Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

3-Hydroxy-4-methoxybenzohydrazide

Muhammad Hanif,[a] Ghulam Qadeer,[a] Nasim Hasan Rama,[a]* Sauli Vuoti[b] and Juho Autio[b]

[a]Department of Chemistry, Quaid-i-Azam Univeristy, Islamabad 45320, Pakistan, and [b]Department of chemistry, University Of Oulu, PO Box 3000, 90014 University Of Oulu, Finland
Correspondence e-mail: nasimhrama@yahoo.com

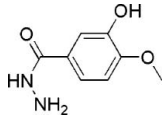
Received 23 October 2007; accepted 25 October 2007

Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.003 Å; R factor = 0.045; wR factor = 0.087; data-to-parameter ratio = 14.2.

The title compound, $C_8H_{10}N_2O_3$, is an important intermediate for the synthesis of biologically active heterocyclic compounds. The planar hydrazide group is oriented at a dihedral angle of 25.15 (3)° with respect to the benzene ring. In the crystal structure, intermolecular N—H···N, N—H···O and O—H···O hydrogen bonds link the molecules.

Related literature

For related literature, see: Zheng *et al.* (2003); Al-Talib *et al.* (1990); Yousif *et al.* (1986); Al-Soud *et al.* (2004); El-Emam *et al.* (2004); Furniss *et al.* (1978). For bond-length data, see: Allen *et al.* (1987).



Experimental

Crystal data

$C_8H_{10}N_2O_3$
M_r = 182.18
Trigonal, $R\overline{3}$
a = 19.4079 (10) Å
c = 11.5250 (4) Å
V = 3759.5 (3) Å^3
Z = 18
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 120 (2) K
0.21 × 0.20 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.977, T_{max} = 0.987
14714 measured reflections
1920 independent reflections
1362 reflections with $I > 2\sigma(I)$
R_{int} = 0.064

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.045
$wR(F^2)$ = 0.087
S = 1.07
1920 reflections
135 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.24 e Å^{-3}
$\Delta\rho_{min}$ = −0.23 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2N···N2^{i}	0.91 (2)	2.24 (2)	3.1274 (19)	165.3 (16)
N2—H2N···N1^{i}	0.91 (2)	2.567 (19)	3.266 (2)	134.5 (15)
N2—H2M···O2^{ii}	0.93 (2)	2.15 (2)	3.0364 (19)	158.6 (17)
N2—H2M···O1^{ii}	0.93 (2)	2.43 (2)	3.1335 (18)	132.6 (15)
N1—H1N···O3^{iii}	0.88 (2)	2.15 (2)	2.9296 (18)	147.6 (16)
O2—H2O···O3^{iv}	0.86 (2)	1.81 (2)	2.6635 (16)	171 (2)

Symmetry codes: (i) $y-\frac{1}{3}, -x+y+\frac{1}{3}, -z+\frac{1}{3}$; (ii) $-y+\frac{4}{3}, x-y+\frac{5}{3}, z+\frac{2}{3}$; (iii) $x-y+\frac{2}{3}, x+\frac{1}{3}, -z+\frac{1}{3}$; (iv) $-y+\frac{4}{3}, x-y+\frac{5}{3}, z-\frac{1}{3}$.

Data collection: *COLLECT* (Bruker, 2000); cell refinement: *EVALCCD* (Duisenberg *et al.*, 2003); data reduction: *EVALCCD*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 2007); software used to prepare material for publication: *SHELXL97*.

The authors gratefully acknowledge funds from the Higher Education Commission, Islamabad, Pakistan.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HK2352).

References

Allen, F. H., Kennard, O., Watson, D. G., Brammer, L., Orpen, A. G. & Taylor, R. (1987). *J. Chem. Soc. Perkin Trans. 2*, pp. S1–19.
Al-Soud, Y. A., Al-Deeri, M. N. & Al-Mosoudi, N. A. (2004). *Farmaco*, **59**, 775–783.
Al-Talib, M., Tastoush, H. & Odeh, N. (1990). *Synth. Commun.* **20**, 1811–1814.
Brandenburg, K. (2007). *DIAMOND*. Version 3.1e. Crystal Impact GbR, Bonn, Germany.
Bruker (2000). *COLLECT*. Bruker AXS BV, Delft, The Netherlands.
Duisenberg, A. J. M., Kroon-Batenburg, L. M. J. & Schreurs, A. M. M. (2003). *J. Appl. Cryst.* **36**, 220–229.
El-Emam, A. A., Al-Deeb, O. A., Al-Omar, M. & Lehmann, J. (2004). *Bioorg. Med. Chem.* **12**, 5107–5113.
Furniss, B. S., Hannaford, A. J., Rogers, V., Smith, P. W. G. & Tatchell, A. R. (1978). Editors. *Vogel's Textbook of Practical Organic Chemistry*, 4th ed., p. 1125. London: Longmann.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXS97*. University of Göttingen, Germany.
Yousif, M. Y., Ismail, A. M., Elman, A. A. & El-Kerdawy, M. M. (1986). *J. Chem. Soc. Pak.* **8**, 183–187.
Zheng, X., Li, Z., Wang, Y., Chen, W., Huang, Q., Liu, C. & Song, G. (2003). *J. Fluorine Chem.* **117**, 163–169.

  doi:10.1107/S1600536807053160

supplementary materials

Acta Cryst. (2007). E**63**, o4506 [**doi:10.1107/S1600536807053160**]

3-Hydroxy-4-methoxybenzohydrazide

M. Hanif, G. Qadeer, N. H. Rama, S. Vuoti and J. Autio

Comment

Aromatic hydrazides are important intermediates in heterocyclic chemistry and have been used for the synthesis of various biologically active five-membered heterocycles such as 2,5-disubstituted-1,3,4-oxadiazoles (Zheng *et al.*, 2003; Al-Talib *et al.*, 1990) and 5-substituted-2-mercapto-1,3,4-oxadiazoles (Yousif *et al.*, 1986; Al-Soud *et al.*, 2004; El-Emam *et al.*, 2004). In view of the versatility of these compounds, we have synthesized the title compound, (I), and reported its crystal structure.

In the molecule of (I) (Fig. 1), the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). The dihedral angle between the planar hydrazidic group (C6/O3/N1/N2) and the benzene ring (C2—C5/C7/C8) is 25.15 (3)°.

In the crystal structure, intermolecular N—H···N, N—H···O and O—H···O hydrogen bonds (Table 1, Fig. 2) link the molecules, in which they seem to be effective in the stabilization of the structure.

Experimental

The title compound, (I), is synthesized by the reaction of methyl ester of 3-hydroxy-4-methoxybenzoic acid with hydrazine hydrate using the reported procedure (Furniss *et al.*, 1978). For the preparation of (I), a mixture of methyl-3-hydroxy-4-methoxybenzoate (1.82 g, 10 mmol) and hydrazine hydrate (80%, 15 ml) in absolute ethanol (50 ml) was refluxed for 5 h at 413–423 K. The excess solvent was removed by distillation. The solid residue was filtered off, washed with water and recrystallized from ethanol (30%) to give the title compound (yield; 1.5 g, 82%, m.p. 475–477 K). Colorless single crystals of (I) were obtained by slow evaporation of an ethanol solution at room temperature.

Refinement

H atoms of OH, NH and NH_2 groups were located in difference syntheses and refined isotropically [O—H = 0.086 (2) Å and U_{iso}(H) = 0.044 (7) Å^2 (for OH); N—H = 0.88 (2) Å and U_{iso}(H) = 0.024 (5) Å^2 (for NH); N—H = 0.91 (2) and 0.93 (2) Å, U_{iso}(H) = 0.019 (5) and 0.027 (5) Å^2 (for NH_2)]. The remaining H atoms were positioned geometrically, with C—H = 0.95 and 0.98 Å for aromatic and methyl H atoms, respectively, and constrained to ride on their parent atoms, with U_{iso}(H) = xU_{eq}(C), where x = 1.2 for aromatic H, and x = 1.5 for methyl H atoms.

Figures

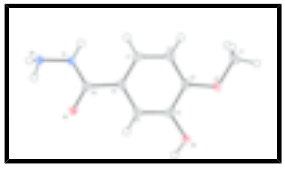


Fig. 1. The molecular structure of the title molecule, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

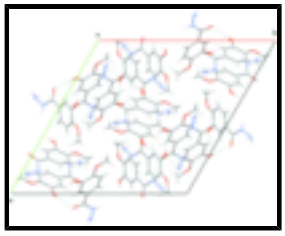


Fig. 2. A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

Fig. 3. The formation of the title compound.

3-Hydroxy-4-methoxybenzohydrazide

Crystal data

$C_8H_{10}N_2O_3$	$Z = 18$
$M_r = 182.18$	$F_{000} = 1728$
Trigonal, $R\bar{3}$	$D_x = 1.448$ Mg m^{-3}
Hall symbol: -R 3	Melting point: 475(2) K
$a = 19.4079$ (10) Å	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å
$b = 19.4079$ (10) Å	Cell parameters from 13690 reflections
$c = 11.5250$ (4) Å	$\theta = 1.0$–27.5°
$\alpha = 90^\circ$	$\mu = 0.11$ mm^{-1}
$\beta = 90^\circ$	$T = 120$ (2) K
$\gamma = 120^\circ$	Block, colorless
$V = 3759.5$ (3) Å^3	0.21 × 0.20 × 0.12 mm

Data collection

Nonius KappaCCD diffractometer	1920 independent reflections
Radiation source: fine-focus sealed tube	1362 reflections with $I > 2\sigma(I)$
Monochromator: horizontally mounted graphite crystal	$R_{int} = 0.064$
Detector resolution: 9 pixels mm^{-1}	$\theta_{max} = 27.5^\circ$
$T = 120(2)$ K	$\theta_{min} = 3.0^\circ$
φ scans and ω scans with κ offset	$h = -24 \rightarrow 25$
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	$k = -25 \rightarrow 25$
$T_{min} = 0.977$, $T_{max} = 0.987$	$l = -14 \rightarrow 12$
14714 measured reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: mixed
$R[F^2 > 2\sigma(F^2)] = 0.045$	H atoms treated by a mixture of independent and constrained refinement

$wR(F^2) = 0.087$	$w = 1/[\sigma^2(F_o^2) + (0.0273P)^2 + 5.5999P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
1920 reflections	$\Delta\rho_{max} = 0.24$ e Å^{-3}
135 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

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 $F^2 > 2\text{sigma}(F^2)$ 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 (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
O1	0.09395 (7)	0.93439 (7)	−0.22631 (10)	0.0177 (3)
O2	0.24707 (7)	1.00363 (7)	−0.25462 (9)	0.0166 (3)
H2O	0.2983 (15)	1.0281 (14)	−0.2516 (19)	0.044 (7)*
O3	0.35414 (6)	0.92873 (6)	0.09783 (9)	0.0144 (3)
N1	0.24700 (9)	0.81514 (8)	0.15538 (11)	0.0143 (3)
H1N	0.1958 (12)	0.7796 (12)	0.1509 (16)	0.024 (5)*
N2	0.29078 (9)	0.78856 (8)	0.22064 (13)	0.0147 (3)
H2N	0.3332 (12)	0.7967 (11)	0.1776 (16)	0.019 (5)*
H2M	0.3109 (12)	0.8204 (12)	0.2860 (18)	0.027 (5)*
C1	0.00948 (10)	0.89463 (11)	−0.21621 (16)	0.0229 (4)
H1A	−0.0118	0.8370	−0.2146	0.034*
H1B	−0.0128	0.9083	−0.2828	0.034*
H1C	−0.0051	0.9113	−0.1444	0.034*
C2	0.13430 (10)	0.91959 (10)	−0.14269 (13)	0.0132 (4)
C3	0.21694 (10)	0.95706 (9)	−0.15902 (13)	0.0126 (4)
C4	0.26263 (10)	0.94487 (9)	−0.07985 (13)	0.0130 (4)
H4	0.3185	0.9699	−0.0910	0.016*
C5	0.22816 (9)	0.89622 (9)	0.01679 (13)	0.0123 (3)
C6	0.28099 (9)	0.88187 (9)	0.09396 (13)	0.0118 (3)
C7	0.14684 (10)	0.86073 (10)	0.03336 (14)	0.0157 (4)
H7	0.1229	0.8281	0.0994	0.019*
C8	0.10022 (10)	0.87259 (10)	−0.04603 (14)	0.0160 (4)
H8	0.0445	0.8483	−0.0339	0.019*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0116 (6)	0.0231 (7)	0.0181 (6)	0.0085 (5)	−0.0025 (5)	0.0038 (5)
O2	0.0117 (6)	0.0203 (7)	0.0145 (6)	0.0057 (6)	0.0019 (5)	0.0062 (5)
O3	0.0126 (6)	0.0125 (6)	0.0172 (6)	0.0056 (5)	0.0002 (5)	0.0016 (5)
N1	0.0118 (8)	0.0130 (7)	0.0168 (7)	0.0051 (7)	−0.0025 (6)	0.0022 (6)
N2	0.0147 (8)	0.0159 (8)	0.0157 (7)	0.0093 (7)	−0.0025 (6)	0.0016 (6)
C1	0.0138 (9)	0.0299 (11)	0.0250 (10)	0.0109 (8)	−0.0036 (7)	0.0019 (8)
C2	0.0148 (9)	0.0132 (8)	0.0135 (8)	0.0084 (7)	−0.0026 (7)	−0.0019 (7)
C3	0.0164 (9)	0.0098 (8)	0.0111 (8)	0.0061 (7)	0.0002 (7)	−0.0009 (6)
C4	0.0109 (8)	0.0127 (8)	0.0148 (8)	0.0055 (7)	0.0002 (6)	−0.0019 (7)
C5	0.0151 (8)	0.0098 (8)	0.0128 (8)	0.0069 (7)	−0.0013 (7)	−0.0020 (6)
C6	0.0142 (9)	0.0114 (8)	0.0107 (8)	0.0071 (7)	0.0010 (6)	−0.0022 (6)
C7	0.0166 (9)	0.0150 (9)	0.0145 (8)	0.0072 (7)	0.0019 (7)	0.0024 (7)
C8	0.0109 (8)	0.0166 (9)	0.0194 (8)	0.0060 (7)	0.0009 (7)	−0.0003 (7)

Geometric parameters (Å, °)

O1—C2	1.3599 (19)	C1—H1C	0.9800
O1—C1	1.425 (2)	C2—C8	1.381 (2)
O2—C3	1.3580 (19)	C2—C3	1.404 (2)
O2—H2O	0.86 (2)	C3—C4	1.373 (2)
O3—C6	1.2464 (19)	C4—C5	1.396 (2)
N1—C6	1.326 (2)	C4—H4	0.9500
N1—N2	1.4114 (19)	C5—C7	1.384 (2)
N1—H1N	0.88 (2)	C5—C6	1.485 (2)
N2—H2N	0.91 (2)	C7—C8	1.385 (2)
N2—H2M	0.93 (2)	C7—H7	0.9500
C1—H1A	0.9800	C8—H8	0.9500
C1—H1B	0.9800		
C2—O1—C1	117.11 (13)	O2—C3—C2	116.99 (14)
C3—O2—H2O	109.1 (15)	C4—C3—C2	119.39 (14)
C6—N1—N2	123.02 (14)	C3—C4—C5	120.97 (15)
C6—N1—H1N	123.1 (12)	C3—C4—H4	119.5
N2—N1—H1N	113.2 (12)	C5—C4—H4	119.5
N1—N2—H2N	107.8 (12)	C7—C5—C4	119.24 (15)
N1—N2—H2M	108.6 (12)	C7—C5—C6	123.13 (14)
H2N—N2—H2M	106.6 (17)	C4—C5—C6	117.55 (14)
O1—C1—H1A	109.5	O3—C6—N1	121.49 (15)
O1—C1—H1B	109.5	O3—C6—C5	121.73 (14)
H1A—C1—H1B	109.5	N1—C6—C5	116.74 (14)
O1—C1—H1C	109.5	C5—C7—C8	120.24 (15)
H1A—C1—H1C	109.5	C5—C7—H7	119.9
H1B—C1—H1C	109.5	C8—C7—H7	119.9
O1—C2—C8	125.10 (15)	C2—C8—C7	120.39 (15)
O1—C2—C3	115.15 (14)	C2—C8—H8	119.8

C8—C2—C3	119.75 (15)	C7—C8—H8	119.8
O2—C3—C4	123.62 (15)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2N···N2^{i}	0.91 (2)	2.24 (2)	3.1274 (19)	165.3 (16)
N2—H2N···N1^{i}	0.91 (2)	2.567 (19)	3.266 (2)	134.5 (15)
N2—H2M···O2^{ii}	0.93 (2)	2.15 (2)	3.0364 (19)	158.6 (17)
N2—H2M···O1^{ii}	0.93 (2)	2.43 (2)	3.1335 (18)	132.6 (15)
N1—H1N···O3^{iii}	0.88 (2)	2.15 (2)	2.9296 (18)	147.6 (16)
O2—H2O···O3^{iv}	0.86 (2)	1.81 (2)	2.6635 (16)	171 (2)

Symmetry codes: (i) *y*−1/3, −*x*+*y*+1/3, −*z*+1/3; (ii) −*y*+4/3, *x*−*y*+5/3, *z*+2/3; (iii) *x*−*y*+2/3, *x*+1/3, −*z*+1/3; (iv) −*y*+4/3, *x*−*y*+5/3, *z*−1/3.

Fig. 1

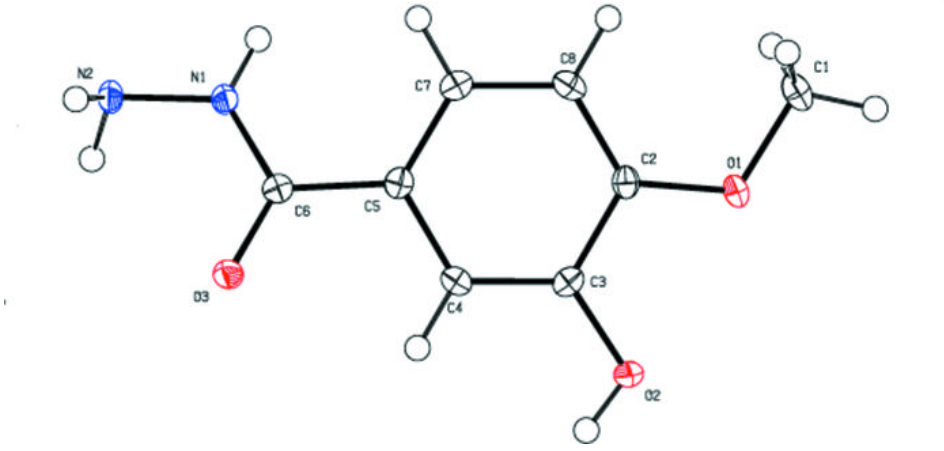


Fig. 2

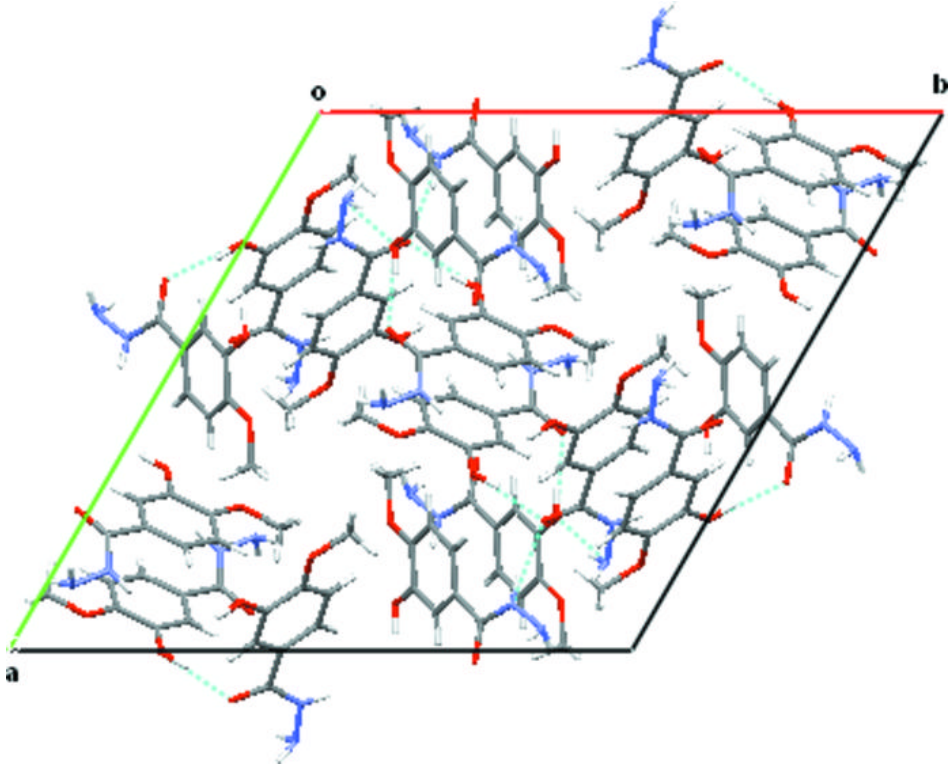
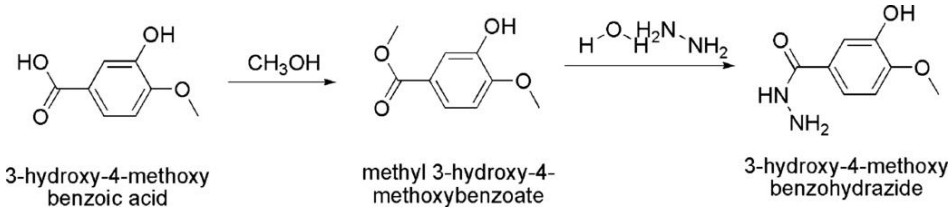


Fig. 3



3-hydroxy-4-methoxy benzoic acid

methyl 3-hydroxy-4-methoxybenzoate

3-hydroxy-4-methoxy benzohydrazide