

3-(4-Hydroxy-3-methoxyphenyl)acrylic acid–2,3,5,6-tetramethylpyrazine (2/1)

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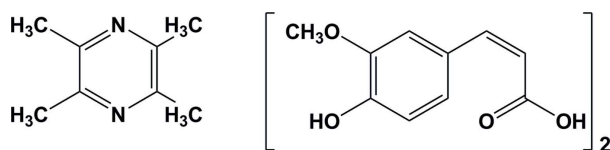
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Key indicators: single-crystal X-ray study; $T = 100$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; disorder in main residue; R factor = 0.054; wR factor = 0.156; data-to-parameter ratio = 11.5.

The asymmetric unit of the title compound, $\text{C}_8\text{H}_{12}\text{N}_2 \cdot 2\text{C}_{10}\text{H}_{10}\text{O}_4$, contains a tetramethylpyrazine molecule, situated about an inversion center, and two substituted acrylic acid derivatives. The dihedral angle between the phenyl and pyrazine rings is 69.45 (9)°. In the crystal, intermolecular $\text{O}-\text{H} \cdots \text{O}$, $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds and weak $\text{C}-\text{H} \cdots \text{O}$ interactions lead to the formation of a supramolecular network. The acrylic acid side chain is positionally disordered [occupancy ratio 0.852 (7):0.148 (7)].

Related literature

For the synthesis of the title compound, see: Tan (2004). For the biological properties of the title compound, see: Tan *et al.* (2003).



Experimental

Crystal data

$0.5\text{C}_8\text{H}_{12}\text{N}_2 \cdot \text{C}_{10}\text{H}_{10}\text{O}_4$
 $M_r = 262.28$
Monoclinic, $P2_1/n$
 $a = 9.4696$ (7) Å

$b = 5.7641$ (4) Å
 $c = 24.3737$ (15) Å
 $\beta = 93.654$ (6)°
 $V = 1327.70$ (16) Å³

$Z = 4$
Cu $K\alpha$ radiation
 $\mu = 0.80$ mm⁻¹

$T = 100$ K
 $0.20 \times 0.05 \times 0.05$ mm

Data collection

Oxford Diffraction Xcalibur Onyx Nova diffractometer
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
 $T_{\min} = 0.953$, $T_{\max} = 0.961$
4780 measured reflections
2398 independent reflections
2004 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.030$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.054$
 $wR(F^2) = 0.156$
 $S = 1.09$
2398 reflections
208 parameters

4 restraints
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.63$ e Å⁻³
 $\Delta\rho_{\min} = -0.40$ e Å⁻³

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

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O2}-\text{H2} \cdots \text{O1}^{\text{i}}$	0.84	1.79	2.613 (5)	167
$\text{O4}-\text{H4} \cdots \text{N1}$	0.82	1.97	2.749 (2)	158
$\text{C3}-\text{H3B} \cdots \text{O4}^{\text{ii}}$	0.98	2.58	3.553 (3)	174
$\text{C14}-\text{H14B} \cdots \text{O4}^{\text{ii}}$	0.98	2.59	3.465 (2)	148

Symmetry codes: (i) $-x, -y + 1, -z$; (ii) $x, y + 1, z$.

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SU2237).

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supplementary materials

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3-(4-Hydroxy-3-methoxyphenyl)acrylic acid-2,3,5,6-tetramethylpyrazine (2/1)

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Comment

The title compound, tetramethylpyrazine ferulate is a pharmacologically significant compound which we found in some prescriptions of traditional Chinese medicine, and which are used to treat stroke patients. In both the *in vivo* and *in vitro* experiments, tetramethylpyrazine ferulate has a remarkable inhibitory effect on ADP induced platelet aggregation (Tan *et al.*, 2003). In order to study further its pharmacological effects the title compound was synthesized by the reaction of 3-(4-hydroxy-3-methoxyphenyl)-2-acrylic acid with tetramethylpyrazine, and its crystal structure is reported on herein.

X-ray crystallographic analysis confirmed the molecular structure and the atom connectivity for the title compound, as illustrated in Fig. 1. The dihedral angle between the mean planes of the pyrazine ring and phenyl ring (C8—C13) is 69.45 (9)°.

In the crystal intermolecular O—H...N hydrogen bonds and weak C—H...O interactions are observed, leading to the formation of a supra-molecular network (Table 1).

Experimental

The title compound was synthesized according to the published procedure (Tan, 2004). Tetramethylpyrazine (2.8 g) was heated with 3-(4-hydroxy-3-methoxyphenyl)-2-acrylic acid (4.0 g) in acetone (45 ml). After refluxing at 333 K for 1 h, the reaction mixture was left to stand for several days, and yellow crystals were finally isolated.

Refinement

The acid side chain is positionally disordered: occupancy of atoms C6/C6A, C/C5A, O1/O1A and O2/O2A were refined to be 0.852 (7)/0.148 (7). The following restraints were also applied: *DFIX* 1.32. 02 C7 C6 C7 C6A; *DFIX* 1.45. 02 C6 C5 C6A C5A; *EADP* C5 C5A. The OH and C-bound H-atoms were included in calculated positions and treated as riding atoms: O—H = 0.82 - 0.84 Å, C—H = 0.95 and 0.98 Å for CH and CH₃ H-atoms, respectively, with $U_{\text{iso}}(\text{H}) = k \times U_{\text{eq}}(\text{C})$, where $k = 1.5$ for OH and CH₃ H-atoms, and $k = 1.2$ for all other H-atoms.

Figures

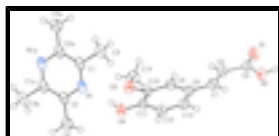


Fig. 1. A view of the centrosymmetric tetramethylpyrazine molecule and one of the ferulate molecules of the title compound. Displacement ellipsoids are drawn at the 50% probability level [Symmetry code: (a) = -x, -y, -z + 1; only the major component of the disordered acrylic acid side chain is shown].

3-(4-Hydroxy-3-methoxyphenyl)acrylic acid–2,3,5,6-tetramethylpyrazine (2/1)

Crystal data

$0.5\text{C}_8\text{H}_{12}\text{N}_2\cdot\text{C}_{10}\text{H}_{10}\text{O}_4$	$F(000) = 556$
$M_r = 262.28$	$D_x = 1.312 \text{ Mg m}^{-3}$
Monoclinic, $P2_1/n$	Cu $K\alpha$ radiation, $\lambda = 1.54180 \text{ \AA}$
Hall symbol: -P 2yn	Cell parameters from 2625 reflections
$a = 9.4696 (7) \text{ \AA}$	$\theta = 3.6\text{--}71.3^\circ$
$b = 5.7641 (4) \text{ \AA}$	$\mu = 0.80 \text{ mm}^{-1}$
$c = 24.3737 (15) \text{ \AA}$	$T = 100 \text{ K}$
$\beta = 93.654 (6)^\circ$	Plate, yellow
$V = 1327.70 (16) \text{ \AA}^3$	$0.20 \times 0.05 \times 0.05 \text{ mm}$
$Z = 4$	

Data collection

Oxford Diffraction Xcalibur Onyx Nova diffractometer	2398 independent reflections
Radiation source: fine-focus sealed tube graphite	2004 reflections with $I > 2\sigma(I)$
Detector resolution: $8.2417 \text{ pixels mm}^{-1}$	$R_{\text{int}} = 0.030$
ω scans	$\theta_{\text{max}} = 68.2^\circ$, $\theta_{\text{min}} = 3.6^\circ$
Absorption correction: multi-scan (<i>CrysAlis PRO</i> ; Oxford Diffraction, 2009)	$h = -6 \rightarrow 11$
$T_{\text{min}} = 0.953$, $T_{\text{max}} = 0.961$	$k = -6 \rightarrow 6$
4780 measured reflections	$l = -29 \rightarrow 29$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.054$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.156$	H-atom parameters constrained
$S = 1.09$	$w = 1/[\sigma^2(F_o^2) + (0.0848P)^2 + 0.4876P]$
2398 reflections	where $P = (F_o^2 + 2F_c^2)/3$
208 parameters	$(\Delta/\sigma)_{\text{max}} = 0.003$
4 restraints	$\Delta\rho_{\text{max}} = 0.63 \text{ e \AA}^{-3}$
	$\Delta\rho_{\text{min}} = -0.40 \text{ e \AA}^{-3}$

Special details

Experimental. *CrysAlisPro* (Oxford Diffraction, 2009) Empirical absorption correction using spherical harmonics, implemented in *SCALE3 ABSPACK* scaling algorithm.

Geometry. Bond distances, angles *etc.* have been calculated using the rounded fractional coordinates. All su's are estimated from the variances of the (full) variance-covariance matrix. The cell e.s.d.'s are taken into account in the estimation of distances, angles and torsion angles

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	-0.0744 (5)	0.5740 (6)	0.06036 (17)	0.0523 (10)	0.852 (7)
O2	0.0563 (4)	0.2666 (5)	0.03930 (15)	0.0489 (9)	0.852 (7)
O3	-0.11323 (15)	0.0544 (3)	0.33773 (5)	0.0432 (4)	
O4	0.04554 (15)	-0.3292 (2)	0.35223 (6)	0.0444 (5)	
C5	-0.0143 (5)	0.3836 (9)	0.07299 (14)	0.0391 (11)	0.852 (7)
C6	-0.0257 (2)	0.2939 (4)	0.12865 (9)	0.0392 (7)	0.852 (7)
C7	0.0333 (2)	0.1014 (4)	0.14611 (9)	0.0506 (7)	
C8	0.0286 (2)	-0.0041 (4)	0.20015 (8)	0.0404 (6)	
C9	-0.0448 (2)	0.0919 (3)	0.24314 (8)	0.0375 (6)	
C10	-0.04259 (19)	-0.0175 (3)	0.29389 (7)	0.0334 (5)	
C11	0.03695 (19)	-0.2208 (3)	0.30294 (7)	0.0347 (5)	
C12	0.1057 (2)	-0.3180 (4)	0.26015 (8)	0.0395 (6)	
C13	0.1010 (2)	-0.2104 (4)	0.20929 (8)	0.0416 (6)	
C14	-0.2088 (2)	0.2438 (4)	0.32912 (9)	0.0462 (7)	
O1A	-0.051 (2)	0.484 (4)	0.0621 (8)	0.045 (6)	0.148 (7)
O2A	0.1074 (19)	0.249 (3)	0.0201 (7)	0.054 (5)	0.148 (7)
C5A	0.028 (3)	0.322 (5)	0.0629 (11)	0.0391 (11)	0.148 (7)
C6A	0.0587 (13)	0.162 (2)	0.1065 (5)	0.038 (4)	0.148 (7)
N1	0.00905 (17)	-0.1036 (3)	0.44970 (6)	0.0393 (5)	
C1	0.0891 (2)	0.0814 (4)	0.46363 (8)	0.0383 (6)	
C2	-0.0802 (2)	-0.1871 (3)	0.48531 (8)	0.0378 (6)	
C3	0.1847 (2)	0.1711 (4)	0.42178 (9)	0.0479 (7)	
C4	-0.1659 (2)	-0.3952 (4)	0.46761 (10)	0.0503 (7)	
H4	0.01920	-0.24080	0.37590	0.0670*	
H6	-0.07890	0.38050	0.15330	0.0470*	0.852 (7)
H2	0.05430	0.33540	0.00890	0.0730*	0.852 (7)
H14A	-0.27540	0.20980	0.29770	0.0690*	
H14B	-0.15560	0.38480	0.32160	0.0690*	
H14C	-0.26120	0.26690	0.36210	0.0690*	
H7	0.08590	0.01970	0.12040	0.0610*	0.852 (7)
H9	-0.09610	0.23230	0.23740	0.0450*	
H12	0.15630	-0.45930	0.26570	0.0470*	
H13	0.14830	-0.27930	0.18020	0.0500*	
H6AA	0.13470	0.06810	0.09570	0.0450*	0.148 (7)
H6AB	-0.05690	0.17360	0.14590	0.0610*	0.148 (7)
H2A	0.09850	0.34570	-0.00580	0.0810*	0.148 (7)

supplementary materials

H3A	0.20300	0.04760	0.39550	0.0720*
H3B	0.13940	0.30260	0.40220	0.0720*
H3C	0.27440	0.22170	0.44030	0.0720*
H4A	-0.12420	-0.46860	0.43620	0.0750*
H4B	-0.26310	-0.34730	0.45700	0.0750*
H4C	-0.16650	-0.50610	0.49810	0.0750*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0654 (19)	0.053 (2)	0.0387 (12)	0.0041 (16)	0.0046 (11)	0.0104 (15)
O2	0.0630 (18)	0.0519 (12)	0.0320 (15)	-0.0025 (11)	0.0044 (11)	0.0042 (11)
O3	0.0487 (8)	0.0467 (8)	0.0339 (7)	0.0155 (6)	0.0009 (6)	0.0038 (6)
O4	0.0586 (9)	0.0409 (8)	0.0337 (7)	0.0124 (6)	0.0032 (6)	0.0103 (6)
C5	0.046 (2)	0.045 (2)	0.0266 (16)	-0.0126 (18)	0.0039 (12)	-0.0014 (14)
C6	0.0447 (13)	0.0429 (13)	0.0302 (12)	-0.0046 (10)	0.0036 (9)	-0.0014 (9)
C7	0.0541 (12)	0.0586 (14)	0.0381 (12)	-0.0193 (11)	-0.0043 (9)	0.0034 (10)
C8	0.0428 (10)	0.0473 (11)	0.0304 (9)	-0.0178 (9)	-0.0024 (8)	0.0015 (8)
C9	0.0425 (10)	0.0327 (9)	0.0357 (10)	-0.0048 (8)	-0.0090 (8)	0.0055 (7)
C10	0.0367 (9)	0.0343 (9)	0.0286 (9)	0.0002 (7)	-0.0027 (7)	0.0003 (7)
C11	0.0366 (9)	0.0357 (10)	0.0312 (9)	-0.0006 (7)	-0.0018 (7)	0.0046 (7)
C12	0.0372 (10)	0.0422 (11)	0.0389 (10)	0.0010 (8)	0.0017 (8)	-0.0008 (8)
C13	0.0409 (10)	0.0502 (12)	0.0339 (10)	-0.0076 (9)	0.0043 (8)	-0.0041 (8)
C14	0.0463 (11)	0.0405 (11)	0.0516 (12)	0.0110 (9)	0.0011 (9)	-0.0011 (9)
O1A	0.054 (10)	0.050 (15)	0.034 (7)	0.014 (10)	0.025 (7)	0.024 (10)
O2A	0.071 (10)	0.057 (7)	0.035 (7)	0.008 (7)	0.011 (6)	0.015 (6)
C5A	0.046 (2)	0.045 (2)	0.0266 (16)	-0.0126 (18)	0.0039 (12)	-0.0014 (14)
C6A	0.037 (7)	0.042 (8)	0.034 (8)	0.011 (5)	0.003 (5)	0.012 (6)
N1	0.0404 (8)	0.0450 (9)	0.0322 (8)	0.0081 (7)	-0.0007 (7)	0.0108 (7)
C1	0.0365 (9)	0.0450 (11)	0.0331 (9)	0.0087 (8)	0.0010 (7)	0.0140 (8)
C2	0.0356 (9)	0.0446 (11)	0.0327 (9)	0.0072 (8)	-0.0007 (7)	0.0122 (8)
C3	0.0478 (11)	0.0549 (13)	0.0420 (11)	0.0058 (9)	0.0107 (9)	0.0151 (9)
C4	0.0486 (12)	0.0520 (13)	0.0498 (12)	-0.0011 (10)	0.0002 (10)	0.0051 (10)

Geometric parameters (\AA , $^\circ$)

O1—C5	1.265 (6)	C11—C12	1.383 (3)
O1A—C5A	1.20 (4)	C12—C13	1.384 (3)
O2—C5	1.283 (6)	C6—H6	0.9500
O2A—C5A	1.39 (3)	C6A—H6AA	0.9500
O3—C14	1.425 (3)	C7—H7	0.9500
O3—C10	1.361 (2)	C7—H6AB	0.9500
O4—C11	1.352 (2)	C9—H9	0.9500
O2—H2	0.8400	C12—H12	0.9500
O2A—H2A	0.8400	C13—H13	0.9500
O4—H4	0.8200	C14—H14B	0.9800
N1—C1	1.340 (3)	C14—H14C	0.9800
N1—C2	1.339 (2)	C14—H14A	0.9800
C5—C6	1.462 (4)	C1—C3	1.498 (3)

C5A—C6A	1.42 (3)	C1—C2 ⁱ	1.393 (3)
C6—C7	1.302 (3)	C2—C4	1.496 (3)
C6A—C7	1.068 (12)	C3—H3A	0.9800
C7—C8	1.454 (3)	C3—H3B	0.9800
C8—C13	1.384 (3)	C3—H3C	0.9800
C8—C9	1.407 (3)	C4—H4A	0.9800
C9—C10	1.387 (3)	C4—H4B	0.9800
C10—C11	1.403 (2)	C4—H4C	0.9800
C10—O3—C14	117.19 (15)	C8—C7—H7	116.00
C5—O2—H2	109.00	C8—C7—H6AB	96.00
C5A—O2A—H2A	109.00	C10—C9—H9	120.00
C11—O4—H4	110.00	C8—C9—H9	120.00
C1—N1—C2	119.49 (16)	C13—C12—H12	120.00
O2—C5—C6	118.7 (4)	C11—C12—H12	120.00
O1—C5—C6	118.3 (4)	C8—C13—H13	119.00
O1—C5—O2	123.0 (4)	C12—C13—H13	119.00
O1A—C5A—O2A	126 (2)	H14A—C14—H14C	109.00
O2A—C5A—C6A	106 (2)	H14B—C14—H14C	110.00
O1A—C5A—C6A	128 (2)	H14A—C14—H14B	109.00
C5—C6—C7	123.3 (3)	O3—C14—H14A	109.00
C5A—C6A—C7	147.1 (16)	O3—C14—H14B	109.00
C6A—C7—C8	167.7 (7)	O3—C14—H14C	109.00
C6—C7—C8	128.0 (2)	N1—C1—C3	117.31 (18)
C9—C8—C13	118.77 (18)	N1—C1—C2 ⁱ	120.61 (17)
C7—C8—C13	117.51 (18)	C2 ⁱ —C1—C3	122.06 (19)
C7—C8—C9	123.72 (19)	N1—C2—C4	117.03 (17)
C8—C9—C10	120.34 (17)	N1—C2—C1 ⁱ	119.90 (17)
O3—C10—C9	125.55 (16)	C1 ⁱ —C2—C4	123.07 (18)
O3—C10—C11	114.63 (15)	C1—C3—H3A	110.00
C9—C10—C11	119.82 (16)	C1—C3—H3B	109.00
O4—C11—C12	118.58 (16)	C1—C3—H3C	109.00
C10—C11—C12	119.59 (17)	H3A—C3—H3B	109.00
O4—C11—C10	121.81 (15)	H3A—C3—H3C	109.00
C11—C12—C13	120.3 (2)	H3B—C3—H3C	109.00
C8—C13—C12	121.10 (19)	C2—C4—H4A	109.00
C7—C6—H6	118.00	C2—C4—H4B	109.00
C5—C6—H6	118.00	C2—C4—H4C	109.00
C5A—C6A—H6AA	107.00	H4A—C4—H4B	110.00
C7—C6A—H6AA	106.00	H4A—C4—H4C	109.00
C6—C7—H7	116.00	H4B—C4—H4C	109.00
C6A—C7—H6AB	96.00		
C14—O3—C10—C9	6.9 (3)	C7—C8—C13—C12	177.84 (19)
C14—O3—C10—C11	-172.83 (16)	C8—C9—C10—C11	2.1 (3)
C1—N1—C2—C4	-179.50 (18)	C8—C9—C10—O3	-177.59 (18)
C2—N1—C1—C2 ⁱ	0.0 (3)	O3—C10—C11—O4	-2.3 (3)
C1—N1—C2—C1 ⁱ	0.0 (3)	O3—C10—C11—C12	175.86 (17)
C2—N1—C1—C3	-178.63 (17)	C9—C10—C11—O4	177.98 (17)

supplementary materials

O2—C5—C6—C7	0.6 (6)	C9—C10—C11—C12	-3.8 (3)
O1—C5—C6—C7	-179.2 (4)	C10—C11—C12—C13	2.7 (3)
C5—C6—C7—C8	-179.8 (3)	O4—C11—C12—C13	-179.10 (17)
C6—C7—C8—C9	0.3 (3)	C11—C12—C13—C8	0.3 (3)
C6—C7—C8—C13	-179.6 (2)	N1—C1—C2 ⁱ —N1 ⁱ	0.0 (3)
C7—C8—C9—C10	-179.05 (18)	N1—C1—C2 ⁱ —C4 ⁱ	-179.47 (18)
C9—C8—C13—C12	-2.1 (3)	C3—C1—C2 ⁱ —N1 ⁱ	178.56 (18)
C13—C8—C9—C10	0.9 (3)	C3—C1—C2 ⁱ —C4 ⁱ	-0.9 (3)

Symmetry codes: (i) $-x, -y, -z+1$.

Hydrogen-bond geometry (\AA , $^\circ$)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O2—H2 \cdots O1 ⁱⁱ	0.84	1.79	2.613 (5)	167
O4—H4 \cdots O3	0.82	2.28	2.685 (2)	111
O4—H4 \cdots N1	0.82	1.97	2.749 (2)	158
C3—H3B \cdots O4 ⁱⁱⁱ	0.98	2.58	3.553 (3)	174
C14—H14B \cdots O4 ⁱⁱⁱ	0.98	2.59	3.465 (2)	148

Symmetry codes: (ii) $-x, -y+1, -z$; (iii) $x, y+1, z$.

Fig. 1

