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5-(But-3-enyl)pyridinium-2-carboxylate–5-butylpyridine-2-carboxylic acid (1/1), a co-crystal from *Fusarium moniliforme*

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Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.004 Å
Disorder in main residue
R factor = 0.063
wR factor = 0.229
Data-to-parameter ratio = 15.7

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

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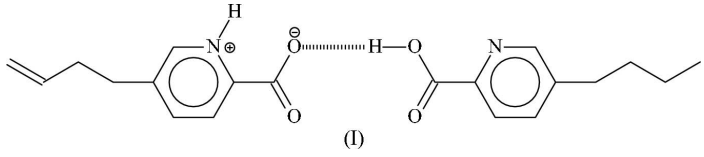
In the title co-crystal, $C_{10}H_{11}NO_2\cdot C_{10}H_{13}NO_2$, the carboxylic acid moiety uses its acid H atom as the donor atom to bind strongly to the negatively charged O atom of the zwitterionic moiety [O···O = 2.557 (2) Å]. Meanwhile, the protonated N atom of the zwitterionic moiety forms a hydrogen bond with the double-bonded O atom of an adjacent zwitterionic moiety [N···O = 2.703 (2) Å] to give rise to a linear chain motif. The butenyl substituent (on the zwitterion) is disordered with respect to a butyl group and the butyl substituent (on the neutral molecule) is disordered with respect to a butenyl group, the site occupancy for both being in an approximate 0.6:0.4 ratio.

Comment

Fusaric (5-butylpyridine-2-carboxylic) and 9,10-dehydrofusaric [5-(but-3-enyl)pyridine-2-carboxylic) acids have been identified by liquid chromatography as the two mycotoxins in infected corn (Abouzeid *et al.*, 2003). The two acids have also been found in rice in the present study, these co-crystallizing in a 1:1 molar stoichiometry, (I) (Fig. 1).



(I)

In the co-crystal, 9,10-dehydrofusaric acid exists to a lesser extent in the neutral and to a greater extent in the zwitterionic form. Similarly, fusaric acid exists in both forms but to a greater extent in the neutral form. The major form of the carboxylic acid moiety engages in a hydrogen-bonding interaction with the negatively charged carboxyl group of the major form of the zwitterionic moiety; the protonated N atom forms a hydrogen bond with the double-bonded O atom of an adjacent zwitterionic moiety to give rise to a linear chain (Fig. 2). Pyridine-2-carboxylic acid itself exists in both forms, as shown by a solid-state ^{13}C NMR study (Hamazaki *et al.*, 1998)

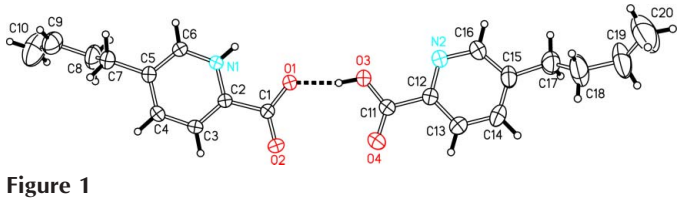


Figure 1
A view of (I). Displacement ellipsoids are shown at the 30% probability level, and H atoms are drawn as spheres of arbitrary radii. The minor disordered component is not shown. The dashed line represents a hydrogen bond.

Experimental

A strain of the endophtic fungus *Fusarium moniliforme* zsu-1 shold was isolated from surface sterilis rice stem. The strain has been deposited at the School of Pharmaceutical Science, Sun Yat-Sen University. The strain was cultured on a PD medium (glucose 2%, potatoes 20 g l^{-1}) and was incubated at 298 K for 15 d. For the extraction and separation of the metabolite, the culture (9 l) was first filtered through cheesecloth. The filtrate was extracted three times by an equal volume of ethyl acetate. The extract was evaporated under reduced pressure and the concentrated extract passed through a silica-gel column. The compound was eluted with petroleum ether/ethyl acetate, and crystals were obtained by recrystallization from methanol. The chemical composition was confirmed by mass spectrometry and by ^{1}H and ^{13}C NMR spectroscopy. The FAB mass spectrum showed $M + 1$ ions at 178 and 180. ^{1}H NMR in DMSO (500 MHz): δ 8.552 (*d*, 1.5 Hz, 2H), 7.966 (*d*, 8.0 Hz, 2H), 7.814 (*dd*, 8.0, 1.5 Hz, 2H), 5.804 (*ddt*, 17.0, 13.5, 6.6 Hz, 1H), 5.008 (*d*, 17.0 Hz, 1H), 4.991 (*d*, 13.5 Hz, 1H), 2.800 (*t*, 7.5 Hz, 2H), 2.658 (*t*, 7.5 Hz, 2H), 2.395 (*q*, 6.6 Hz, 2H), 1.586 (quintet, 7.5 Hz, 2H), 1.317 (sextet, 7.5 Hz, 2H), 0.904 (*t*, 7.5 Hz, 3H); ^{13}C NMR, DEPT in DMSO (500 MHz): δ 166.0, 149.4, 149.3, 146.1, 146.0, 141.5, 140.6, 137.2, 136.9, 136.7, 124.2, 124.1, 115.7, 34.0, 32.3, 31.6, 31.2, 21.5, 13.5. The 1:1 molar ratio of the two components of the co-crystal was confirmed by the relative ratio of the number of H atoms on the terminal olefinic bond to that on the methyl C atom. Additionally, the peaks of the M^{+1} ion in the mass spectrum were of the same intensity.

Crystal data

$C_{10}H_{11}NO_2{\cdot}C_{10}H_{13}NO_2$
M_r = 356.41
Monoclinic, $P2_1/n$
a = 12.010 (2) Å
b = 10.401 (1) Å
c = 16.988 (2) Å
β = 108.178 (2)°
V = 2016.2 (4) Å^3
Z = 4
D_x = 1.174 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 827 reflections
θ = 2.5–26.2°
μ = 0.08 mm^{-1}
T = 295 (2) K
Block, colourless
0.48 × 0.45 × 0.29 mm

Data collection

Bruker SMART 1K area-detector diffractometer
φ and ω scans
Absorption correction: none
13 186 measured reflections
4315 independent reflections
2231 reflections with $I > 2\sigma(I)$
R_{int} = 0.027
θ_{max} = 26.9°
$h = -15 \rightarrow 14$
$k = -12 \rightarrow 13$
$l = -21 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.229
S = 1.01
4315 reflections
275 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1215P)^2 + 0.3711P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.31 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—H3o···O1	0.86 (1)	1.71 (1)	2.557 (2)	168 (4)
N1—H1n···O2^{i}	0.85 (1)	1.98 (2)	2.703 (2)	141 (2)

Symmetry code: (i) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{3}{2} - z$.

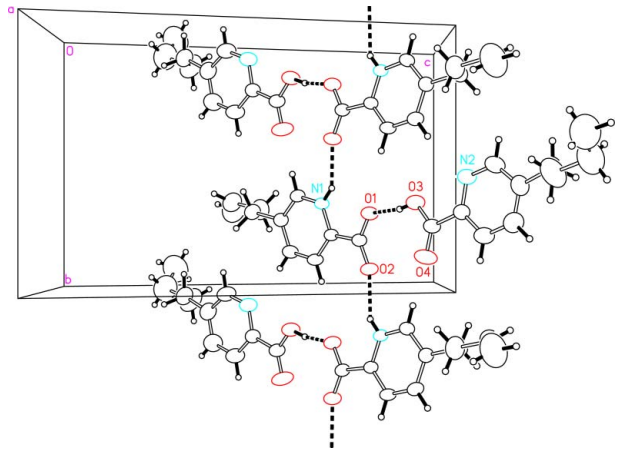


Figure 2
A view of the hydrogen-bonded chain structure (dashed lines). Only the major disordered component is shown.

The asymmetric unit is disordered in the alkyl chains of the zwitterion and neutral molecule. The butenyl chain is disordered over two sites, as is the butyl chain; the occupancies refined to 0.59 (1):0.41 (1) for both. The other disorder model, in which the butenyl chain is disordered with respect to the butyl chain of the same moiety, was ruled out as the occupancies could not be refined. For both chains, the C—C single-bond distances were restrained to 1.500 (5) Å and the C═C double-bond distances to 1.350 (5) Å. The displacement parameters of the primed atoms were set equal to those of the unprimed atoms. Additionally, the displacement parameters were restrained to be approximately isotropic; the atoms along the chain were further restrained to have similar displacement parameters. The H atoms were positioned geometrically (C—H = 0.96 Å for the methyl H atoms, 0.97 Å for the methylene H atoms and 0.93 Å for the aromatic H atoms) and were included in the refinement in the riding-model approximation; their displacement parameters were set at $1.2U_{eq}$ of the parent atoms for the methylene and aromatic H atoms, and at $1.5U_{eq}$ for the methyl H atoms. The nitrogen- and oxygen-bound H atoms were located in a difference Fourier map, and were refined with a distance restraint of 0.85 (1) Å.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT-Plus* (Bruker, 1999); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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References

Abouzeid, M. A., Abd-Elrahman, D. G., Hassan, A. A., Youssef, K. A. & Hammad, A. A. (2003). *Int. J. Agric. Biol.* **5**, 397–404.
Bruker (1999). *SAINT-Plus* (Version 6.45) and *SMART* (Version 5.054). Bruker AXS Inc., Madison, Wisconsin, USA.
Hamazaki, H., Hosomi, H., Takeda, S., Kataoka, H. & Ohba, S. (1998). *Acta Cryst.* C**54**, IUC9800049.
Johnson, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.