroxyisophthalic acid co-crystals using pyrazine derivatives. J. Mol. Struc. **1150** (2017) 96–102.
20. Li, Y.; Wang, J.: The crystal structure of 4-(methoxycarbonyl) benzoic acid, $C_9H_8O_4$. Z. Kristallogr. **234** (2019) 349–350.