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Crystal structure of 6-(carboxymethyl)-2,3,4-trimethoxybenzoic acid, $C_{12}H_{14}O_7$

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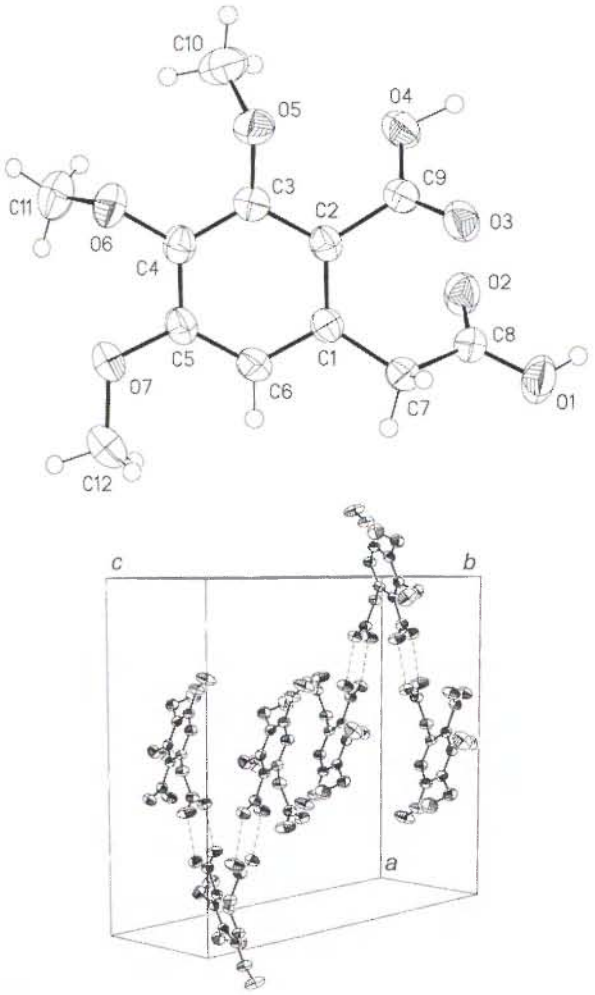

Abstract

$C_{12}H_{14}O_7$, orthorhombic, *Pbca* (no. 61), a = 17.62(1) Å, b = 7.040(4) Å, c = 20.51(1) Å, V = 2544.2 Å^3, Z = 8, $R_{gt}(F)$ = 0.041, $wR_{ref}(F^2)$ = 0.099, T = 293 K.

Source of material

A solution of sodium hydroxide (5 %, 110 ml) was added to the solution of 6-[(methoxycarbonyl)methyl]-2,3,4-trimethoxybenzoic acid (3 g, 0.01 mol) in methanol (35 ml). The reaction mixture was refluxed for 1 h and methanol was rotary-evaporated. Acidification of the aqueous layer directly afforded 6-(carboxymethyl)-2,3,4-trimethoxybenzoic acid (2.5 g, 0.0092 mol) as white solid. Recrystallization from ethyl acetate gave crystals suitable for X-ray structure analysis.

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Experimental details

The hydrogen atoms bonded to oxygen atoms were refined freely due to their importance in the hydrogen bonding.

Discussion

The reported compound commonly known as 4,5,6-trimethoxyhomophthalic acid is the key intermediate for the synthesis of naturally occurring biological active isocoumarins and 3, 4-dihydroisocoumarins. The most important naturally occurring isocoumarins synthesized by the title compound is (±)-kigelin [1].

In the title crystal structure, the bonds lengths within phenyl ring lie between 1.383(3) Å and 1.401(3) Å which highlights the aromatic character (figure, top). The valence angle C1–C6–C5 (121.9(2)°) is larger than the standard value of 120°. The opening of this angle is due to the presence of the methoxy and methyl carboxyl groups on C1 and C5, respectively, which involves a decrease of the ring angles of C1 (118.4(2)°) and C5 (119.9(2)°). The C8—O1 (1.298(3) Å) and C9—O4 (1.297 (3) Å) bond distances are compatible with respective distances in related structures [2,3] and smaller than those usually observed in carboxylic acids (1.365 Å).

The structure is influenced by quite interesting intra- and intermolecular hydrogen bonding. The carboxyl H atom forms intramolecular bond to the corresponding methoxy O atoms, i.e. O–H···O (d(H2···O5) = 2.757 Å and the crystal structure is stabilized by intermolecular O–H···O hydrogen bonds, whereas the carboxyl H atom of one molecule A interacts with the O atom of the methyl carboxyl group of one neighboring molecule B (d(H2A···O2B) = 2.631 Å) and the H atom of the methyl carboxyl group of the molecule B interacts with the O atom of the carboxyl group of molecule A (d(H1B ··O3A) = 2.648 Å). Simultaneously, the methyl carboxyl group present on molecule A interacts with the carboxyl group of another neighboring molecule C in quite similar fashion. Thus, each molecule has hydrogen bonding interactions with two neighboring molecules, giving a zigzag appearance in cell.

Table 1. Data collection and handling.

Crystal:	colorless needle, size 0.13 × 0.15 × 0.25 mm
Wavelength:	Mo K_α radiation (0.71069 Å)
μ:	1.18 cm^{-1}
Diffractometer, scan mode:	Stoe IPDS II, ω
$2\theta_{max}$:	49.36°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	26888, 2147
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1570
$N(param)_{refined}$:	180
Programs:	SIR97 [4], SHELXL-97 [5]

Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{iso}
H(6)	8c	1.0645	0.3764	0.6626	0.047
H(7A)	8c	0.9299	0.3082	0.7599	0.049
H(7B)	8c	0.9606	0.4724	0.7161	0.049
H(10A)	8c	0.9259	–0.4713	0.5554	0.107
H(10B)	8c	0.9913	–0.3418	0.5288	0.107
H(10C)	8c	0.9081	–0.2635	0.5326	0.107
H(11A)	8c	1.1593	–0.2624	0.4970	0.092
H(11B)	8c	1.1583	–0.0428	0.5097	0.092
H(11C)	8c	1.0854	–0.1448	0.4835	0.092
H(12A)	8c	1.2480	0.3348	0.6049	0.114
H(12B)	8c	1.1983	0.3332	0.6682	0.114
H(12C)	8c	1.1692	0.4380	0.6056	0.114
H(1)	8c	0.767(2)	0.509(4)	0.734(2)	0.11(1)
H(2)	8c	0.769(2)	–0.097(5)	0.634(2)	0.11(1)

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	8c	0.9715(1)	0.2137(3)	0.6736(1)	0.027(1)	0.038(1)	0.038(1)	0.0028(9)	–0.0041(8)	–0.0007(9)
C(2)	8c	0.9414(1)	0.0369(3)	0.65686(9)	0.028(1)	0.040(1)	0.035(1)	0.0003(9)	–0.0011(8)	0.0012(9)
C(3)	8c	0.9865(1)	–0.0948(3)	0.6234(1)	0.037(1)	0.034(1)	0.036(1)	–0.0004(9)	–0.0032(9)	0.0023(9)
C(4)	8c	1.0597(1)	–0.0507(3)	0.6041(1)	0.032(1)	0.040(1)	0.036(1)	0.0068(9)	–0.0010(8)	0.001(1)
C(5)	8c	1.0887(1)	0.1283(3)	0.6192(1)	0.027(1)	0.046(1)	0.039(1)	0.0006(9)	0.0000(8)	0.001(1)
C(6)	8c	1.0446(1)	0.2572(3)	0.6532(1)	0.030(1)	0.040(1)	0.047(1)	–0.0030(9)	–0.0028(9)	–0.005(1)
C(7)	8c	0.9306(1)	0.3568(3)	0.7157(1)	0.031(1)	0.043(1)	0.048(1)	–0.0007(9)	–0.0027(9)	–0.008(1)
C(8)	8c	0.8515(1)	0.4090(3)	0.6979(1)	0.033(1)	0.039(1)	0.044(1)	0.0009(9)	0.002(1)	–0.008(1)
C(9)	8c	0.8612(1)	–0.0107(3)	0.6717(1)	0.035(1)	0.038(1)	0.040(1)	–0.0042(9)	–0.001(1)	–0.002(1)
C(10)	8c	0.9449(2)	–0.3437(4)	0.5534(1)	0.084(2)	0.058(2)	0.072(2)	–0.018(2)	0.013(2)	–0.024(2)
C(11)	8c	1.1288(2)	–0.1573(4)	0.5114(1)	0.063(2)	0.069(2)	0.053(2)	0.007(1)	0.015(1)	–0.008(1)
C(12)	8c	1.1971(1)	0.3304(4)	0.6214(2)	0.044(1)	0.080(2)	0.103(2)	–0.023(1)	0.020(1)	–0.024(2)
O(1)	8c	0.8154(1)	0.4944(3)	0.74457(8)	0.0394(9)	0.093(2)	0.061(1)	0.0182(9)	–0.0028(8)	–0.031(1)
O(2)	8c	0.82339(8)	0.3759(2)	0.64432(7)	0.0362(8)	0.059(1)	0.0441(9)	0.0093(7)	–0.0035(7)	–0.0060(7)
O(3)	8c	0.83274(8)	0.0247(2)	0.72524(7)	0.0386(8)	0.061(1)	0.0418(9)	–0.0075(7)	0.0064(6)	–0.0041(7)
O(4)	8c	0.82307(9)	–0.0829(2)	0.62360(8)	0.0372(9)	0.075(1)	0.0500(9)	–0.0150(8)	0.0026(7)	–0.0166(8)
O(5)	8c	0.95896(8)	–0.2763(2)	0.61753(8)	0.0531(9)	0.0353(9)	0.057(1)	–0.0070(7)	0.0070(7)	–0.0030(7)
O(6)	8c	1.10415(8)	–0.1903(2)	0.57715(7)	0.0439(9)	0.047(1)	0.051(1)	0.0123(7)	0.0074(7)	–0.0027(7)
O(7)	8c	1.16124(7)	0.1602(2)	0.60017(8)	0.0305(8)	0.060(1)	0.063(1)	–0.0079(7)	0.0103(7)	–0.0099(9)

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References

1. Saeed, A.; Somia, E.: Synthesis of (±)-Kigelin. J. Braz. Chem. Soc. **16** (2005) 739-742.
2. Smith, G.; Kennard, C. H. L.: 4-chloro-2-methylphenoxyacetic acid. Cryst. Struct. Commun. **10** (1981) 295-299.
3. Kennard, C. H. L.; Smith, G.: 2-Chlorophenoxyacetic acid. Acta Crystallogr. **B37** (1981) 1456-1458.
4. Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R.: SIR97: a new tool for crystal structure determination and refinement. J. Appl. Crystallogr. **32** (1999) 115-119.
5. Sheldrick, G. M.: SHELXL-97. Program for the Refinement of Crystal Structures. University of Göttingen, Germany 1990.