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(2-Ethoxycarbonyl-3,5-dihydroxyphenyl)-acetic acid monohydrate, an intermediate in the Pechmann reaction

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.045
wR factor = 0.113
Data-to-parameter ratio = 12.3

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

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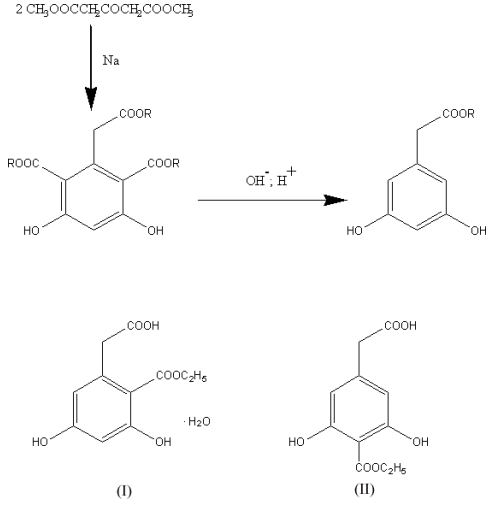
The title compound, $C_{11}H_{12}O_6\cdot H_2O$, contains a water molecule of hydration and consists of a mostly planar six-membered ring and pendant ester, with a nearly perpendicular orientation of the carboxylic acid group. The structure of this compound was incorrectly reported in the early literature. The crystal structure involves a variety of hydrogen bonds.

Comment

The Pechmann reaction (Cornelius & von Pechmann, 1886) (see Scheme) was one of the earliest biomimetic syntheses, and involves conversion of an aliphatic ester to an aromatic phenolic acid. The reaction and its variants find wide application in classical synthetic chemistry. While repeating the reaction of the Scheme (R = Et), following a more recent procedure (Theilacker & Schmid, 1950), we isolated, from the acid hydrolysis, about 5% of a colorless crystalline fraction that was soluble in hot water but insoluble in chloroform. Initially thought to be inorganic, the material, after recrystallization from water, fused at about 443 K and melted completely by 473 K. The compound slowly turned brown on standing in air. X-ray crystallographic analysis revealed the monohydrated structure, (I), shown below, arising in the second step from incomplete hydrolysis and decarboxylation.



(I) (II)

Compound (I) was not found in the Cambridge Structural Database (Allen, 2002). However, Jerdan (1899) described a number of intermediates from the Pechmann reaction and their transformation products. He ascribed structure (I) to one of them, melting at 417–419 K. Most interestingly, Jerdan described another intermediate, 4-monoethylic hydrogen *para*-orcinoldicarboxylate, as a monohydrate, melting at 463 K that was soluble in water but insoluble in chloroform. He assigned structure (II) to this compound. Since his description

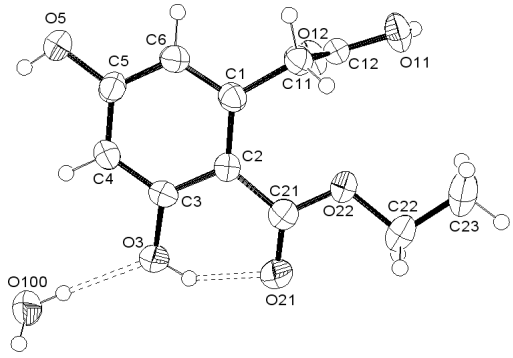


Figure 1
ORTEP-3 (Farrugia, 1997) view of (I), shown with 50% probability displacement ellipsoids. H atoms are represented by spheres of arbitrary radii. Hydrogen bonds are indicated by dashed lines.

closely matches the properties of our product, it is likely that Jerdan's assignments are incorrect. In fact, some of Jerdan's other intermediates have also been reassigned (Asahina & Nogami, 1940; Theilacker & Schmid, 1950). Compound (I) was previously used as a reactant to form 2,4-dihydroxy-6-methylbenzoic acid ethyl ester (Asahina & Nogami, 1942).

The water molecule of solvation is stabilized by hydrogen bonds (Table 1), by interaction with the hydroxy groups of the acid, as is normally the case with compounds containing water molecules of solvation. This results in a chain structure with the hydroxy part of the acid molecule pointing to and interacting with water molecules of solvation, and the hydrophobic end of the acid molecules on adjacent chains facing each other. Parallel chains are held together, *via* hydrogen bonding, by the expected carboxylic acid dimerization.

Experimental

Crystals of the title compound were obtained by recrystallization from water of the product obtained following a literature procedure (Theilacker & Schmid, 1950).

Crystal data

$C_{11}H_{12}O_6\cdot H_2O$
M_r = 258.22
Monoclinic, $P2_1/c$
a = 12.091 (3) Å
b = 7.658 (1) Å
c = 13.784 (2) Å
β = 108.57 (1)°
V = 1209.8 (4) Å^3
Z = 4
D_x = 1.418 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 10–15°
μ = 0.12 mm^{-1}
T = 293 (2) K
Prism, white
0.20 × 0.15 × 0.10 mm

Data collection

Enraf–Nonius TurboCAD-4 diffractometer
Non-profiled $\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.976, T_{max} = 0.988
2218 measured reflections
2113 independent reflections
1235 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 25.0°
$h = 0 \rightarrow 14$
$k = 0 \rightarrow 9$
$l = -16 \rightarrow 15$
3 standard reflections
frequency: 166 min
intensity decay: 2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.113
S = 1.01
2113 reflections
172 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0485P)^2 + 0.1688P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.15 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H31···O21	0.82	1.78	2.514 (2)	147
O5—H5···O100^{i}	0.82	1.83	2.639 (3)	168
O11—H11C···O12^{ii}	0.82	1.86	2.678 (3)	171
O100—H101···O5^{iii}	0.88 (4)	1.94 (4)	2.812 (3)	174 (4)
O100—H102···O3	0.82 (3)	2.01 (4)	2.835 (3)	178 (4)

Symmetry codes: (i) $-x, y-\frac{1}{2}, \frac{5}{2}-z$; (ii) $1-x, -y, 2-z$; (iii) $x, 1+y, z$.

The water H atoms were refined independently and resulted in the O—H distances listed in Table 1 and an H—O—H angle of 109 (3)°.

Data collection: *CAD*-4 *EXPRESS* (Enraf–Nonius, 1994); cell refinement: *CAD*-4 *EXPRESS*; data reduction: *XCAD*4 (Harms & Wocadlo, 1995); program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 for Windows (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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