FENPYROXIMATE

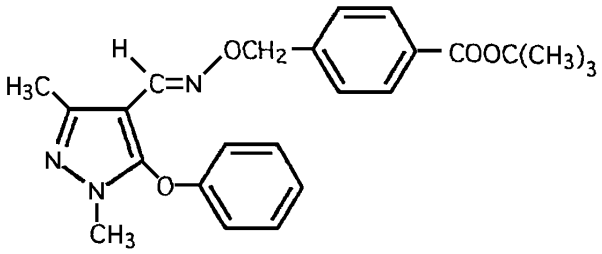
IDENTITY

ISO common name: Fenpyroximate (draft)
Chemical name
IUPAC: *tert*-butyl (*E*)-Æ-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluate
CA: (*E*)-1,1-dimethylethyl 4-[[[[(1,3-dimethyl-5-phenoxy-1*H*-pyrazol-4-yl)methylene]amino]oxy]methyl]benzoate

CAS No.: 111812-58-9

Synonyms: Danitron, Kiron, Naja, Dynamite, NNI-850

Structural formula:



Molecular formula: $C_{24}H_{27}N_3O_4$
Molecular weight: 421.50

Physical and chemical properties

Pure active ingredient

Vapour pressure at 25°C:	5.6×10^{-8} mm Hg	
n-Octanol/water partition coefficient:	log P_{ow} = 5.01	
Solubility in water at 25°C:	pH 5	0.021 mg/l
	pH 7	0.023 mg/l
	pH 9	0.030 mg/l

Technical material

Physical state:	solid
Colour:	off-white to pale yellowish
Odour:	practically odourless
Purity:	95.9-99.8%
Density:	1.237-1.257 g/cm^3
Melting point:	99.3-101.7 °C

Solubility in organic solvents at 25°C:	n-Hexane	3.5 g/l
	Methanol	15.3 g/l
	Ethanol	16.5 g/l
	Acetonitrile	37.4 g/l
	Acetone	150 g/l
	Ethyl acetate	201 g/l
	Benzene	207 g/l
	Toluene	268 g/l
	Chloroform	1197 g/l
Flammability:	Not applicable	
Hydrolysis:	Half-life (25°C) at	pH 5: 180 days pH 7: 226 days pH 9: 221 days
Photolysis:	Half-life at pH 7: 1.5 hours (in aqueous solution irradiated with a xenon lamp of 603 watts, 290-800 nm)	
Storage stability:	Stable for more than 1 year	

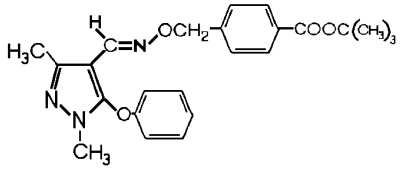
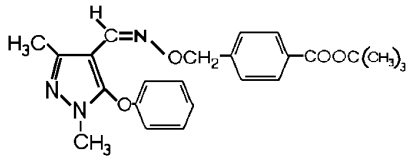
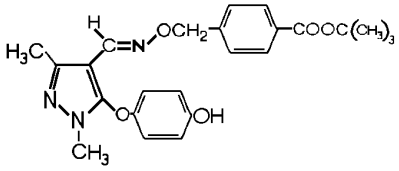
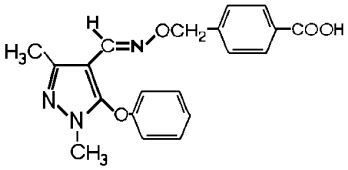
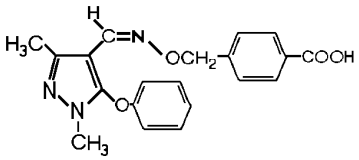
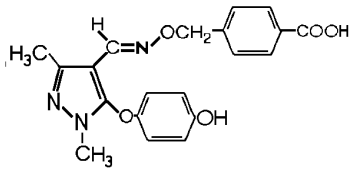
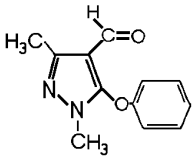
Formulation

Fenpyroximate is formulated as a 5% suspension concentrate.

METABOLISM AND ENVIRONMENTAL FATE

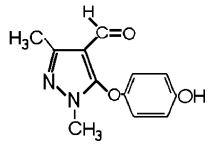
The labelled compounds [*pyrazole*-^{14}C] and [*benzyl*-^{14}C]fenpyroximate were used in a series of studies on metabolism in rats and plants (citrus, apples and grapes), and degradation in soil and water. The chemical names and structures of fenpyroximate and its metabolites are shown in Table 1.

Table 1. Chemical names and structures of fenpyroximate and its metabolites

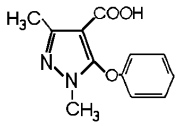
tert-butyl (*E*)-Æ-(1,3,-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluate (fenpyroximate)		
tert-butyl (*Z*)-Æ-(1,3,-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluate (M-1)	(A)	
tert-butyl (*E*)-4-([1,3,-dimethyl-5-(4-hydroxyphenoxy)pyrazol-4-yl)methyleneamino-oxymethyl)benzoate (M-2)	(B)	
(*E*)-Æ-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluic acid	(C)	
(*Z*)-Æ-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluic acid	(D)	
(*E*)-Æ-(1,3-dimethyl-5-(4-hydroxy-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluic acid (M-5)	(E)	
1,3-dimethyl-5-phenoxypyrazole-4-carbaldehyde	(F)	

fenpyroximate

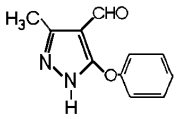
1,3-dimethyl-5-(4-hydroxyphenoxy)pyrazole-4-carbaldehyde (G)



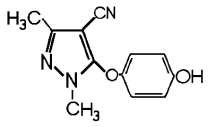
1,3-dimethyl-5-phenoxypyrazole-4-carboxylic acid (H)



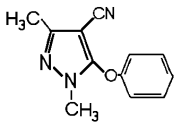
3-methyl-5-phenoxypyrazole-4-carbbaldehyde (M-9) (I)



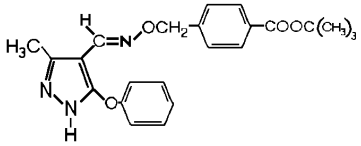
1,3-dimethyl-5-(4-hydroxyphenoxy) pyrazole-4-carbonitrile (M-10) (J)



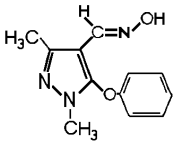
1,3-dimethyl-5-phenoxypyrazole-4-carbonitrile (K)



tert-butyl (*E*)-Æ-(3-methyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluate (L)

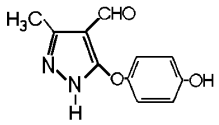


(*E*)-1,3-dimethyl-5-phenoxy-pyrazole-4-carbaldehyde oxime (M-13) (M)



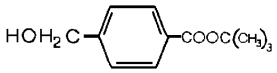
fenpyroximate

(N)



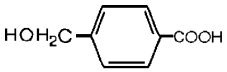
3-methyl-5-(4-hydroxyphenoxy)-pyrazole-4-carbaldehyde (M-14)

(O)



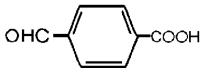
tert-butyl Æ-hydroxy-*p*-toluate (M-15)

(P)



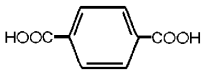
Æ-hydroxy-*p*-toluic acid (M-16)

(Q)



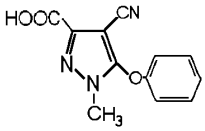
4-formylbenzoic acid (M-17)

(R)



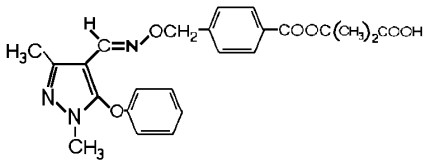
terephthalic acid (M-8)

(S)



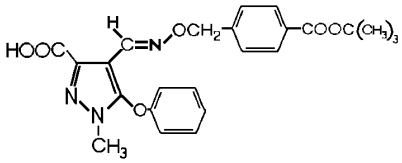
4-cyano-1-methyl-5-phenoxy-pyrazole-3-carboxylic acid (M-21)

(T)



(*E*)-2-[4-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethylene-amino-oxymethyl)benzoyloxy]-2-methylpropionic acid (M-22)

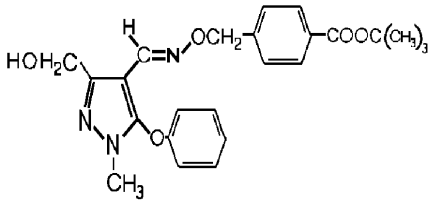
(U)



(*E*)-4-[-4(*tert*-butoxycarbonyl)benzloxyiminomethyl]-1-methyl-5-phenoxypyrazole-3-carboxylic acid (M-19)

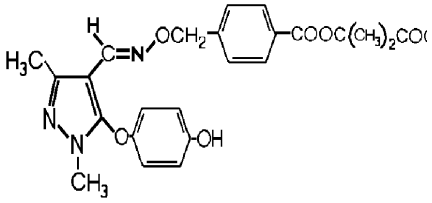
tert-butyl (*E*)-Æ-(3-hydroxymethyl-1-methyl-5-phenoxyprazol-4-ylmethyleneamino-oxy-*p*-toluate (M-20)

(V)



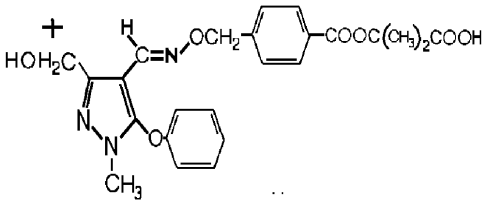
(*E*)-2-[-[1,3-DIMETHYL-5-(4-hydroxyphenoxy)pyrazole-4-ylmethyleneamino-oxymethyl]benzoyloxy]-2-methyl-propionic acid

(W)



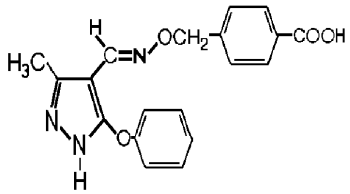
(*E*)-2-[4-[(3-hydroxymethyl-1-methyl-5-phenoxypyrazol-4-yl)-methyleneamino-oxymethyl]-benzoyloxy]-2-methylpropionic acid

(X)



(*E*)-Æ-(1,3-methyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluic acid

(Y)



Animal metabolism

A metabolic study was undertaken with the objective of determining the distribution, elimination and biotransformation of [*pyrazole*-^{14}C]fenpyroximate administered orally to male and female rats at various doses.

The rats were divided into three groups (A, B, C). Group A was dosed orally with [*pyrazole*-^{14}C]fenpyroximate suspended in 1% aqueous Tween 80 at 2 mg/kg bw. Group B received 14 consecutive daily doses of unlabelled fenpyroximate followed by a single dose of radiolabelled material at 2 mg/kg bw. Group C was dosed orally with 400 mg/kg bw of [*pyrazole*-^{14}C]fenpyroximate suspended in aqueous Tween 80 solution.

In a preliminary experiment it was determined that negligible amounts of radioactivity were expired as CO_2 or volatile organic compounds after the oral administration of [*pyrazole*-^{14}C]fenpyroximate at 2 mg/kg bw.

After dosing with labelled fenpyroximate, urine and faeces were collected at intervals up to 168 hours, when the animals were killed for assay of the radioactivity in various tissues.

After the administration of fenpyroximate at 2 mg/kg, radioactivity was rapidly excreted. After 7 days, 70-85% of the dose was eliminated in the faeces and 12-18% in the urine. Residues at 7 days in fat were 0.025 and 0.011 ì g/g fenpyroximate equivalents in males and females respectively. Residues in liver were 0.003 ì g/g in both males and females. No residues were detected in other tissues. Similar results were obtained by multiple dosing of the unlabelled compound followed by a single dose of labelled fenpyroximate at 2 mg/kg. Residues expressed as fenpyroximate equivalents were 0.016 and 0.008 ì g/g in the fat and 0.005 and 0.003 ì g/g in the liver of males and females respectively. Slower excretion was observed after a single administration at 400 mg/kg, but after 168 hours 75-77% of the dose was eliminated in the faeces and 11-12% in the urine. Residues in the tissues were generally low at 168 hours, and parts of the gastrointestinal tract showed the highest concentrations of radioactivity at 1-4% of the dose. The delayed movement of fenpyroximate through the gastrointestinal tract at 400 mg/kg is probably due to its toxic effect.

The major urinary metabolites were 1,3-dimethyl-5-phenoxypyrazole-4-carboxylic acid (H) and 4-cyano-1-methyl-5-phenoxypyrazole-3-carboxylic acid (S). A large amount of (apparently unabsorbed) fenpyroximate was present in the faeces; the major faecal metabolites were (*E*)-Æ-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluic acid (C) and (*E*)-2-[4-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxymethyl)benzoyloxy]-2-methylpropionic acid (T).

Residues in the tissues were generally very low at 168 hours, with the highest concentrations of radioactivity in all groups in the liver, kidneys, fat and urinary bladder. In all groups in which radioactivity was detectable, the concentration in the plasma was about twice that in the blood, indicating that nearly all of the radioactive material in the blood was in the plasma.

Urine, plasma, cage rinses and washes, and carbon dioxide trapping solutions were analyzed directly by LSC. Urine and faeces were extracted with various solvents to determine the total extractable residues, and the metabolites in the extracts were identified by TLC and HPLC (Sharp, 1991a).

A similar study was carried out with [*benzyl*-^{14}C]fenpyroximate. Similar patterns of excretion and tissue distribution were observed. The major urinary metabolite was terephthalic acid (R). As with [*pyrazole*-^{14}C]fenpyroximate large amounts of the parent compound were present in the faeces. Major metabolites were C and (*Z*)-Æ-(1,3-dimethyl-5-phenoxypyrazole-4-ylmethyleneamino-oxy)-*p*-toluic acid (D) (Sharp, 1991b).

Further studies to elucidate the metabolic fate in rats were carried out with fenpyroximate labelled in the pyrazole ring, the phenoxy group and the *tert*-butyl group.

Fenpyroximate is metabolized by oxidation of the *tert*-butyl and pyrazole-3-methyl groups, *p*-hydroxylation of the phenoxy moiety, *N*-demethylation, hydrolysis at the ester and methyleneamino-oxy bonds, and conjugation. *E/Z* isomerization also occurs, giving the faecal metabolites A and D.

The proposed metabolic pathways of fenpyroximate in rats are shown in Figure 1, which includes the 3 metabolites W, X and Y which were subsequently identified by NMR spectrometry (Nishizawa *et al.*, 1993).

Plant metabolism

Metabolism studies were carried out with ^{14}C-labelled fenpyroximate, solutions of the product being sprayed on citrus, apple trees and grape vines.

Citrus. Satsuma tangerine trees were sprayed with [*pyrazole*-^{14}C]fenpyroximate at application rates of 22. 4 ± 1. 5 mg/tree (group 1) and 33.5 ± 0.5 mg /tree (group 2) at a concentration of 5 g/hl. Group 1 trees received 61.9 ± 4.3 ì Ci/tree and fruit were harvested after 0, 3, 7, 14 and 28 days. Group 2 trees received 703.5-705.9 ì Ci/tree and the fruit were harvested at maturity, 137 days after treatment. Two untreated trees served as controls. Leaves, fruit and soil samples were collected. The fruit were separated into pulp and peel, each sample was homogenized and the residues quantitatively determined by combustion and liquid scintillation spectroscopy. Table 2 shows the results (Krautter *et al.*, 1989).

Table 2. Mean residues of ^{14}C expressed as fenpyroximate in tangerine plant tissues and soil (Krautter *et al.*, 1989).

Sample	^{14}C as mg/kg pyroximate at interval, days					
	Group 1					Group 2
	0	3	7	14	28	137
Leaves	5.33	5.54	3.37	2.27	1.78	1.37
Peel	0.49	0.63	0.52	0.48	0.49	0.37
Fruit (pulp)	N.D.[1]	N.D.[1]	N.D.[1]	N.D.[1]	N.D.[1]	N.D.[2]
Soil	5.50	8.40	7.04	5.91	7.42	4.59

[1] LOD 0.03 mg/kg
[2] LOD 0.004 mg/kg

The samples were investigated further at another laboratory (Izawa *et al.*, 1990). The radioactivity in the fruit pulp was too low for further analysis. Extracts of leaves and peel were analysed by thin-layer co-chromatography and autoradiography (TLC-ARG). The level of fenpyroximate in the peel was 0.44 mg/kg at day 0 and 0.12 mg/kg at day 137: the half-life was 38.4 days. In the leaves the residues at days 0 and 137 were 4.88 and 0.24 mg/kg respectively, and the half-life was 8.8 days. The major metabolites in the leaves and peel were the *Z*- isomer of fenpyroximate (A) and *tert*-butyl (*E*)-4-(3-methyl-5-phenoxypyrazol-4-ylmethyleneamino-oxymethyl)benzoate (demethyl-fenpyroximate, L). The results are shown in Table 3 (Izawa *et al.*, 1990).

Figure 1. Proposed metabolic pathways of fenpyroximate in rats.

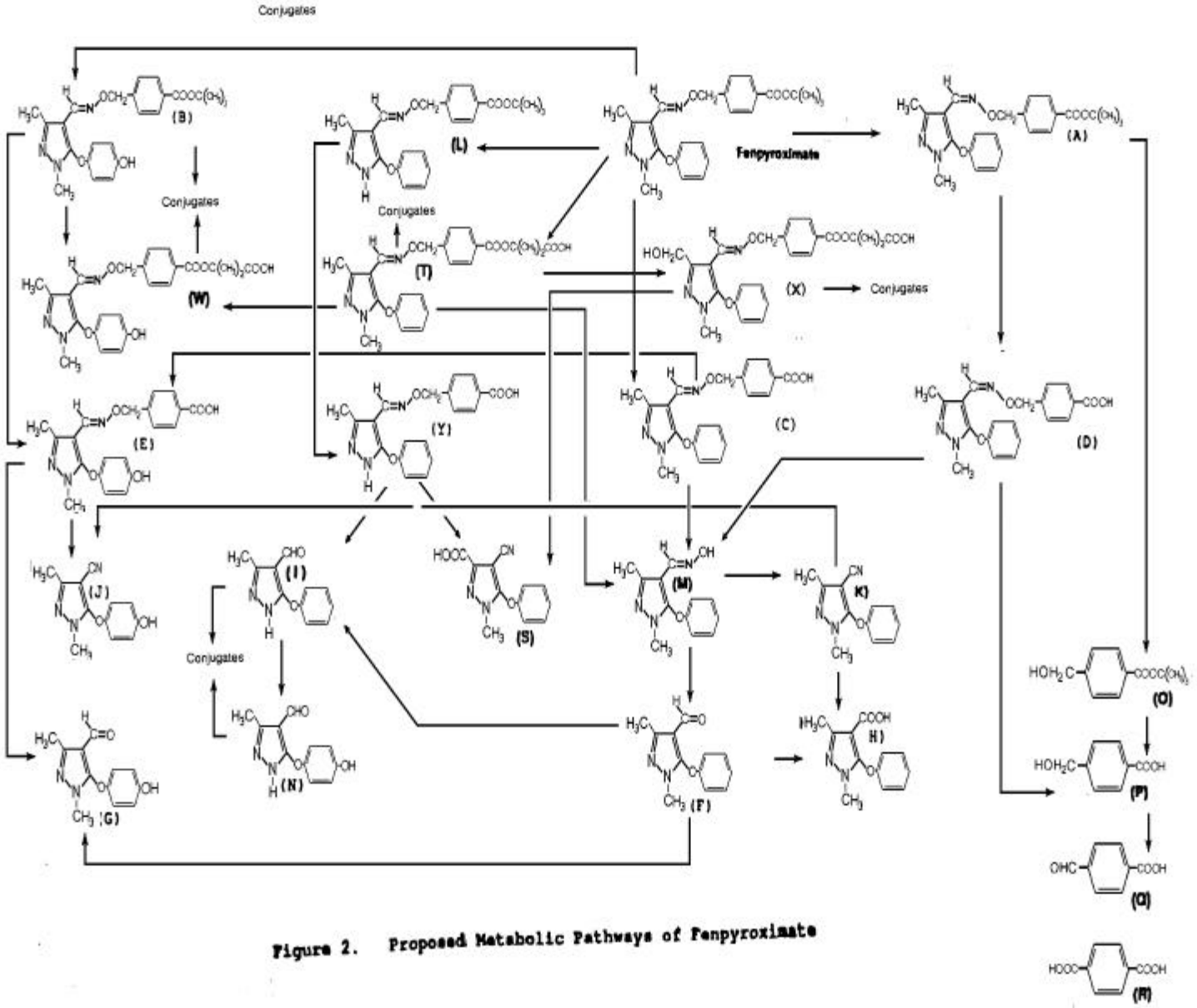


Figure 2. Proposed Metabolic Pathways of Fenpyroximate

fenpyroximate

fenpyroximate

Table 3. Radioactivity in citrus leaves and peel after [^{14}C]fenpyroximate application (Izawa *et al.*,1990).

Sample	^{14}C expressed as mg/kg fenpyroximate (fresh weight) at interval, days					
	Group 1					Group 2
	0	3	7	14	28	137
Leaves, total	5.33	5.54	3.37	2.27	1.78	1.37
Extractable	5.28 (99.1)	4.89 (88.3)	2.58 (76.6)	1.53 (67.4)	1.33 (74.7)	1.05 (76.6)
Unextractable	0.05 (0.9)	0.65 (11.7)	0.79 (23.4)	0.74 (32.6)	0.45 (25.3)	0.32 (23.4)
Peel, total	0.49	0.63	0.52	0.48	0.49	0.36
Extractable	0.49 (100)	0.62 (98.4)	0.50 (96.2)	0.46 (95.8)	0.46 (93.9)	0.33 (91.9)
Unextractable	0 (0)	0.01 (1.16)	0.02 (3.8)	0.02 (4.2)	0.03 (6.1)	0.03 (8.1)

Values in parentheses represent % of total radioactivity in each sample

Table 4. Concentration of fenpyroximate and its metabolites in citrus peel and leaves after ^{14}C-fenpyroximate application.

Compound	Days after application					
	0	3	7	14	28	137
Peel						
Fenpyroximate	0.44 (90)	0.52 (84)	0.42 (84)	0.32 (70)	0.30 (65)	0.12 (36)
A	0.05 (10)	0.03 (5)	0.02 (4)	0.05 (11)	0.02 (4)	0.02 (6)
K	nd	nd	nd	nd	nd	0.01 (3)
L	nd	nd	nd	nd	0.02 (4)	0.06 (18)
Leaves						
Fenpyroximate	4.88 (92)	3.37 (69)	1.01 (39)	0.56 (37)	0.51 (38)	0.24 (23)
A	0.23 (4)	0.29 (6)	0.15 (6)	0.23 (15)	0.25 (19)	0.13 (12)
I	n.d	0.20 (4)	0.13 (5)	0.08 (5)	<0.06	<0.01
K	n.d	<0.06	<0.06	<0.06	<0.06	<0.01
L	0.12 (2)	0.44 (9)	0.27 (10)	0.09 (6)	<0.06	0.08 (8)

Values in parentheses represent % of the extractable radioactivity

The other minor metabolites in the peel, (*E*)-Æ-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluic acid (C), 1,3-dimethyl-5-phenoxypyrazole-4-carbaldehyde (F), 1,3-dimethyl-5-phenoxypyrazole-4-carboxylic acid (H), 3-methyl-5-phenoxypyrazole-4-carbaldehyde (I), (*E*)-1,3-dimethyl-5-phenoxypyrazole-4-carbaldehyde oxime (M), 3-methyl-5-(4-hydroxyphenoxy)-pyrazole-4-carbaldehyde (N), (*E*)-4-[4-(-*tert*-butoxycarbonyl)benzyloxyiminomethyl]-1-methyl-5-phenoxypyrazole-3-carboxylic acid (U) and *tert*-butyl (*E*)-Æ-(3-hydroxymethyl-1-methyl-5-phenoxypyrazole-4-ylmethyleneamino-oxy)-*p*-toluate (V) were detected at concentrations of less than 0.01 mg/kg at day 137 (Izawa *et al.*, 1991a).

In another study with [*benzyl*-^{14}C]fenpyroximate, satsuma mandarin trees were sprayed at the rate of 1 mg/tree (experiment 1 10 ì Ci/tree; experiment 2 35 ì Ci/tree). Fruit and leaves were collected

after 0, 3, 7, 14 and 28 days in experiment 1 and 98 days in experiment 2. The radioactivity in all pulp samples was less than 0.01 mg fenpyroximate equivalents/kg. In the peel the residues of fenpyroximate were 1.12 mg/kg just after application and 0.09 mg/kg at day 98, and in the leaves 9.75 mg/kg at day 0 and 0.21 mg/kg at day 98. The concentrations of the extractable and unextractable radioactivity in the peel and of the identified metabolites in the extracts are shown below (Izawa *et al.*, 1991b).

Table 5. Concentration of fenpyroximate and metabolites in citrus peel after [*benzyl*-^{14}C]fenpyroximate application.

Compound or fraction	^{14}C expressed as mg/kg fenpyroximate (fresh weight) at interval, days				
	0	7	14	28	98
Fenpyroximate	1.12 (100)	0.81 (83)	0.83 (79)	0.53 (70)	0.09 (53)
Metabolite A	nd	0.04 (4)	0.05 (5)	0.02 (3)	0.01 (6)
Metabolite L	nd	0.12 (12)	0.12 (11)	0.10 (13)	0.04 (24)
Extractable	1.12	0.98	1.05	0.76	0.17
Unextractable	0.01	0.04	0.11	0.11	0.04

Values in parentheses represent % of the extractable radioactivity

The other minor metabolites, B, C, O, Q, U and V were less than 0.01 mg/kg at day 98.

From these results, fenpyroximate was shown to be metabolized in citrus trees by hydrolysis of the ester and methyleneamino ether links, *N*-demethylation, oxidation, and conjugation of the polar metabolites (Izawa *et al.*, 1991).

Apple trees were sprayed with a 5% SC formulation of [*pyrazole*-^{14}C]fenpyroximate at the maximum recommended rate of 7.5 g ai/hl (37.5 g ai/ha/m crown height) and 908.6 ì Ci/tree (Galicia & Wyss-Benz, 1992). Fruit and leaves were collected 0, 7, 14, 28 and 57 days (harvest) after application. The total radioactivity in the fruit was 0.128 mg/kg fenpyroximate equivalents at day 0 and 0.032 mg/kg at day 57. In leaves, the total radioactivity decreased from 10.33 mg/kg at day 0 to 0.51 mg/kg at day 57. The total radioactivity in the juice was 0.003 mg/kg at day 57. Unchanged fenpyroximate and metabolite A were the major residues in both fruit and leaves. The concentrations of radioactivity in various fractions derived from the fruit are shown in Table 6.

The study was reported as being in compliance with GLP according to the OECD, Switzerland, and the EPA.

Table 6. Concentration of fenpyroximate and metabolites in apples after treatment with [*pyrazole*-^{14}C]fenpyroximate.

	mg fenpyroximate equivalents/kg fresh fruit at interval, days				
	0	7	14	28	57
Total in fruit	0.128	0.108	0.081	0.061	0.032
Fenpyroximate	0.119	0.094	0.062	0.043	0.015
Metabolite A	0.007	0.009	0.009	0.008	0.005
Unknown 1	-	-	-	0.001	-
Unknown 2	-	-	-	0.004	0.001
Unknown 3	-	-	0.003	-	-

fenpyroximate

	mg fenpyroximate equivalents/kg fresh fruit at interval, days				
	0	7	14	28	57
Unknown 9	-	0.001	-	-	-
Aqueous phase	-	0.002	0.003	0.003	0.005
Juice	0.001	0.001	0.001	0.002	0.003
Unextractable	-	-	-	0.001	0.001

In leaves, the residues of fenpyroximate and A were 0.221 and 0.091 mg/kg at day 57 respectively, and 5 unidentified metabolites were found in washed and extracted fractions, but none of the minor metabolites were present at harvest. The proposed degradation pathway of fenpyroximate (pyrazole labelled) in apples is as follows.

Parent ----------➢ A
(Isomer of parent)
↓
Unknown metabolites

The metabolism of [*benzyl*-^{14}C]fenpyroximate by apples investigated with a similar experimental design (Wyss-Benz & Mamouni, 1992a). [^{14}C]fenpyroximate was applied at the rate of 37.5 g ai/ha/m crown height and 955 ì Ci/tree. The total radioactivities at day 0 were equivalent to 0.12 mg fenpyroximate/kg in fruits and 12.2 mg/kg in leaves, decreasing to 0.036 and 0.628 mg/kg respectively at day 57. The radioactivity in the juice was equivalent to 0.02 mg/kg at day 57. The major residual products were unchanged fenpyroximate and metabolite A in both fruits and leaves. The concentrations of radioactivity in the various fractions are shown in Table 7.

Table 7. Concentration of fenpyroximate and metabolites in apples after treatment with [*benzyl*-^{14}C]fenpyroximate.

	mg fenpyroximate equivalents/kg fresh fruit at interval, days				
	0	7	14	28	57
Total in fruit	0.120	0.140	0.110	0.075	0.036
Fenpyroximate	0.109	0.113	0.086	0.053	0.017
Metabolite A	0.005	0.017	0.013	0.011	0.007
Unknown 1	-	0.001	-	-	0.001
Unknown 2	0.004	0.004	0.003	0.003	0.001
Aqueous phase	0.002	0.004	0.004	0.003	0.007
Juice	-	-	0.001	0.001	0.002
Unextractable	-	-	0.001	0.001	0.002

In leaves, the residues of fenpyroximate and A were 0.219 and 0.162 mg/kg respectively at day 57, and 7 unknown metabolites were found.

Grapes. A 5% SC formulation of [*pyrazole*-^{14}C]fenpyroximate was applied by hand spraying to two vines in the field at the maximum recommended field rate of 7.5 g ai/hl and 731 ì Ci/vine. Samples of bunches and leaves were taken 0, 7, 14, 28 and 57 days (harvest) after application. The samples were rinsed with acetone/water and the radioactivity determined by LSC. Bunches were separated into grapes and stems, grapes were homogenized and separated into juice and cake, and washings as well as extracts were analysed. The highest total radioactivity in grape bunches was 0.195 mg/kg fenpyroximate equivalents at day 7, decreasing to 0.081 mg/kg at day 57. Leaves accounted for 6.234 mg/kg at day 0 and 0.971 mg/kg at day 57. The concentrations of ^{14}C residues in grape bunches and individual fractions are shown in Table 8.

Table 8. ^{14}C residues in grape bunches treated with [*pyrazole*-^{14}C]fenpyroximate.

	mg fenpyroximate equivalents/kg fresh fruit at interval, days				
	0	7	14	28	57
Total	0.097	0.195	0.102	0.051	0.081
Fenpyroximate	0.096	0.140	0.067	0.028	0.031
Metabolite A	-	0.004	0.004	0.002	0.004
Unknown 1	-	0.001	-	0.002	0.002
Unknown 3	-	0.015	0.010	0.002	0.016
Unknown 5	-	0.001	0.001	-	0.001
Unknown 6	-	-	-	-	0.001
Unknown 8	-	-	-	-	0.001
Aqueous phase	0.001	0.014	0.011	0.008	0.010
Juice	-	0.005	0.005	0.004	0.007
Unextractable	-	0.004	0.004	0.003	0.006

In the leaves, the residues of fenpyroximate and A were 0.326 and 0.052 mg/kg respectively at day 57. Seven unknown metabolites found at day 57 were in the range 0.002-0.14 mg/kg (Wyss-Benz & Mamouni, 1992b).

In another study with the same experimental design but using [*benzyl*-^{14}C]fenpyroximate the labelled compound was applied to vines in the field at the rate of 37.5 g ai/ha/m crown height and 770 ì Ci/vine. Samples were taken at days 0, 7, 14, 28 and 57 (harvest). The total radioactivities at day 0 were 0.086 mg/kg fenpyroximate equivalents in grape bunches and 7.49 mg/kg in leaves, decreasing to 0.060 and 1.16 mg/kg respectively at day 57. The concentrations of radioactivity in various fractions derived from the fruit are shown in Table 9.

Table 9. ^{14}C residues in grape bunches treated with [*benzyl*-^{14}C]fenpyroximate.

	mg fenpyroximate equivalents/kg fresh fruit at interval, days				
	0	7	14	28	57
Total	0.086	0.144	0.075	0.087	0.60
Fenpyroximate	0.079	0.109	0.049	0.053	0.027
Metabolite A	0.004	0.013	0.007	0.016	0.006
Unknown 1	-	-	-	-	0.001
Unknown 2	-	0.001	0.002	0.001	0.002
Unknown 3	-	0.008	0.004	0.006	0.006
Unknown 5	-	0.001	-	-	0.001
Unknown 6	-	0.001	0.001	0.002	-
Aqueous phase	0.001	0.005	0.005	0.007	0.006
Juice	-	0.004	0.005	0.006	0.005
Unextractable	-	0.001	0.001	0.002	0.002

In the leaves, the residues of fenpyroximate and A were 0.64 and 0.054 mg/kg respectively at day 57. Eight metabolites were found in the range 0.005-0.132 mg/kg. The juice was not extracted because the level of radioactivity was so low, <0.008 mg/kg (Wyss-Benz & Mamouni, 1992c).

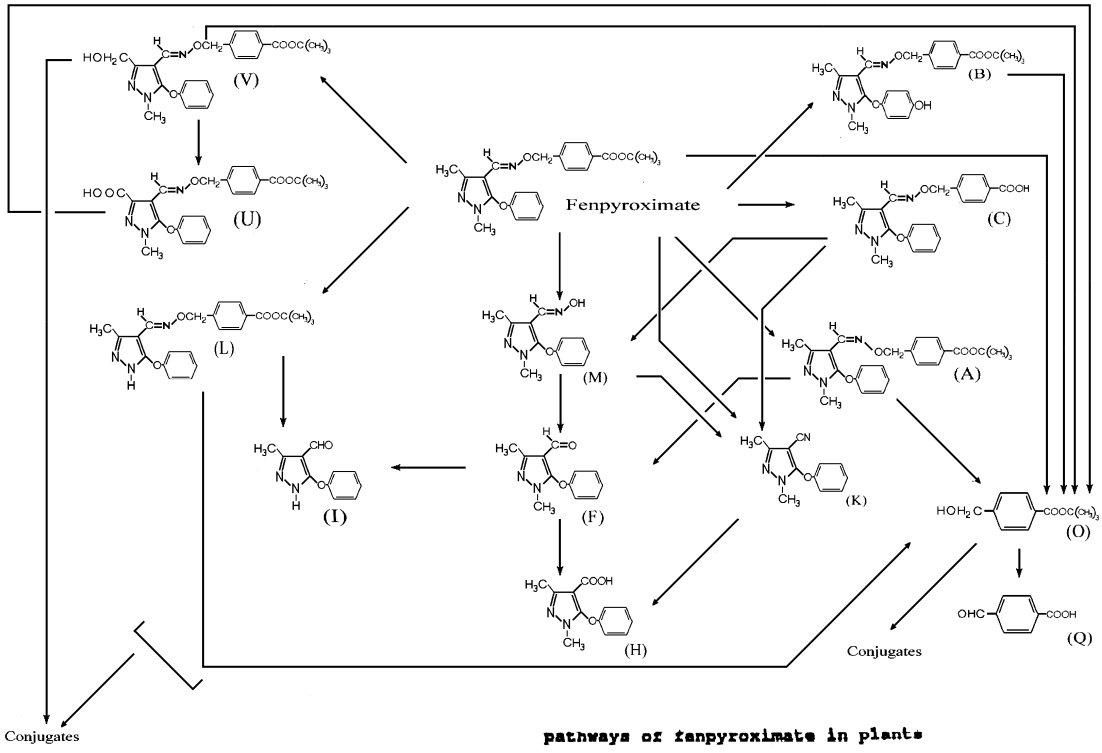
The proposed metabolic pathways of fenpyroximate in plants are shown in Figure 2.

Environmental fate in soil

The degradation of fenpyroximate was studied in upland soils (25 g diluvial and volcanic ash) under laboratory conditions to determine the fate in the field and environment. Soil samples fortified with pyrazole- and benzyl-labelled fenpyroximate (1.30-2.20 mg/kg) were incubated at 25°C for 112 days in the dark, in bottles with traps for CO_2 and volatile organic material.

The compound was degraded with a half-life of 34.3-49.7 days in diluvial soil and 26.3-35.6 days in volcanic ash soil. Eleven degradation products were identified by thin-layer co-chromatography from the pyrazole label, seven from the benzyl. The major degradation products were C, H and K. The other minor products were identified as A, B, F, I, L, M, P, U and V. The $^{14}CO_2$ liberated during the incubation of [*pyrazole*-^{14}C]fenpyroximate amounted to 17.1% of the applied radioactivity in diluvial soil and 16.8% in volcanic soil. With [*benzyl*-^{14}C]fenpyroximate the $^{14}CO_2$ amounted to 64.6% of the applied radioactivity in diluvial soil and 51.2% in volcanic soil. The structures of the identified degradation products suggest that the degradation pathway of fenpyroximate consists in hydrolysis of the ester, isomerization, cleavage to form the oxime, *N*-demethylation, oxidation of the methyl group at the 3-position on the pyrazole ring, hydroxylation of the phenyl ring, and mineralization to CO_2. The degradation products in both soils were determined by TLC with ARG (autoradiography) and radioassay. At day 112 46-58% of the radioactivity from the pyrazole label and 21.3-41.5% of that from the benzyl label was unextractable; most of it was in the humin, humic acid and fulvic acid fractions (Hirano *et al.*, 1990; Izawa *et al.*, 1993).

Figure 2. Proposed metabolic pathways of fenpyroximate in plants.



Three fresh field soils (clay loam, silt loam and sandy loam, with the characteristics shown in Table 10) were treated with [*pyrazole*-^{14}C]fenpyroximate at a rate of 0.2 mg/kg dry soil, corresponding to the highest recommended application rate (150 g ai/ha), and incubated in the dark for 100 days at 20°C under aerobic conditions. The half-lives of fenpyroximate were 16.9, 10.1 and 21.3 days respectively, and the times for the disappearance of 90% of the initial concentration (DT 90) were 186.4, 111.9 and more than 100 days. The degradation products A, C, F, H and K were identified, and five unknown products were found (Römbke and Möllerfeld, 1992a).

Table 10. Characteristics of soils (Römbke and Möllerfeld, 1992a).

%	Clay loam	Silt loam	Sandy loam
Sand	20.2	11.2	30.6
Silt	49.5	65.7	49.7
Clay	30.3	23.1	19.7
Water capacity	55.9	54.1	52.8
Microbial biomass	67.1 initial 47.0 final	29.6 initial 26.4 final	30.4 initial 15.2 final
pH	6.9	6.3	5.9

Both the quantities of degradation products and their rate of formation were different in the three soils, being for example lower in sandy loam than in clay loam (Römbke and Möllerfeld, 1992a)

Another study was carried out to calculate the half-life (DT 50) and DT 90 values using a single standardized sandy soil treated with unlabelled fenpyroximate at the maximum recommended rate of 150 g ai/ha (0.2 mg ai/kg). Portions of 100 g dry weight were incubated in glass tubes (140 cm x 7.5 cm diameter) at 20°C for 100 days in the dark under aerobic conditions.

Fenpyroximate was determined by HPLC. The DT 50 and DT 90 values, calculated by BBA methods, were 159 and more than 200 days, respectively (Römbke and Brodesser, 1992).

The adsorption/desorption of fenpyroximate loamy sand, sandy loam, clay loam and loam was studied in accordance with OECD Guidelines, using ^{14}C-labelled fenpyroximate.

The four soils were sterilized at 120°C for 60 min, because fenpyroximate is readily degraded by soil micro-organisms. Duplicate samples of the soils were agitated for 16 hours with [^{14}C]fenpyroximate solution in a water bath. The amount of fenpyroximate adsorbed was calculated from the difference between the amount recovered from control solutions with no soil and the amount in the supernatants.

The adsorption coefficients (K_{oc}) were 4.53 x 10^4 in sandy loam, 5.36 x 10^4 in loam, 7.95 x 10^4 in clay loam and 12.4 x 10^4 in loamy sand (Takemoto *et al.*, 1990).

In another study the adsorption/desorption of [*pyrazole*-^{14}C]fenpyroximate was determined on sand, sandy loam, clay loam and loam.

The pH of the four soils was between 7.0 and 7.8; the three loams had organic matter contents ranging from 1.4% to 2.1%, and the sand 0.33%. The soils were sterilized by autoclaving for ninety-minute periods daily for three consecutive days.

The adsorption coefficients in this study ranged between 37,000 and 64,000, showing that fenpyroximate was readily adsorbed by the four soils tested; it was not readily desorbed. Fenpyroximate was immobile in the soils studied.

Degradation of fenpyroximate to A and C was observed in all the soils as well as in control solutions (McCann, 1992).

A laboratory column leaching study was carried out with three different sandy soils (German Standard Soils 2.1, sand; 2.2., loamy sand; and 2.3 sandy loam). The soils were characterized by the relative amount of sand, silt and clay, cation exchange capacity, pH (6.1-6.7), maximum water capacity, percentage of organic carbon, and microbial biomass.

The air-dried soils were packed in glass columns with a height of 35 cm and a diameter of 5 cm, and saturated with water. Fenpyroximate was then added as an SC formulation (5.2%) at the highest recommended field application rate of 150 g ai/ha (0.029 mg/column), and the columns kept at 20 ± 2°C in the dark. A total of 393 ml water, equal to 200 mm rainfall, was added dropwise to the soil columns during a period of 2 days. The leachate was collected and analysed by reversed-phase HPLC with UV detection. The fenpyroximate in the soil column (divided into six sections) was also measured at the end of the watering period. The concentration of fenpyroximate in the leachate of the sand was 0.21 mg/l (0.27% of the applied amount), and below the detection limit of 0.1 mg/l (<0.13%) in the other leachates (Römbke, 1992).

An aged column leaching study was carried out according to BBA Guidelines, using a German Standard loamy sand and a glass column with a height of 35 cm and a diameter of 5 cm. The test substance, [*pyrazole*-^{14}C]fenpyroximate, was added at 0.026 mg/column (= 150 g ai/ha) to the standard soil and incubated for 30 days, at which time fenpyroximate and its degradation products

were determined. Aged soil mixture (100 g) was added to a column filled to a height of 28 cm with the same but untreated soil and the column irrigated with 393 ml water for two days. Fenpyroximate and its degradation products were determined in the leachate.

After collecting the leachate the columns were divided into 5 cm sections which were analysed for fenpyroximate and the main degradation products.

The microbial biomass was measured at the beginning and end of the incubation period. The total radioactivity found in the leachate was 1.7% of the amount applied, too low for the identification of products. The total radioactivity detected in the soil was 111.9% of that applied, distributed as follows.

Depth, cm	Extract, %	Residue, %	Total, %
0-5	106.6	2.0	108.6
5-10	2.4	0.3	2.7
10-15	0.6	0	0.6

No activity was detected below 15 cm (Römbke and Möllerfeld, 1992b).

Approximately 5.1% of the total radioactivity could be attributed to the compounds A (3.5%), C (0.4%), H (0.1%) and K (1.1%). The distribution of identified compounds in the top 10 cm of the soil columns was as follows.

Depth, cm	% of applied ^{14}C found as			
	A	C	H	Fenpyroximate
0-5	2.9	0.5	0.1	103.1
5-10	0.2	0.3	0.1	1.6

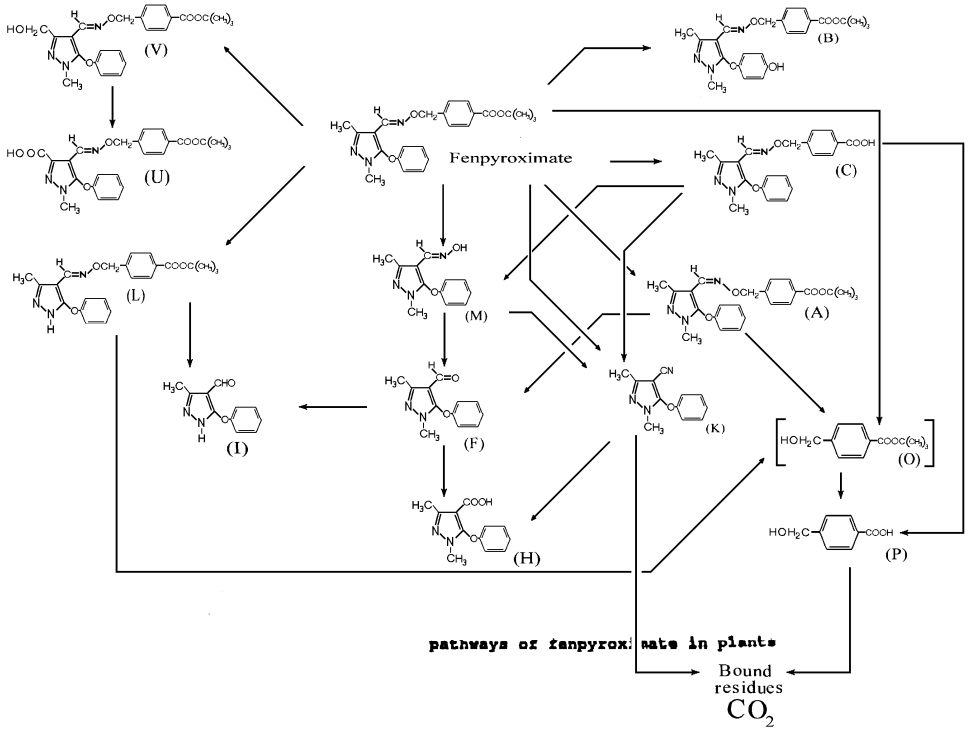
A similar study was carried out with [*benzyl*-^{14}C]fenpyroximate. A small amount of radioactivity was found in the leachate (11%). The major degradation products found after extraction of the soil columns were A and C (Römbke and Möllerfeld, 1992c).

The proposed degradation pathways of fenpyroximate in soil are shown in Figure 3.

Environmental fate in water/sediment systems

In a study of the hydrolysis of fenpyroximate in water according to OECD Guidelines solutions of [*pyrazole*-^{14}C]fenpyroximate (10 ì g/ml) in pH 4.0, 7.0 and 9.0 buffers at 50°C and in pH 7.0 buffer at 40° and 60°C were incubated in the dark. At intervals, the pH 4 and pH 7 solutions were extracted with ethyl acetate, and the pH 9 solution with the same solvent after the addition of 0.5 ml of 1 N HCl.

Figure 3. Degradation pathways of fenpyroximate in soil.



The extracts were analysed by HPLC. The degradation products C and F were identified, C accounting for 60 and 80% of the radioactivity at pH 7.0 and 9.0 after 7 days. The results at 50°C are shown in Table 11 (Nishizawa *et al.*, 1990a).

Table 11. Distribution of radioactivity after incubation of fenpyroximate in buffer solutions at 50°C.

Compound	% of original radioactivity								
	pH 4, at days			pH 7, at days			pH 9, at days		
	1	3	7	1	3	7	1	3	7
Fenpyroximate	82.1	34.3	12.5	88.2	51.3	20.7	74.0	46.0	15.6
C	22.4	39.8	36.8	15.2	29.8	59.8	29.0	46.7	79.2
F	5.4	7.3	34.1	--	--	--	--	--	--

The half-lives of fenpyroximate at 50°C and pH 4.0, 7.0 and 9.0 were 2.28, 3.01 and 2.64 days respectively. The half-life at pH 7 was 10.9 days at 40° and 1.21 days at 60° (Table 12), and was estimated to be 65.7 days at 25° by extrapolation (Nishizawa *et al.*, 1990a).

Table 12. Concentrations of fenpyroximate and compound C in buffer solutions at pH 7 at 40° and 60°C.

Time (days)	% of original radioactivity			
	40°C		60°C	
	Fenpyroximate	Compound C	Fenpyroximate	Compound C
0.5			77.9	23.8
1			57.4	37.8
3	84.7	22.8	18.2	78.7
7	57.3	42.4		
14	39.6	59.6		
21	25.2	53.3		

The hydrolysis of [*pyrazole*-^{14}C]fenpyroximate was studied in sterile aqueous solutions buffered at pH 5, 7 and 9 for 30 days. The solutions were fortified at 9.5 ì g/ml and maintained in a dark chamber at 25 ± 1°C. Duplicate samples were collected after 0, 1, 2, 4, 7, 14, 21 and 30 days, and analysed by HPLC. The samples remained sterile over the course of the study and the pH did not change appreciably.

The half-lives of fenpyroximate were calculated to be 180 days at pH 5, 226 days at pH 7 and 221 days at pH 9. The degradation products A and C were identified at pH 5 and 9, and C also at pH 7 (Saxena and McCann, 1992).

A study of photolysis was carried out to predict the effects of photodegradation in the environment. When fenpyroximate was exposed to sunlight (8 h daily) in a 10 ì g/ml aqueous solution it decomposed with a half-life of 2.6 days and was reduced to 1.7 ì g/ml by the 7th day. Compound A was recognized as a main product at 5.7 and 6.5 ì g/kg at 3 and 7 days respectively (Table 13).

Table 13. Effect of sunlight (8 h/day) on fenpyroximate in water.

Compounds	Concentration, ì g/ml				
	Light, days			Dark, days	
Days	0	3	7	3	7
Fenpyroximate	9.5	4.3	1.7	9.8	9.5
A	<0.5	5.7	6.5	<0.5	<0.5

In an extension of this study aqueous solutions buffered at pH 7 containing pyrazole-, benzyl- or phenyl-labelled fenpyroximate (10 mg/l) were irradiated with a xenon lamp (160,000 lux hr/cm^2) at 25°C for 0, 1, 3 or 6 h. After irradiation, samples were extracted with ethyl acetate, radioactivity was measured by LSC, and products were identified by TLC. The half-life of fenpyroximate was calculated from a decay curve.

Table 14. Photodegradation of [^{14}C]fenpyroximate in water under irradiation with a xenon lamp.

Compound	Radioactivity, % of original										
	[Pyrazole-^{14}C], hours				[Benzyl-^{14}C], hours				[Phenyl-^{14}C], hours		
	0	1	3	6	0	1	3	6	0	3	6
Fenpyroximate	95.1	62.8	46.8	30.0	92.6	75.7	47.4	27.1	96.4	50.7	37
A	0.8	20.4	41.5	47.5	0.7	14.7	41.8	58.3	1.2	41.3	54.3
C + D	2.6	1.8	1.6	1.7	2.5	2.4	1.4	1.9	3.2	1.1	1.4
F	<0.2	0.6	2.2	2.9	--	--	--	--	<0.2	3.5	6.6
M	<0.2	0.2	0.8	0.6	--	--	--	--	<0.2	0.2	<0.2
O	--	--	--	--	<0.2	<0.2	0.5	1.0	--	--	--
Others	0.2	2.9	0.9	2.5	<0.2	<0.2	2.5	5.6	<0.2	1.1	1.7
Half-life of fenpyroximate, h			2.9				2.8			3.1	

Half-lives from 2.8 to 3.1 hours were calculated for the three labelled compounds, and A was again the main product. The addition of acetone (2%), a photo-sensitizer, accelerated the degradation of fenpyroximate. Compounds F, K, M and O, in addition to A, were identified as photodegradation products (Nishizawa *et al.*, 1990b).

An additional study, according to EPA guidelines, investigated the photodegradation of [*pyrazole*-^{14}C]fenpyroximate in 0.01 M phosphate buffer solution (10 mg/l) at pH 7.0. The study was in two parts: (1) to determine the first order rate constant and half-life of fenpyroximate, and (2) to determine the half-life of A, its geometric isomer.

In part 1, duplicate samples were collected after 0.5, 1, 2, 3, and 4 hours of continuous irradiation with a xenon lamp (603 watts, 290-300 nm) to estimate the half-life of fenpyroximate. In part 2 the samples were collected after 4, 12, 24, 48 and 73 hours of continuous irradiation to generate the isomer A and estimate its half-life. Samples were extracted with ethyl acetate and analysed by HPLC.

The half-life of fenpyroximate was estimated to be 1.5 hours, and that of A 10.5 hours. Only one other degradation product (K) accounted for more than 10% of the original radioactivity. Volatile radioactivity accounted for less than 1% of that originally present (Swanson, 1993).

The proposed degradation pathways of fenpyroximate in water are shown in Figure 4.

Figure 4. Degradation of fenpyroximate in water

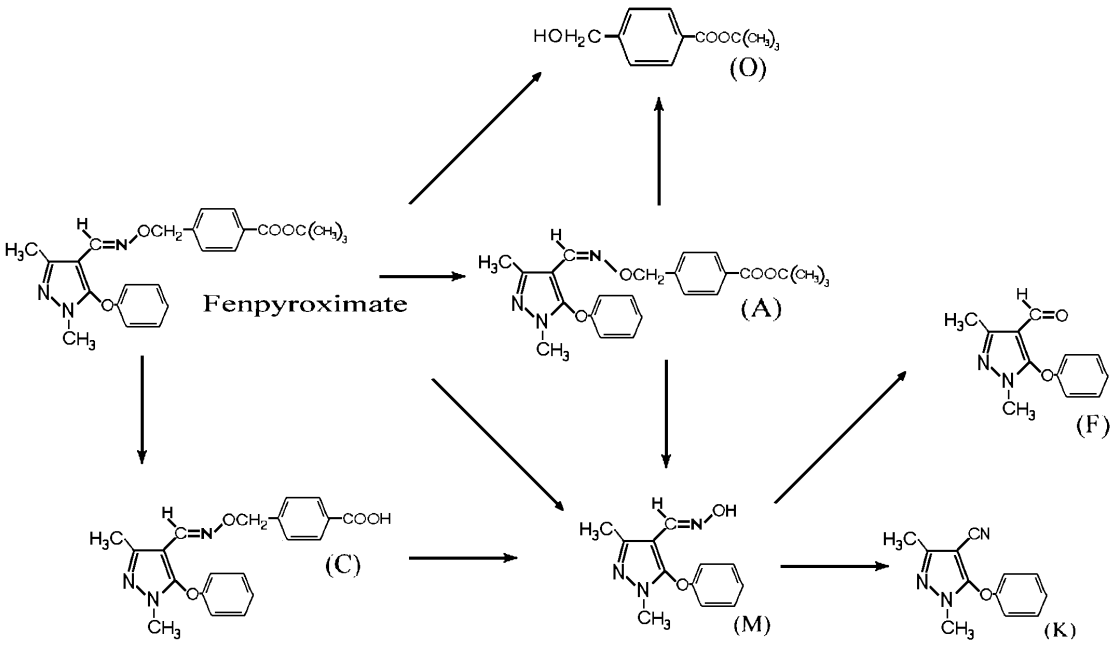


Figure 5. Proposed metabolic pathways of fenpyroximate in water

METHODS OF RESIDUE ANALYSIS

Analytical methods

The following methods were used to determine residues in supervised trials.

Fruits, vegetables and tea. The homogenized sample is extracted with methanol and filtered by suction through Celite. After concentration in a rotary evaporator, the extract is partitioned with n-hexane and acetonitrile and cleaned up on a silica gel/alumina column, eluting with n-hexane/ethyl acetate. After evaporation of the eluant, the residue is redissolved in 1,4-dioxane and analysed by GLC with an NPD. Fenpyroximate and its *Z*- isomer (A) are determined in the same extract (Nihon Nohyaku, 1989a). The reported recoveries and limits of detection are shown Table 15.

Table 15. Recoveries and limits of detection of fenpyroximate and its *Z*- isomer.

Sample	Added, mg/kg	Recovery, %		Limit of detection
		Fenpyroximate	*Z*- isomer	
Orange peel	0.2	93	87	0.02
Orange pulp	0.1	92	81	0.01
Apple	0.1	105	88	0.01
Strawberry	0.1	91	78	0.01
Tea	0.2	78	85	0.02

The parent compound, its *Z*- isomer and demethyl-fenpyroximate can be determined in the same extract by HPLC using an ultraviolet photometric detector. Homogenized samples are extracted with acetonitrile, partitioned in hexane/water and cleaned up on a silica gel/alumina column, using n-hexane/ethyl acetate (7:3) as eluant. The residue, dissolved in acetonitrile/water (3:2), is cleaned up on C_{18} and silica cartridges, again eluting with n-hexane/ethyl acetate. The eluant is evaporated and the residue dissolved in acetonitrile for HPLC analysis on a 4 x 250 mm RP-18 column, with detection at 258 nm. The L0D is 0.02 mg/kg. Recoveries are shown in Table 16 (Nihon Nohyaku, 1989b).

Table 16. Recoveries of fenpyroximate, its *Z*- isomer and demethyl-fenpyroximate from mandarin orange pulp and grapes.

Sample	Added, mg/kg	Recovery %		
		Fenpyroximate	*Z*- isomer	Demethyl-fenpyroximate
Orange pulp	0.1	96	98	88
Grapes	0.1	103	90	78

In another method GLC with an NPD is used to determine fenpyroximate and its *Z*- isomer, and HPLC with an ultraviolet detector to determine demethyl-fenpyroximate. The homogenized sample is extracted with acetonitrile and the extract cleaned up by solid-phase chromatography on a silica gel/alumina column, silica cartridge and/or C_{18} cartridge. The reported recoveries were 99% for the GLC determination and 80% (from green peppers) for the HPLC. The reported limit of detection by both methods was 0.01 mg/kg (Nihon Nohyaku, 1989c).

The analytical methods of the Deutsche Forshungsgemeinschaft were adapted for the residue determination of fenpyroximate and its *Z*- isomer in orange pulp and peel, apple fruit, mash and cider and grapes and wine, and the processing products of hops (dregs, yeast and beer) (Specht, 1992a-d).

Homogenized samples are extracted with acetone, after the addition of sufficient water to bring the acetone: water ratio to 2:1 v/v. The extract is saturated with sodium chloride and partitioned with dichloromethane. Beer is simply diluted with sodium chloride solution and extracted with dichloromethane. The solvent is evaporated and the residue cleaned up by automated gel-permeation chromatography on Bio Beads S-X3 polystyrene gel, using a mixture of cyclohexane and ethyl acetate (1 + 1) as eluant. The fraction containing the residue is concentrated and, after supplemental clean-up on a small silica gel column, analysed by GLC using a wide-bore capillary column and nitrogen-sensitive alkali flame ionization detector. The limits of determination of both compounds were 0.05 mg/kg for grapes, wine, orange pulp and peel, and apple fruit, mash and cider; 0.1 mg/kg for dregs and yeast from hops, and 0.01 mg/kg for beer.

Recoveries of fenpyroximate and the isomer were in the range 74 to 100% from orange pulp and peel at fortification levels of 0.05, 0.5 and 5.0 mg/kg (Specht, 1992a), from grapes and wine at 0.05 and 0.5 mg/kg and from grapes at 2.0 mg/kg (Specht, 1992c). Recoveries from apple fruit, mash and cider at 0.05 and 0.5 mg/kg and from fruit at 5 mg/kg ranged from 70 to 100% (Specht, 1992b). Recoveries from beer at 0.01 and 0.10 mg/l and from dregs and yeast at 0.1 and 1.0 mg/kg ranged from 79% to 115% (Specht, 1992d). All the studies were carried out in compliance with GLP.

A simplified HPLC method was used for residue analysis in several supervised trials. Samples were extracted with acetonitrile and concentrated. The concentrate was cleaned up on a C_{18} cartridge eluted with methanol, then on a silica gel cartridge eluted with diethyl ether/n-hexane. HPLC was on an RP-18 column with a UV detector (wavelength 258 nm). The LOD was 0.005 mg/kg. Recoveries at 0.2 mg/kg fortification levels from citrus pulp and peel and 0.2-0.5 mg/kg from apples were reported to be over 90% for fenpyroximate, its *Z*- isomer and demethyl-fenpyroximate (Iawamoto and Matano, 1993a,b).

Soil. The parent compound and its degradation products A, C, H and K are easily extractable from soil. Samples are extracted with a mixture of acetonitrile and 1M aqueous ammonium chloride (4:1). The extract is cleaned up by partition of an acidic aqueous solution (1M HCl) with dichloromethane, followed by column chromatography on silica gel/alumina and Florisil. The carboxyl groups of C and H are methylated with diazomethane before column chromatography. The residues are determined in a single aliquot by gas chromatography with an NPD. Recoveries at fortification levels of 25 and 250 ì g/kg ranged from 90 to 100% for fenpyroximate and from 72 to 100% for the other compounds (Nishizawa *et al.*, 1992).

Water. For the analysis of water for fenpyroximate and its *Z*- isomer samples are extracted with n-hexane, cleaned up on a silica gel cartridge, and determined by HPLC with UV detection. The recoveries from river water, well water and distilled water were 82-87% for fenpyroximate and 78-85% for the isomer at 5 ì g/l. The reported limit of detection was 0.1 ì g/l for both compounds (Funayama *et al*., 1991).

Stability of pesticide residues in stored analytical samples

Fenpyroximate and its degradation products were added to soil at 250 ì g/kg, and samples stored at -20°C for 120 days were analysed in duplicate. The results were 86-88% of the initial values for fenpyroximate, and 90-116% for the other compounds.

The stability of pyrazole-labelled fenpyroximate was studied in apples and grapes stored at about -20°C for approximately three years. The studies were reported to be in compliance with GLP.

Apples were treated with [*pyrazole*-^{14}C]fenpyroximate, harvested at maturity 57 days after treatment, and then analysed. After 3 years frozen storage, apples of the same batch were analysed by the same procedure. The nature and relative levels of the metabolites remained unchanged. The variation in the residues (Table 17) was attributed to inhomogeneity of the sub-samples (Wyss-Benz, 1993a).

Bunches of grapes from vines treated 57 days previously were analysed. Replicate samples were analysed after storage at about -20° for 3 years (Wyss-Benz, 1993b). The results are shown in Table 17.

Table 17. Total ^{14}C residues before and after frozen storage (Wyss-Benz, 1993a,b).

Sample	Residue[1] October 1990	Residue[1] September 1993
Apples	0.031	0.020
Grapes	0.070	0.045

[1] Total ^{14}C expressed as mg fenpyroximate/kg fresh wt

In a storage stability study on apples fortified with fenpyroximate, the *Z*- isomer and demethyl-fenpyroximate, homogenized samples were stored at -20°C until analysis after 18 and 145 days. The remaining levels of fenpyroximate, *Z*- isomer and demethyl compound were 68.0-68.1, 71.0-72.2 and 57.2-66.3% of the initial values respectively (Iawamoto and Matano, 1993b).

Grapes fortified with fenpyroximate, the *Z*- isomer and *N*-demethyl-fenpyroximate were stored at -20°C. Fenpyroximate and the *Z*- isomer were determined after storage for 77 days and *N*-demethyl-fenpyroximate after 119 days. The mean remaining levels of the three compounds were 76.1, 87.6 and 49.7% of the initial values respectively (Iawamoto and Matano, 1993e,d).

A study to determine the effect of storage at -18°C on the residues of fenpyroximate and the *Z*- isomer in dried hop cones was carried out using the analytical method DFG S 19. Untreated and fortified samples were analysed in duplicate. Samples were spiked to obtain a level of 9.6 mg/kg fenpyroximate and 9.68 mg/kg of the *Z*- isomer.

No significant decrease of fenpyroximate, the isomer or their sum was observed during a storage period of 24 months (Weber, 1994).

Table 18. Stability of residues in stored hop samples (dried cones).

Compound	% of initial residue, storage time (months)					
	1 day	3	6	12	18	24
Fenpyroximate	97	85	97	88	91	109
Z- isomer (A)	75	89	78	60	90	66
Sum of A and fenpyroximate	104	107	95	105	108	105

The stability of fenpyroximate was also studied in stored citrus samples. Pulp samples fortified with fenpyroximate and the *Z*- isomer (0.4 mg/kg and 0.079 mg/kg respectively) and stored at -20°C for 140 days contained 65 and 62% of the initial level respectively. In peel, fenpyroximate and the *Z*- isomer were added at 1.0 and 0.195 mg/kg respectively: after storage at -20°C for 188 days 73 and 72% of these levels remained respectively (Iawamoto and Matano, 1993a).

Residue definition

Fenpyroximate is the major component of the residues remaining in crop commodities. The *Z*- isomer (compound A) and *N*-demethyl-fenpyroximate (compound L) were the only metabolites found at analytically significant levels, and only in mandarin peel. Compound L was not detected in any other commodities and compound A was at levels near or below the limit of determination. The residue should therefore be defined as fenpyroximate.

USE PATTERN

Fenpyroximate is a non-systemic miticide for the control of immature and adult stages. It is registered in several countries, principally for the control of the European red mite (*Panonychus ulmi*) and the two-spotted mite (*Tetranichus urticae*), on pome fruits, citrus, grapes and hops. It is applied as a foliar spray. It is available as a 5% suspension concentrate. Registered uses are listed in Table 19.

Table 19. Registered uses of fenpyroximate on fruit and hops. All formulations are 5% SC. All applications are foliar.

Crop	Country	Application			PHI, days
		Kg ai/ha	Spray conc., kg ai/hl	No.	
Citrus	Brazil	0.15	0.005	1	15
	Chile	-	0.0025	1	14
	Greece	0.12-0.16	0.004-0.005	1	14
	Italy	0.1	0.005	1	14
	Japan		0.003-0.005	1	14
	Peru		0.005	-	-
	Spain	0.2	0.005	1	14
Pome fruits	Argentina		0.0025-0.0037	1	14
	Chile		0.0025	1	21
	Malaysia	0.01-0.02	0.005	1	7
	New Zealand	0.05-0.075	0.0025	1	14
	Peru		0.005		
	Portugal	0.05-0.075	0.005-0.0075	1	14
	Spain	0.11	0.008	1	7
Apple	Brazil	0.06	0.005	1	15
	France	0.06-0.08	0.008	1	21
	Germany	0.112	0.0075	1	21
	Greece	0.06-0.11	0.004-0.005	1	7
	Italy	0.075	0.005	1	14
	Japan		0.003-0.005	1	14
	Portugal	0.05-0.08	0.005-0.008	1	28
	Switzerland	0.1-0.15	0.005-0.008	1	21
	UK	0.1	-	1	14
Grapes	Chile		0.0025	1	30

Crop	Country	Application			PHI, days
		Kg ai/ha	Spray conc., kg ai/hl	No.	
	Germany	0.105-0.120	0.0075	1	35
	Italy	0.05		1	14
	Japan		0.003-0.005	1	14
	Peru		0.005	-	-
	Portugal	0.05-0.08		1	14
	Spain	0.04		1	14
	Switzerland	0.1-0.15	0.005-0.008	1	21
Hops	Germany	0.225-0.263	0.0075	1	21
	Italy	0.05		1	14
	Japan		0.005	1	14

RESIDUES RESULTING FROM SUPERVISED TRIALS

Residue data were provided from trials on citrus fruits, apples, grapes and hops. In many of the trials the *Z*- isomer was also determined. Results are shown in Tables 20-23, in which residues from treatments according to GAP are underlined.

Citrus fruit (Table 20). Fenpyroximate 5% SC is registered for use on citrus fruits in several countries. One application is recommended at rates of 0.1-0.2 kg ai/ha and PHIs of 14 or 15 days.

A summary report of six supervised trials carried out on mandarins in Italy in 1991 was provided. Three trials were with one application at the recommended rate (0.1 kg ai/ha) and the other three were at a double rate. Residues were determined in the pulp and peel. No data were available on whole fruit.

Another study was carried out on satsuma mandarins growing in a greenhouse with fenpyroximate 5% SC applied at the GAP concentration of 0.005 kg ai/hl in Japan. Residues of fenpyroximate 14 or more days after application in whole fruit, pulp and peel were 0.019-0.21, <0.005-0.027 and 0.068-0.98 mg/kg respectively. Residues in the whole fruit were estimated from the weight ratio of pulp to peel.

Samples were analysed by HPLC 130 days after sampling. Recoveries were determined by fortification of control samples with fenpyroximate, the *Z*- isomer and *N*-demethyl-fenpyroximate. Mean recoveries were fenpyroximate 98% (pulp and peel), *Z*- isomer 76% (pulp and peel) and *N*-demethyl fenpyroximate 78% (peel) and 100% (pulp) (Iawamoto and Matano, 1993a).

Oranges, Sweet. Summary data on supervised trials were provided from Brazil, Greece and Italy. Four supervised field trials were carried out in Brazil with 2 applications between 0.08 and 0.36 kg ai/ha. Samples were analysed by HPLC with an LOD of 0.05 mg/kg. Recoveries were 77-87% for fenpyroximate and 87-89% for the *Z*- isomer. In the trials in Greece and Italy analyses were by the DFG S 19 method: residues in the whole fruit were not determined.

Table 20. Residues of fenpyroximate and its *Z*- isomer in citrus treated with fenpyroximate 5% SC.

Country, year, crop	Application	PHI, days	Fenpyroximate	*Z*- isomer	Ref.

	kg ai/ha	kg ai/hl	No		Pulp	Peel	Whole fruit	Pulp	Peel	
Brazil (1989-1990) Oranges	0.08	0.005	2	15	<0.05	0.2		<0.05	0.05	R.08
				30	<0.05	<0.05		<0.05	<0.05	
	0.16	0.01	2	15	<0.05	0.1		<0.05	0.06	R.09
				30	<0.05	<0.05		<0.05	<0.05	
	0.18	0.005	2	16	<0.05	0.38		<0.05	0.08	R.10
				29	<0.05	0.18		<0.05	0.05	
	0.36	0.01		16	0.08	0.73 0.85		<0.05	0.21 (2)	R.11
				29	<0.05	0.59		<0.05	0.13	
Greece 1992 Oranges	0.15	0.005	1	0	<0.01	0.35		<0.01	<0.01	R.12
				2	<0.01	0.37		<0.01	<0.01	
				9	<0.01	0.3		<0.01	<0.01	
				16	<0.01	0.26		<0.01	<0.01	
				22	<0.01	0.13		<0.01	<0.01	
				28	<0.01	0.18		<0.01	<0.01	
	0.31	0.01	1	0	<0.01	0.31		<0.01	<0.01	R.13
				2	<0.01	0.28		<0.01	<0.01	
				9	<0.01	0.19		<0.01	<0.01	
				16	<0.01	0.24		<0.01	<0.01	
				22	<0.01	0.19		<0.01	<0.01	
				28	<0.01	0.23		<0.01	<0.01	
Italy 1990 Oranges	0.077	0.0075	2	21	0.05	0.38		<0.05	<0.05	R.14
				64	<0.05	0.39		<0.05	<0.05	
				113	<0.05	0.35		<0.05	<0.05	
	0.077	0.0075	2	21	<0.05	0.3		<0.05	<0.05	R.15
				63	<0.05	0.26		<0.05	<0.05	
				105	<0.05	0.36		<0.05	<0.05	
	0.077	0.0075	2	21	0.06	0.54		<0.05	<0.05	
				63	<0.05	0.53		<0.05	<0.05	R-16
				84	<0.05	0.4		<0.05	<0.05	
	0.15	0.015	2	21	0.08	0.73		<0.05	<0.05	
				64	<0.05	0.77		<0.05	<0.05	R-17
				113	<0.05	0.62		<0.05	<0.05	
	0.15	0.015	2	21	<0.05	0.96		<0.05	<0.05	
				63	<0.05	0.57		<0.05	<0.05	R-18
				105	<0.05	0.71		<0.05	<0.05	
				21	0.08	0.83		<0.05	<0.05	
				63	<0.05	0.75		<0.05	<0.05	R-19
				84	<0.05	0.72		<0.05	<0.05	
Italy 1991 Mandarins	0.10	0.006	1	28	0.01	0.35		<0.01	<0.01	R-01

Country, year, crop	Application			PHI, days	Fenpyroximate			*Z*- isomer		Ref.
	kg ai/ha	kg ai/hl	No		Pulp	Peel	Whole fruit	Pulp	Peel	
					<0.01	0.42		<0.01	0.02	R-03
	0.20	0.013	1	28	0.03 0.03	0.78 0.86		<0.01 <0.01	<0.01 0.03	R-02 R-04
	0.10	0.006	1	0	0.03	0.52		<0.01	0.02	R-05
				5	0.02	0.5		<0.01	0.02	
				10	<0.01	0.36		<0.01	<0.01	
				14	<0.01	0.34		<0.01	<0.01	
				25	0.02	0.24		<0.01	<0.01	
				28	<0.01	0.13		<0.01	0.01	
	0.20	0.013	1	0	0.05	0.45		<0.01	<0.01	
				5	0.06	0.63		<0.01	<0.01	R-06
				10	0.03	0.57		<0.01	0.04	
				14	0.03	0.83		<0.01	0.03	
				21	0.02	0.59		<0.01	0.03	
				28	0.01	0.59		<0.01	0.03	
Japan 1989 Mandarins, Greenhouse	0.25	0.005	1	7	0.006 0.006	0.15 0.14	0.028	<0.005 (2)	<0.005 (2)	R-07
				14	<0.005 (2)	0.15 0.14	0.026	<0.005 (2)	<0.005 (2)	
				21	0.009 (2)	0.08 0.068	0.019	<0.005 (2)	<0.005 (2)	
				30	0.008 0.007	0.17 (2)	0.037	0.005 (2)	0.008 0.007	
				44	0.007 (2)	0.21 0.18	0.04	<0.005 (2)	0.007 0.008	
	0.5	0.005	1	7	0.027 0.024	0.99 0.96	0.20	<0.005 (2)	0.024 0.022	
				14	0.023 0.019	0.98 0.97	0.21	<0.005 (2)	0.045 0.043	
				21	0.01 0.01	0.69 0.66	0.15	<0.005 (2)	0.035 0.033	
				30	0.01 0.01	0.67 0.65	0.12	<0.005 (2)	0.04 (2)	
				44	<0.005 (2)	0.72 0.68	0.13	<0.005 (2)	0.044 0.042	

Apples (Table 21). Supervised trials were carried out in Australia to determine residues of fenpyroximate, its *Z*- isomer and the demethyl metabolite in apples following the application of fenpyroximate approximately 4 weeks before harvest at rates of 0.083 and 0.16 kg ai/ha. Information on GAP in Australia was not provided. The metabolites were not detected at the limit of determination of 0.01 mg/kg (Bull and Holding, 1992).

In Belgium, two supervised trials were carried out to establish a decary curve and to determine fenpyroximate and its isomer in apples. No information on GAP was provided. No residues of the metabolite were found above the limit of determination of the method (0.02 mg/kg). Residues of

fenpyroximate were 0.10 and 0.08 mg/kg after 14 and 21 days from treatment at 0.090 kg ai/ha, close to the French GAP rate (Benet and Deerecke, 1992).

Nine trials were carried out on apples in France at rates of 0.06, 0.08, 0.17 and 0.24 kg ai/ha. Samples were analysed according to GLP, by a modified HPLC method. No residues of the two metabolites were found above the limit of determination (0.02 mg/kg), except a residue of 0.03 mg/kg of the *Z*- isomer after treatment at the highest rate. Residues of fenpyroximate from treatment according to GAP (single applications of 0.06-0.08 kg ai/ha) were 0.02-0.09 mg/kg at the GAP PHI of 21 days (Benet and Masserot, 1991).

Eleven supervised trials were carried out in Germany (1989-90) on four varieties (Golden Delicious, James Grieve, Gloucester and Jonathan) at different locations. The application rates were 0.064-0.15 kg ai/ha. Residues of fenpyroximate 21 days after the last application approximating the GAP rate of 0.112 kg ai/ha were <0.05-0.24 mg/kg. Residues of the *Z*- isomer were all below 0.05 mg/kg (Burstell *et al*., 1991a,b,1992a).

Two supervised field trials were carried out in Japan, with single applications at 0.005 kg ai/hl, in accordance with GAP. Residues of fenpyroximate 15 days after application were 0.05 and 0.11 mg/kg. Residues of the *Z*- isomer were <0.005 and 0.006 mg/kg.

In New Zealand, 14 trials were carried out from 1991 to 1994. Apple trees were treated with fenpyroximate as recommended, one application at 0.0025 kg ai/hl, and at a double concentration. Residues of fenpyroximate in samples treated at the GAP concentration were <0.01-0.13 mg/kg after the registered PHI of 14 days. Metabolites were not determined.

Table 21. Residues of fenpyroximate and its isomer in apples treated with fenpyroximate 5% SC

Country, Year	Application			PHI, days	Residues mg/kg		Ref.
	kg ai/ha	kg ai/hl	No		Fenpyroximate	Z- isomer	
Australia 1992	0.083	0.005	1	0	0.09, 0.07, 0.1, 0.13	<0.01 (4)	R-20
				7	0.08, 0.10, 0.05, 0.06	<0.01 (4)	
				14	0.14, 0.12, 0.08, 0.18	<0.01 (4)	
				24	0.06 (2), 0.03, 0.17	<0.01 (4)	
	0.16	0.01	1	0	0.34, 0.30, 0.23 (2)	<0.01 (4)	
				7	0.19, 0.33, 0.29, 0.22	<0.01 (4)	
				14	0.19 (2), 0.18, 0.17	<0.01 (4)	
				24	0.12, 0.19, 0.08 (2)	<0.01 (4)	
Belgium 1991	0.090	0.006	1	7	0.12	<0.02	R-21
				14	0.10	<0.02	
				21	0.08		
				28	0.05		
	0.18	0.012	1	7	0.19	<0.02	
				14	0.17	<0.02	
				21	0.14		
				28	0.18		
France 1989	0.06	0.006	1	0	0.1	<0.02	R-22
				7	0.08		
				14	0.03		

Country, Year	Application			PHI, days	Residues mg/kg		Ref.
	kg ai/ha	kg ai/hl	No		Fenpyroximate	Z- isomer	
				21	0.02		
				29	0.03		
	0.06		2	48	0.05	<0.02	
				53	0.07		
				69	0.03		
	0.08	0.008	2	48	0.08	<0.02	
				53	0.03		
				69	0.04		
France 1990	0.08	0.008	1	0	0.11, 0.12	<0.02 (2)	R-22
				7	0.05, 0.08	<0.02 (2)	
				14	0.06, 0.10	<0.02 (2)	
				20-21	0.05, 0.09	<0.02 (2)	
				29	0.03, 0.06	<0.02 (2)	
	0.06	0.006	2	24	0.11	<0.02	
				68	0.05	<0.02	
	0.08	0.008	2	24	0.16	<0.02	
				68	0.07	<0.02	
	0.17	0.006	2	45	0.08	<0.02	
	0.23-0.24	0.008	2	45	0.19	0.03	
France 1991	0.08	0.008	1	30	0.03		R-23
				50	0.03		
				75	<0.02		
				106	<0.02		
				120	<0.02		
				144	<0.02		
Germany 1989	0.1125	0.0075	2	0	0.1, 0.19	<0.01, 0.01	R-24
				7	0.12, 0.18	<0.01, 0.01	
				14	0.11, 0.1	<0.01, 0.01	
				21	0.1, 0.09	<0.01 (2)	
	0.0643-0.0868	0.0075-0.0073	2	0	0.12	<0.01	
				7	0.12	0.01	
				14	0.08	0.01	
				21	0.09, 0.12	0.01	
	0.1- 0.115	0.0075-0.0076	2	0	0.21	<0.01	
				7	0.19	0.01	
				14	0.15	0.01	
				21	0.16	0.01	
	0.15	0.001	2	0	0.23, 0.24	0.02	R-25
				7	0.23	0.01	
				14	0.24	0.02	
				21	0.24	0.02	

Country, Year	Application			PHI, days	Residues mg/kg		Ref.
	kg ai/ha	kg ai/hl	No		Fenpyroximate	Z- isomer	
	0.095, 0.132	0.01	2	0	0.12	<0.01	
				7	<0.01 (2)	<0.01	
				14	0.12	0.01	
				21	0.12	0.01	
Germany 1990	0.064	0.0075	1	0	0.15	<0.05	R-26
				7	0.11	<0.05	
				14	0.16	<0.05	
				28	0.12	<0.05	
				42	0.09	<0.05	
				56	0.06	<0.05	
				70	<0.05	<0.05	
				81	<0.05	<0.05	
				92	<0.05	<0.05	
	0.1125	0.0075	1	0	0.13	<0.05	R-26
				7	0.14	<0.05	
				14	0.11	<0.05	
				28	0.08	<0.05	
				42	0.06	<0.05	
				56	<0.05	<0.05	
				70	<0.05	<0.05	
				84	<0.05	<0.05	
				91	<0.05	<0.05	
	0.075	0.0075	2	0	0.13	<0.05	R-27
				7	0.08	<0.05	
				14	0.08	<0.05	
				21	0.06	<0.05	
				28	<0.05	<0.05	
	0.081	0.0075	2	0	0.24	<0.05	
				7	0.21	<0.05	
				14	0.18	<0.05	
				21	0.15	<0.05	
				28	0.13	<0.05	
	0.1125	0.0075	2	0	0.21	<0.05	
				7	0.17	<0.05	
				14	0.13	<0.05	
				21	0.08	<0.05	
				28	0.11	<0.05	
	0.114	0.0076	2	0	0.05	<0.05	
				7	<0.05	<0.05	
				14	<0.05	<0.05	
				21	<0.05	<0.05	

Country, Year	Application			PHI, days	Residues mg/kg		Ref.
	kg ai/ha	kg ai/hl	No		Fenpyroximate	Z- isomer	
				28	<0.05	<0.05	
Japan 1990	0.14	0.005	1	15	0.11	0.006	R-28
				30	0.08	0.005	
				45	0.034	<0.005	
				60	0.042	<0.005	
	0.25	0.005	1	15	0.048	<0.005	
				30	0.028	<0.005	
				45	0.007	<0.005	
				60	<0.005	<0.005	
New Zealand 1991/92		0.0025 (3 trials)	1	7-9	0.07, 0.09, 0.12		R-29
				14	0.12, 0.13, 0.03		
				28	<0.01 (3)		
				42-43	<0.01 (2), 0.01		
		0.005 (3 trials)	1	7-9	0.1, 0.07, 0.06		
				14	0.05, 0.04, 0.02		
				21	<0.01		
				28	0.03 (2), <0.01		
				42-43	<0.01 (2), 0.01		
				52-56	<0.01 (3),		
New Zealand 1993/94		0.0025 (4 trials)	1	7-9	0.05, 0.06, 0.01 (2)		R-30
				14	0.03 (2), <0.01, 0.04		
				21	0.04 (2), 0.02, <0.01		
				28	0.03, 0.02, <0.01 (2)		
				35	0.02 (2), 0.01,<0.01		
				42-43	0.02 (3), <0.01		
				49	0.02, 0.01, <0.01		
				52-56	0.01, <0.01 (2)		
		0.005 (4 trials)	1	7-9	0.11, 0.07, 0.06, 0.05		
				14	0.08, 0.06 (2), 0.03		
				21	0.03, 0.04, 0.05, 0.06		
				28	0.03 (2), 0.05, 0.02		
				35	0.03 (2), 0.04, 0.01		
				42-43	0.04, 0.03 (2), <0.01		
				49	0.03, 0.02, 0.01		
				52-56	0.03, 0.01, <0.01		

Grapes (Table 22). Fenpyroximate 5% SC is registered for use on vines in Chile, Peru, Japan and

several European countries.

In France, six supervised trials (two designed to establish decay curves) were carried out on vines in 1989 and 1990. Grapes and wine were analysed for fenpyroximate and its two major metabolites. For the dissipation studies, fenpyroximate was applied at rates of 0.06 kg ai/ha in 1989 and 0.08 kg ai/ha in 1990. Residues of fenpyroximate in grapes decreased from 0.1 to 0.07 mg/kg in 30 days when the vines were treated at 0.08 kg ai/ha. After treatment at 0.06 kg/ha all residues after 7 days and later were <0.02 mg/kg. The other trials were with two applications of 0.06 or 0.08 kg ai/ha and harvest was after 36 to 55 days. Residues of fenpyroximate in the grapes ranged between <0.02 and 0.14 mg/kg. Residues of the metabolites were <0.02 mg/kg. There was no information on GAP in France.

Eight supervised field trials were carried out at different locations in Germany. Grapes were analysed for fenpyroximate and its *Z*- isomer. The last treatment was at the beginning of ripening and sampling was at intervals up to 35 days (maturity). The vines were treated twice at 0.14 or 0.18 kg ai/ha, or once at 0.045 kg ai/ha and again at 0.135 kg/ha. Residues of fenpyroximate and the metabolite after 35 days were 0.06-0.4 mg/kg and ≤0.01 mg/kg respectively.

Six trials were carried out in Italy on wine grapes at application rates of 0.064-0.19 kg ai/ha. The GAP rate is 0.05 kg ai/ha. Grapes samples were taken at the GAP PHI of 14 days. Residues of fenpyroximate and its isomer were 0.07-0.57 mg/kg and <0.01 mg/kg respectively.

In residue trials in Japan (1988 and 1989) in greenhouses fenpyroximate was applied once or twice at the GAP concentration of 0.005 kg ai/hl (a single application is GAP). Samples were taken 13, 20 and 29 days after application. Residues of fenpyroximate were 0.06-0.05 mg/kg from single applications and about 1.2 mg/kg from two applications. Residues of the *Z*- isomer were <0.005-0.014 mg/kg (Iwamoto and Matano, 1993c,d).

Table 22. Residues of fenpyroximate and its isomer in grapes from supervised trials.

Country, Year, Location	Application			PHI, days	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		Fenpyroximate	*Z*- isomer	
France 1989	0.06	0.006	1	0	0.05	<0.02	R-31
				7	<0.02	<0.02	
				14	<0.02	<0.02	
				21	<0.02	<0.02	
				29	<0.02	<0.02	
		0.006	2	36	0.05	<0.02	
				37	0.07	<0.02	
				47	<0.02	<0.02	
France 1990	0.06	0.006	2	42	0.05	<0.02	
				46	0.07	<0.02	
				55	0.06	<0.02	
France 1990	0.08	0.008	1	0	0.1	<0.02	
				7	0.05	<0.02	
				14	0.05	<0.02	
				21	0.08	<0.02	
				30	0.07	<0.02	

Country, Year, Location	Application			PHI, days	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		Fenpyroximate	*Z*- isomer	
France 1989	0.08	0.008	2	36	<0.02	<0.02	
				37	0.14	<0.02	
				47	<0.02	<0.02	
France 1990	0.08	0.008	2	42	0.08	<0.02	
				46	0.05	<0.02	
				55	0.04	<0.02	
Germany 1989 (Mussbach)	0.14	0.023	2	0	0.17	<0.01	R-32
				7	0.12	<0.01	
				14	0.11	<0.01	
				28	0.09	<0.01	
				35	0.06	<0.01	
Germany 1989 (Kappelrodeck)	0.14	0.023	2	0	0.41	<0.01	R-33
				7	0.41	<0.01	
				14	0.27, 0.34	0.01	
				28	0.32	0.01	
				35	0.4	<0.01	
Germany 1989 Pfeddersheim	0.18	0.03	2	0	0.2	<0.01	R-34
				7	0.12, 0.17	<0.01	
				14	0.14	<0.01	
				28	0.21	<0.01	
				35	0.15	<0.01	
Willsbach	0.18	0.03	2	0	0.19 (2)	<0.01	R-35
				7	0.18	<0.01	
				14	0.24	<0.01	
				28	0.16	<0.01	
				35	0.13, 0.14	<0.01	
Germany 1989 Mussbach	0.18	0.03	2	0	0.26	<0.01	R-36
				7	0.16	<0.01	
				14	0.1 (2)	<0.01	
				28	0.13	<0.01	
				35	0.13	<0.01	
Germany 1989 Kappelrodeck	0.18	0.03	2	0	0.29	<0.01	R-37
				7	0.3 (2)	<0.01	
				14	0.18	<0.01	
				28	0.12	<0.01	
				35	0.16	<0.01	
Germany 1991 Nittel	0.045-0.135	0.015-0.225	2	0	0.22	0.02	R-38
				7	0.16	0.02	
				14	0.16	0.02	
				28	0.1	0.01	
				35	0.08	0.01	

Country, Year, Location	Application			PHI, days	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		Fenpyroximate	*Z*- isomer	
Mühlhofan	0.045-0.135	0.015-0.225	2	0	0.36	0.04	
				7	0.29	0.03	
				14	0.17	0.02	
				28	0.12	0.02	
				35	0.11	0.01	
Italy 1991	0.081	0.0062	1	14	0.47	0.02	R-39
	0.16	0.012	1	14	0.57	0.03	
	0.094	0.0063	1	14	0.17	0.01	
	0.19	0.013	1	4	0.52	0.03	
	0.064	0.0064	1	14	0.07	<0.01	R-40
	0.13	0.013	1	14	0.19	<0.01	R-41
Japan 1988 (greenhouse)	0.2	0.005	1	14	0.38, 0.41	<0.005	R-42
				21	0.45, 0.41	0.01	
				30	0.36, 0.33	0.01	
				60	0.062, 0.058	0.007, 0.006	
Japan 1989 (greenhouse)	0.2	0.005	1	13	0.43 (2)	<0.005 (2)	R-43
				20	0.53, 0.5	<0.005 (2)	
				29	0.51, 0.49	0.01, 0.009	
		0.005	2	13	1.1, 1.2	0.015, 0.013	R-43
				20	1.1, 1.2	0.014 (2)	

Hops. Fenpyroximate 5% SC is registered for use on hops at dosage rates between 0.225 and 0.263 kg ai/ha in Germany, 0.05 kg ai/ha in Italy, and at 0.005 kg ai/hl in Japan. Several supervised trials were carried out on hops at rates between 0.375 and 0.75 kg ai/ha (1 application) in Germany, but only one, at 0.23 kg ai/ha, within the range covered by GAP. In this trial residues of fenpyroximate were <0.5-1.6 mg/kg in green hops and 1.2-4.3 mg/kg in dried hops 21 days after application. Residues of the *Z*-isomer were <0.05 and <1 mg/kg in green and dried hops respectively.

Table 23. Residues of fenpyroximate and its isomer in hops from supervised trials.

Country, Year, Location	Application			PHI, days	Residues in green and [dried] hops, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		Fenpyroximate	Z- isomer	
Germany, 1989, Gambach	0.375	0.0125	1	0	5.2, 7.6	<0.5 (2)	R-44, R-45
				7	1.6, 3.8	<0.5 (2)	
				14	0.9, 3.1	<0.5 (2)	
				21	0.8, 3.2, [6.4], [<1]	<0.5 (2), [<1] (2)	
Oberrunseried	0.375	0.0086	1	0	2.7, 2.6	<0.5 (2)	R-46, R-47
				7	1.6, 1.1	<0.5 (2)	
				14	1.5, 1.1	<0.5 (2)	
				21	0.5, 0.8, [2.1], [2.1]	<0.5 (2), [<1] (2)	
Germany, 1990, Gambach	0.375	0.0188	1	0	3.1, 1.8	<0.5 (2)	R-48
				7	3.7, 2.1	<0.5 (2)	
				14	3.7, 2.5	<0.5 (2)	
				21	1.1, <0.5, [6.8, 8.2]	<0.5 (2), [<1] (2)	
Germany, 1990, Gambach	0.75	0.0375	1	0	11.6	<0.5	R-48
				7	11.3	<0.5	
				14	15.8	<0.5	
				21	10.4 [28.7]	<0.5 [1.7]	
Germany, 1990, Tannant Red	0.375	0.015	1	0	5.3	<0.5	R-48
				7	2.5	<0.5	
				14	2.4	<0.5	
				21	2.1, [7.0]	<0.5, [<1]	
Germany, 1990, Lindau-Bodenegg	0.375	0.0094	1	0	4.7	<0.5	R-48
				7	3.5	<0.5	
				14	13.7	<0.5	
				21	4.9, [<1]	<0.5, [<1]	
Germany, 1990, Lindau-Bodenegg	0.75	0.0188	1	0	25.9	<0.5	
				7	24.1	<0.5	
				14	12.1	<0.5	
				21	9.2, [25]	<0.5, [1.7]	
Germany, 1991	0.23	0.0075	1	0	11.3, 6.6, <0.5	<0.5 (3)	R.49
				7	1.5, 2.3, 2.6	<0.5 (3)	
				14	<0.5, 1.2, 1.7	<0.5 (3)	
				21	<u>≤0.5</u>, <u>0.7</u>, <u>1.6</u>, [1.2, 3.7, 4.3]	<0.5 (3), [<1] (3)	
Germany, 1991	0.46	0.015	1	0	9.8, 6.8, 14.7	<0.5 (3)	
				7	4.2, 4.0, 4.0	<0.5 (3)	

Country, Year, Location	Application			PHI, days	Residues in green and [dried] hops, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		Fenpyroximate	*Z*- isomer	
				14	1.3, 2.5, 2.3	<0.5 (3)	
				21	0.6, 1.5, 3.1, [2.5, 4.9, 3.6]	<0.5 (3), [<1] (3)	

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No data were provided.

In processing

Apples. Processing trials were carried out in Germany to determine residues of fenpyroximate and its *Z*- isomer in fruit, purée, cider, wet pomace and washings after two applications of fenpyroximate 5% SC at 0.075-0.08 kg ai/ha (Table 24). The last treatment was 21 days before harvest. The washed apples were finely chopped and cider was prepared using a household juice press. The cider was pasteurized at 75°C for 25 minutes. Other samples of washed apples were cut into small pieces and boiled for 20 minutes. Apple purée (mash) was separated from peel and pips using a sieve. Samples were analysed by GLC, using a nitrogen-selective detector (method DFG S 19, in accordance with GLP Guidelines). Recoveries were 79-92% for the active ingredient and between 71 and 88% for the *Z*- isomer (Burstell *et al*., 1992b).

Table 24. Residues of fenpyroximate and its isomer in apples and processed products.

Sample	Residues, mg/kg			
	Fenpyroximate		*Z*- isomer mg/kg	
	Trial 1 (0.075 kg ai/ha)	Trial 2 (0.08 kg ai/ha)	Trial 1	Trial 2
Fruit	0.06	0.15	<0.05	<0.05
Cider	<0.05	<0.05	<0.05	<0.05
Apple purée	<0.05	<0.05	<0.05	<0.05
Pomace, wet	0.13	0.39	<0.05	<0.05
Washings from apples	<0.05	<0.05	<0.05	<0.05
Washings from purée	<0.05	<0.05	<0.05	<0.05

Residues of fenpyroximate in the purée and cider were below the limit of determination, but were concentrated about twofold in wet pomace.

Grapes. Residues of fenpyroximate and its metabolite A (the *Z*- isomer) were investigated in grapes and wine.

In two trials on *Vitis vinifera* vines treated with fenpyroximate 5% SC at 0.18 kg ai/ha (Table 22, Trials R-34, 4-35), grapes collected 35 days after application and wine made from them were analysed by HPLC (Table 25).

Table 25. Residues of fenpyroximate and its isomer in grapes and wine from vines treated at 0.18 kg ai/ha.

Sample	Residues, mg/kg			
	Trial R-34		Trial R-35	
	Fenpyroximate	*Z*- isomer	Fenpyroximate	*Z*- isomer
Grape	0.15	<0.01	0.13, 0.14	<0.01
Wine	<0.01	<0.01	<0.01	<0.01

Fenpyroximate residues were reduced in wine. No data were provided on residues in raisin culls or raisin waste, which could be used as animal feed in some countries.

Hops. In trials in Germany hops treated at 0.46 and 0.75 kg ai/ha 21 days before harvest were used to brew beer. Residues were determined in dried hops, spent hops, yeast, sludge and beer. The results are shown in Table 26 (Secker, 1994).

Table 26. Residues of fenpyroximate and its isomer in processed products of hops.

Sample	Residues, mg/kg							
	Trial 1[1]		Trial 2[2]		Trial 3[2]		Trial 4[2]	
	Fenpyrox.	*Z*- isomer	Fenpyrox.	*Z*- isomer	Fenpyrox.	*Z*- isomer	Fenpyrox.	*Z*- isomer
Dried hops	37.4	1.2	6.4	<1.0	9.0	<1.0	11.4	<1.0
Sludge	4.7	0.4	1.0	0.2	0.9	0.1	1.6	0.2
Spent hops	5.8	0.4	0.8	0.2	1.4	<0.1	1.6	0.3
Yeast	0.4	<0.1	<0.1	<0.1	0.4	<0.1	0.4	<0.1
Beer	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

[1] Treatment at 0.75 kg ai/ha
[2] Treatment at 0.46 kg ai/ha

The results show clearly that even at the exaggerated application rates (the maximum GAP rate is 0.263 kg ai/ha) no residues could be measured in beer. In yeast, which is of minor importance in the human diet, the highest residues of fenpyroximate were 0.4 mg/kg. In spent hops, which are used in animal feed, maximum combined residues of fenpyroximate and the *Z*- isomer were about 2 mg/kg from treatment at 0.46 kg/ha and 6 mg/kg from 0.75 kg/ha.

Residues in the edible portion of food commodities

The only data provided, apart from the processing trials just described, were on residues in orange pulp. These were all below 0.1 mg/kg.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

No information was provided.

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs have been reported.

Country	Commodity	MRL, mg/kg
Belgium	Pome fruits	0.2
	Others	0.01
Brazil	Citrus fruits	0.5
	Apple	0.1
France	Apple	0.2
	Grapes	0.2
Japan	Satsuma mandarin	0.5
	Citrus fruits (except Satsuma mandarin)	1.0
	Apple	1.0
	Grapes	2.0
	Hops	15
Spain	Citrus fruits	0.3
	Pome fruits	0.3
	Grapes	0.3
Switzerland	Apple	0.2
	Grapes	0.2

APPRAISAL

The fate of fenpyroximate has been studied in rats, mandarins, apples, grapes, soil and water.

The principal metabolites identified are indicated below.

A: *tert*-butyl (*Z*)-Æ-(1,3,-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluate
C: (*E*)-Æ-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluic acid
F: 1,3-dimethyl-5-phenoxypyrazole-4-carbaldehyde
H: 1,3-dimethyl-5-phenoxypyrazole-4-carboxylic acid
K: 1,3-dimethyl-5-phenoxypyrazole-4-carbonitrile
L: *tert*-butyl (*E*)-Æ-(3-methyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluate

Male and female rats were dosed orally once with fenpyroximate labelled with ^{14}C in both the pyrazole and benzyl rings at a 2 mg/kg or 400 mg/kg bw. Another group of animals received a daily dose of 2 mg/kg bw of the unlabelled compound for 14 days, followed by a single administration of [*pyrazole*-^{14}C]fenpyroximate at the same level. Fenpyroximate was rapidly excreted in the urine and faeces.

Following [*pyrazole*-^{14}C]fenpyroximate administration at 2 mg/kg, radioactivity was rapidly excreted in faeces and urine. After 168 hours, 70-85% of the dose had been excreted in the faeces and 12-18% in the urine. Negligible amounts of radioactivity were expired as CO_2 or volatile organic compounds. Similar results were obtained after multiple dosing with unlabelled fenpyroximate followed by a single dose of fenpyroximate at 2 mg/kg.

Although slower excretion was observed after a single administration at 400 mg/kg, 75-77% of the dose was excreted in the faeces and 11-12% in the urine after 168 hours. Tissue residues were generally low at 168 hours, and the highest concentration of radioactivity (1-4% of the dose) was in the gastrointestinal tract. The major urinary metabolites were 1,3-dimethyl-5-phenoxypyrazole-3-carboxylic acid (H) and 4-cyano-1-methyl-5-phenoxypyrazole-3-carboxylic acid. High levels of

unchanged fenpyroximate were present in the faeces, owing to the excretion of the unabsorbed compound.

A similar pattern of excretion and tissue distribution were observed after administration of [*benzyl*-^{14}C]fenpyroximate. The major urinary metabolite was terephthalic acid and large amounts of unchanged fenpyroximate were found in the faeces.

The principal metabolic pathways were isomerization, cleavage of the oxime ether bond between the benzyl and pyrazole rings, hydrolysis of the ester, oxidation of the *tert*-butyl group and *N*-demethylation of the pyrazole ring.

Low residues were found in the tissues: liver 0.1-0.25%; kidney 0.05-0.1 %; and fat 0.4-0.8% of the initial dose.

No metabolism studies were submitted for other animals.

The fate of residues in plants was studied in mandarins, apples and grapes, using [*pyrazole*-^{14}C] and [*benzyl*-^{14}C]fenpyroximate. Labelled fenpyroximate was applied to mandarins at approximately the recommended rate, and samples were collected at 0, 3, 7, 14, 28 and 137 days after treatment. Radioactivity was not detected in the pulp (LOD 0.03 mg/kg at 28 days and 0.004 mg/kg at 137 days after treatment). The radiocarbon concentration on and in treated leaves gradually decreased. Loss from the peel was slower. The half-life of fenpyroximate was 38.4 days in the peel and 8.8 days in the leaves. The principal ^{14}C residues were fenpyroximate and its *Z*- isomer, although *N*-demethyl-fenpyroximate was found at analytically significant levels in early trials on mandarins.

The *Z*- isomer (compound A) generally occurred at levels of ≤10% of those of fenpyroximate in the peel and leaves at short PHIs (3-7 days). *N*-demethyl fenpyroximate (compound L) occurred at comparable or slightly higher levels at PHIs of 28-137 days.

Labelled fenpyroximate was applied to apples at the maximum recommended field rate of 7.5 g ai/hl, and samples were analyzed at intervals. Fenpyroximate and its *Z*- isomer were the main ^{14}C residues in apples at harvest. Several metabolites were also found, but were of minor importance. The total radioactivity in the fruits decreased from 0.13 mg fenpyroximate equivalents/kg at day 0 to 0.003 mg/kg at day 57 (harvest).

Metabolism studies on grapes were carried out using pyrazole- and benzyl-labelled fenpyroximate. Fenpyroximate and its *Z*- isomer were again the main residues in grapes and stems at harvest. Several metabolites were detected at lower levels. After the application of labelled fenpyroximate at the recommended rate (37.5 g ai/ha) the highest total radioactivity found in grape bunches was 0.19 mg/kg fenpyroximate equivalents at day 7, and 0.08 mg/kg at day 57 (harvest).

In summary, plant metabolism studies indicated that the major residual compounds in crop commodities are unchanged fenpyroximate and its *Z*- isomer. Although the proportion of the *Z*-isomer increased with time, its residues were generally less than 20% of the fenpyroximate levels in fruits at PHIs up to 28 days. Leaves showed the same pattern of metabolites as fruits, but with higher levels of ^{14}C. Residues of *N*-demethyl-fenpyroximate (compound L) were of the same order as, or slightly higher than, those of the *Z*- isomer.

Although compounds A and L were the main metabolites in plants, compound A was a minor metabolite in animals and compound L was not found.

Studies of the fate of fenpyroximate in soil (sandy, silty and clay) showed that the degradation pathways consist of hydrolysis of the ester, isomerization or cleavage of the oxime group, *N*-

demethylation, oxidation of the methyl group at the 3-position on the pyrazole ring and hydroxylation of the phenyl ring, with final mineralization to CO_2. Compounds A, C, H and K were the major degradation products. The half-life was 10 to 50 days, except in sandy soil where it was 159 days. Fenpyroximate was strongly adsorbed to soil, to an extent depending on the content of soil organic matter.

The adsorption/desorption of [*pyrazole*-^{14}C]fenpyroximate was studied in four different soil types. The K_{oc} values were all 37,000 or more, showing that fenpyroximate is immobile in all the soils tested (loamy sand, sandy loam, clay loam and loam).

The leaching behaviour of fenpyroximate and its aged residues was studied in various soils. The results showed that small amounts of fenpyroximate move only through very sandy soils with low organic matter contents. The compound can therefore be classified as weakly mobile.

Environmental fate in water. The hydrolysis of fenpyroximate was studied in buffered sterile and unsterilized aqueous solutions at various Ph values and temperatures. Compounds A, C and F were identified as degradation products. The studies were too short to estimate half-lives.

The photolysis of fenpyroximate in solution was studied with irradiation by sunlight and a xenon lamp. The predominant product of photodegradation was compound A. Degradation was apparently by isomerization, oxime-ether cleavage and hydrolysis. The half-life was 2.6 days in sunlight and 1.5 hours under irradiation with a xenon lamp (603 watts, 290-300 nm) at pH 7.

The analytical methods for fenpyroximate and its isomer used in the reported studies were based on extraction with methanol or acetone, partitioning with hexane or acetonitrile, and clean-up on some combination of C_{18} cartridges, SX-3 gel, silica gel and alumina columns. Determination was by GLC or HPLC. The GLC methods determine fenpyroximate and its *Z*- isomer, while HPLC (with UV detection) determines fenpyroximate, its *Z*- isomer and *N*-demethyl-fenpyroximate in the same extract.

Recoveries of fenpyroximate and its *Z*- isomer from fruits were above 70% with LODs of 0.02-0.05 mg/kg. The limits of determination reported for other commodities were 0.1 mg/kg for dregs and yeast, 1 mg/kg for dried hops, 0.5 mg/kg for green hops, and 0.01 mg/kg for beer.

The storage stability of pyrazole-labelled fenpyroximate was investigated on apples and grapes stored at -20ºC. After about 3 years approximately 65% of the initial residue remained. In another study apples and grapes fortified with a solution of fenpyroximate and its metabolites were stored at -20ºC. The proportions of the original residues remaining in apples after 145 days were fenpyroximate 68%, *Z*- isomer 71%, and *N*-demethyl fenpyroximate 60%, and in grapes stored for 77 days fenpyroximate 76%, *Z*- isomer 87%, and *N*-demethyl-fenpyroximate 50%.

The stability of fenpyroximate residues at -20ºC was also studied in citrus samples (peel and pulp) fortified with fenpyroximate and its *Z*- isomer. The proportions of both compounds remaining were 65% in pulp stored for 140 days and 72% in peel stored for 188 days. Fenpyroximate and the *Z*-isomer were stable in hops (dried cones) stored at -18ºC for 2 years with about 100% of the residues remaining. The studies showed that fenpyroximate can be considered to be reasonably stable during these periods.

Results of residue trials were available for citrus (oranges and mandarins), apples, grapes and hops. For many trials only summary reports were supplied and few trials were according to GAP. Often representative chromatograms were not provided although control values and percentage recoveries were submitted.

Fenpyroximate is registered for use on citrus fruits in Brazil, Chile, Greece, Italy, Japan, Peru

and Spain with application rates from 0.1 to 0.2 kg ai/ha, and PHIs of 14-15 days. The Meeting received data from supervised trials in Brazil, Greece and Italy: residues were determined separately and the peel/pulp ratios were not reported. Supervised trials on mandarins treated at the recommended rate (0.005 kg ai/hl) were carried out in Japan in greenhouses, this being a minor use in that country. These trials were the only ones in which residues in the whole fruit were reported. Since the other trials showed that the residues occur principally in the peel and pulp:peel ratios were not reported, the Meeting could not estimate a maximum residue level.

Apples. Numerous field trials have been conducted in Australia, Belgium, France, Germany, Japan and New Zealand. No GAP was reported for Australia. A trial in Belgium was evaluated against GAP in France and Switzerland. Several trials in France and Germany were carried out according to GAP in those countries (0.008 kg ai/hl, 21 days PHI). In supervised trials in Japan fenpyroximate was applied at the recommended rate (0.005 kg ai/hl). The *Z*- isomer was determined in most of these trials and was below the limit of determination in almost every sample. Supervised trials according to GAP carried out in New Zealand showed parent residues from <0.01 to 0.13 mg/kg at the New Zealand PHI of 14 days; the *Z*- isomer was not determined. The storage period before analysis was not reported. The Meeting estimated a maximum residue level of 0.2 mg/kg.

Grapes. Supervised trials on vines were conducted in France, Germany, Italy and Japan. Those in France and Italy which approximated Portuguese GAP showed residues of <0.02 and 0.08 mg/kg (France) and 0.07, 0.17 and 0.47 mg/kg (Italy). Residues in two (greenhouse) trials in Japan in accordance with GAP were 0.38 to 0.53 mg/kg. Residues of fenpyroximate in all the trials complying with GAP ranged from <0.02 to 0.53 mg/kg. The Meeting concluded that the data were insufficient to estimate a maximum residue level for a major crop.

Hops. Results of nine German trials (1989-1991) were submitted to the Meeting, but only one trial was in accordance with GAP. The Meeting could not estimate a maximum residue level.

The Meeting received data from processing studies on apples. Residues of fenpyroximate in apple puree and cider were below the limit of determination. In two domestic processing trials with fruit containing 0.06 mg/kg and 0.15 mg/kg, the fenpyroximate residues in wet pomace were concentrated by factors ranging from 2.2 to 2.6. In the absence of the study details and because the studies did not represent a commercial process, the Meeting could not draw conclusions from the data.

Supervised trials on grapes were carried out in Germany to study the fate of fenpyroximate in processed products. Only summary reports were available, where critical supporting information was lacking. Residues of fenpyroximate in wine were below the limit of determination (<0.01 mg/kg), when made from grapes containing residues of fenpyroximate of 0.13-0.15 mg/kg. No data on processing to pomace were provided. In the absence of the study details the Meeting could not draw conclusions from the data.

Processing studies on hops showed that even with high fenpyroximate residues in the hops no residues could be detected in beer. A residue of 0.4 mg/kg was found in yeast, which is of minor importance in the human diet. The highest residue found in spent hops was 6 mg/kg, from dried hops with a fenpyroximate residue of 37.4 mg/kg.

No information was provided on residues of fenpyroximate occurring in commerce or at consumption.

Since metabolism studies showed that the *Z*- isomer was always less than 20% of the residue and in almost all supervised trials its residues were near the limit of determination, the Meeting concluded that the residue should be defined as fenpyroximate.

The Meeting considered the need to include livestock metabolism and animal transfer studies in accordance with FAO guidelines in future submissions. The Meeting was informed that animal studies were not available. Additional residue data on citrus fruits (oranges, whole fruit) with relevant information on GAP are needed, as are additional supervised trials data on grapes and hops reflecting GAP. Complete trial details should be provided, including the analytical methods used, validations thereof, and sample chromatograms.

RECOMMENDATIONS

The Meeting estimated a maximum residue level of 0.2 mg/kg for apples but this cannot be recommended for use as an MRL owing to the lack of critical supporting data.

FURTHER WORK OR INFORMATION

Desirable

1. An additional processing study on apples, conducted with apples containing residues at or above the estimated maximum residue level (0.2 mg.kg), reflecting commercial processing.

2. An additional study on processing grapes to wine and raisins, including data on by-products. Complete trial details should be provided.

3. Information on residues of fenpyroximate in foods in commerce or at consumption.

REFERENCES

Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080102, R-01. Unpublished.

Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080103, R-02. Unpublished.

Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080202, R-03. Unpublished.

Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080203, R-04. Unpublished.

Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080302, R-05. Unpublished.

Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080303, R-06. Unpublished.

Iawamato, T. and Matano, O. 1993a. Residue determination of fenpyroximate in or on Satsuma mandarin treated with fenpyroximate 5% SC at 50 ppm (ai). Japan Plant Protection Association, Japan and The Institute of Environmental Toxicology, Japan. Rep. No-4056, R-07. Unpublished.

Hoechst, 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90BRA004000102, R-08. Unpublished.

Hoechst, 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90BRA004000202, R-09. Unpublished.

Hoechst, 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90BRA004000302, R-10. Unpublished.

Hoechst, 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90BRA004000402, R-11. Unpublished.

Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER92GRC002000102, R-12. Unpublished.

Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER92GRC002000103, R-13. Unpublished.

Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA008080102, R-14. Unpublished.

Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA008080202, R-15. Unpublished.

Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA008080302, R-16. Unpublished.

Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA009080102, R-17. Unpublished.

Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA009080202, R-18. Unpublished.

Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA009080302, R-19. Unpublished.

Bull, M.S. and Holding, R.K. 1992. Residues of fenpyroximate and its metabolites (M1 & 12) in pome fruit following application of NNI-850. Ciba-Geigy, Australia. Rep. No. 92/12/1378, R-20. Unpublished.

Benet, F. and Decraecke, H. 1992. Recherche de residus de fenpyroximate et de ses deux metabolites dans des pommes. ICI, France. Rep. No.RE-9205-H, R-21. Unpublished.

Benet, F. and Massenot, F. 1991a. Recherche de residus de fenpyroximate dans des pommes. ICI, France. Rep. No. RE-9109-H, R-22. Unpublished.

Benet, F. and Massenot, F. 1991b. Recherche de residus de fenpyroximate et de ses deux metabolites dans les pommes. ICI, France. Rep. No. RE-9117-H, R-23. Unpublished.

Burstell, H. Raquet, H. and Werner, H. 1991a. Investigation of residues in apples following application of Hoe 094552 for the control of spider mites. Hoechst AG, Germany. Rep No. DEU89I801, R-24. Unpublished.

Burstell, H. Raquet, H. and Werner, H. 1991b. Investigation of residues in apples following application of Hoe 094552 for the control of spider mites. Hoechst AG, Germany. Rep No. DEU89I811, R-25. Unpublished.

Burstell, H. Raquet, H. and Werner, H. 1992a. Investigation of residues in apples following a single application of Hoe 094552. Hoechst AG, Germany. Rep No. ERDEU90DEU812, R-26. Unpublished.

Burstell, H. Raquet, H. and Werner, H. 1992b. Investigation of residues in processed apples following two applications of Hoe 094552. Hoechst AG, Germany. Rep No. ERDEU90DEU801, R-27. Unpublished.

Iawamoto, T. and Matano, O. 1993b. Residue determination of fenpyroximate in or on apples treated with fenpyroximate 5% SC at 50 ppm (ai). Japan Plant Protection Association, and The Institute of Environmental Toxicology, Japan. Rep. No.R-4058, R-28. Unpublished.

Patterson, T.M., 1992. The analysis of apple for fenpyroximate residues. Ciba-Geigy New Zealand Limited, New Zealand. Rep. No.91/35B, R-29. Unpublished.

Patterson, T.M., 1994. The analysis of apple for fenpyroximate residues. Ciba-Geigy New Zealand Limited, New Zealand. Rep. No.93/35B, R-30. Unpublished.

Benet, F. and Massenot, F. 1992. Recherche de residus de fenpyroximate et de ses deux metabolites dans du raisin et du vin. ICI, France. Rep. No. RE-9206-H, R-31. Unpublished.

Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU813020102, R-32. Unpublished.

Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU813020202, R-33. Unpublished.

Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU803020102, R-34. Unpublished.

Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU813020202, R-35. Unpublished.

Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU805020102, R-36. Unpublished.

Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU805020202, R-37. Unpublished.

Raquet, H. Werner, H.J. and Burstell, H 1994. Fenpyroximate (50 g/l) water miscible suspension concentrate. Investigation of residues in grapes following two applications of Hoe 094552. Hoechst Schering AgroEvo GmbH, Germany. Rep. No. ER91DEU814, R-38. Unpublished.

Sochor, H. 1994. Investigation of residues in vine grapes following one application of Hoe 094552. Hoechst, Germany. Rep. No.ER91ITA004, R-39. Unpublished.

Hoechst. 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA104080102, R-40. Unpublished.

Hoechst. 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA104080103, R-41. Unpublished.

Iawamoto, T. and Matano, O. 1993c. Residue determination of fenpyroximate in or on grapes treated with fenpyroximate 5% SC at 50 ppm (ai)-Ishikawa- Japan

Plant Protection Association, and The Institute of Environmental Toxicology, Japan. Rep. No.R-4059, R-42. Unpublished.

Iawamoto, T. and Matano, O. 1993d. Residue determination of fenpyroximate in or on grapes treated with fenpyroximate 5% SC at 50 ppm (ai)-Fukui- Japan Plant Protection Association, and The Institute of Environmental Toxicology, Japan. Rep. No.R-4060, R-43. Unpublished.

Hoechst. 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU804030102, R-44. Unpublished.

Hoechst. 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU804030202, R-45. Unpublished.

Hoechst. 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU804030302, R-46. Unpublished.

Hoechst. 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU804030402, R-47. Unpublished.

Sochor, A. 1994. Fenpyroximate, water miscible suspension 50 g/l. Investigation of residues in processed and no processed hops following one application. Hoechst, Germany. Rep. No. ER90DEU804, R-48. Unpublished.

Sochor, A. 1994. Fenpyroximate, water miscible suspension 50 g/l. Investigation of residues in processed and no processed hops following one application. Hoechst, Germany. Rep. No. ER91DEU804, R-49. Unpublished.

Funayama, S., Kojima, Y. and Uchida, M. 1991. Liquid chromatographic determination of fenpyroximate in water. Nihon Nohyaku, Japan. Rep. No. ILSRE91-023A, Unpublished.

Galicia, H. & Wyss-Benz, M. 1992. ^{14}C-fenpyroximate (NNI-850) [pyrazole labeled]: Plant metabolism study in field grown apple. RCC Umweltchemie AG, Switzerland. Rep. No. RCC-274961, Unpublished.

Hirano, A., Izawa, Y., Funayama. S. and Uchida, M. 1990. Degradation of [pyrazole-^{14}C] and [benzyl-^{14}C] fenpyroximate in soils under laboratory condition. Nihon Nohyaku, Japan. Rep. No.ILSR-M-90-059A, Unpublished.

Izawa, Y., Hirano, A., Funayama. S. and Uchida, M. 1990. Metabolism of fenpyroximate (NNI-850) in citrus. Nihon Nohyaku, Japan. Rep. No.ILSR-M-90060A, Unpublished.

Izawa, Y., Hirano, A., Funayama. S. and Uchida, M. 1991a. Metabolism of [pyrazole-^{14}C] fenpyroximate (NNI-850) in citrus grown in the greenhouse. Nihon Nohyaku, Japan. Rep. No.ILSR-M-91-0190, Unpublished.

Izawa, Y., Hirano, A., Funayama. S. and Uchida, M. 1991b. Metabolism of [benzyl-^{14}C] fenpyroximate (NNI-850) in citrus. Nihon Nohyaku, Japan. Rep. No.ILSR-M-91-020A, Unpublished.

Izawa, Y., Hirano, A., Funayama. S. and Uchida, M. 1993. Degradation of fenpyroximate in upland soils under laboratory conditions. J. Pesticide Sci., 18,67-75.

Krautter, G., Downs, J. and Lawrence, L. J. 1983. Metabolism of [14C]NNI-850 in tangerine trees under commercial conditions. PTRL, USA. Rep. No.1139. Unpublished.

Krautter, G., Downs, J. and Lawrence, L. J. 1989. Metabolism of [14C]NNI-850 in tangerine trees grown outside. PTRL, USA. Rep. No.1172. Unpublished.

McCann, D. J. 1992. Sorption/desorption of pyrazole-^{14}C-fenpyroximate on soils by batch equilibrium method. Battelle, USA. Rep. No SC910124. Unpublished.

NIHON NOHYAKU Co., Ltd. 1989a. Residue analysis of fenpyroximate and its metabolite in fruits (GLC method). Nihon Nohyaku, Japan. Rep. No. A-4001. Unpublished.

NIHON NOHYAKU Co., Ltd. 1989b. Residue analysis of fenpyroximate and its metabolite in fruits (HPLC method). Nihon Nohyaku, Japan. Rep. No. A-4002. Unpublished.

NIHON NOHYAKU Co., Ltd. 1989c. Residue analysis of fenpyroximate and its metabolite in fruits (GLC and HPLC method). Nihon Nohyaku, Japan. Rep. No. A-4003. Unpublished.

Nishizawa, H., Nakayama, M., Nakano, A., Susuki, T. and Uchida, M. 1990a. Hydrolysis of fenpyroximate in water. Nihon Nohyaku, Japan. Rep. No. ILSR-E-90056. Unpublished.

Nishizawa, H., Hirano, A., Hasegawa, T., Susuki, T. and Uchida, M. 1990b. Photodegradation of fenpyroximate in water. Nihon Nohyaku, Japan. Rep. No.ILSR-E-90-057A. Unpublished.

Nishizawa, H., Shigemura, M., Kitaura, T. and Uchida, M. 1992. Analytical method of fenpyroximate and its metabolites in soil. Nihon Nohyaku, Japan. Rep. No.ILSR-R92-001A. Unpublished.

Nishisawa, H., Motoba, K., Susuki, T., Ohshima, T. and Uchida, M. 1993. Metabolism of fenpyroximate in rats. J. Pesticide Sci., 18, 59-66.

Römbke, J. 1992. Determination of soil column leaching of fenpyroximate (normal study). Batelle, Germany. Rep. No. BE-ME-107-90-01-LEAS. Unpublished.

Römbke, J. and Brodesser, J. 1992. Determination of the degradation in soil of fenpyroximate. Batelle, Germany. Rep. No.BE-EM-107-90-01-SAB1.1. Unpublished.

Römbke, J. and Möllerfeld, J. 1992a. Determination of degradation and metabolism in soil of pyrazole-^{14}C-fenpyroximate. Battelle, Germany. Rep. No.BE-ME-107-90-01-SAB1. Unpublished.

Römbke, J. and Möllerfeld, J. 1992b. Determination of the

soil column leaching of pyrazole ^{14}C-fenpyroximate (aging study). Battelle, Germany. Rep. No.BE-ME-107-90-01-LEA3. Unpublished.

Römbke, J. and Möllerfeld, J. 1992c. Determination of the soil column leaching of benzyl-^{14}C-fenpyroximate (aging study). Battelle, Germany. Rep. No.BE-ME-107-90-01-LEA4. Unpublished.

Saxena, A. & McCann, D. 1992. Hydrolysis of pyrazole-^{14}C-fenpyroximate in buffered aqueous solutions. Batelle, USA. Rep. No.SC900192. Unpublished.

Sharp, D. E., 1991a. Metabolism and disposition of [pyrazole-^{14}C] NNI-850 in rats. Hazleton Laboratories America, Inc., USA. Rep. No. HLA 6283-102. Unpublished.

Sharp, D. E., 1991b. Metabolism and disposition of [benzyl-^{14}C] NNI-850 in rats. Hazleton Laboratories America, Inc., USA. Rep. No. HLA 6283-101. Unpublished.

Specht, W. 1992a. Validation of method DFG S 19 for the determination of the residue of fenpyroximate (HOE 094552) and metabolite M-1 (HOE 112573) in orange (pulp and peel). Dr. Specht & Partner, Germany. Rep. No. HOE 9039V, Az.77546A/90. Unpublished.

Specht, W. 1992b. Validation of method DFG S 19 for the determination of the residue of fenpyroximate (HOE 094552) and metabolite M-1 (HOE 112573) in apple (fruit, mash and cider). Dr.Specht & Partner, Germany. Rep. No. HOE 9032V, Az.77539A/90. Unpublished.

Specht, W. 1992c. Validation of method DFG S 19 for the determination of the residue of fenpyroximate (HOE 094552) and metabolite M-1 (HOE 112573) in vine (grape, cider and wine) Dr.Specht & Partner, Germany. Rep. No. HOE 9030V, Az.77537A/90. Unpublished.

Specht, W. 1992d. Validation of method DFG S 19 for the determination of the residue of fenpyroximate (HOE 094552) and metabolite M-1 (HOE 112573) in processing products of hops (dregs, yeast and beer). Dr.Specht & Partner, Germany. Rep. No. HOE 92117V, Az.93232A/92. Unpublished.

Specht, W. & Winkelmann, 1987. Organochloride, organophosphorus, nitrogen-containing and other pesticides Gas-chromatographic determination after clean-up by gel permeation chromatography and silica gel minicolumn chromatography. In: Manual of pesticide residue analysis, edited by Thier, H. and Zeumer, H. Vol. 1, VCH publishers, New York.Swanson, M.B 1993. Direct photolysis of pyrazole-^{14}C-fenpyroximate in a buffered aqueous solution under artificial sunlight. Battelle, USA. Rep. No.SC910077. Unpublished.

Takemoto, Y., Funayama, S. and Uchida, 1990. Soil adsorption/desorption of fenpyroximate. Nihon Nohyaku, Japan. Rep. No.ILSR-M-90-058A. Unpublished.

Weber, H. 1993. Validation of method DFG S 19 for the determination of the residues of fenpyroximate (HOE 094552) and metabolite M-1 (HOE 112573) in soil. Dr. Specht & Partner, Germany. Rep. No. HOE 9236V, Az.96006A/92. Unpublished.

Weber, H. 1994. Storage stability of fenpyroximate (HOE 094552) and M-1 (HOE 112573) in hop (dried cone). Interim. report. Dr. Specht & Partner, Germany. Rep. No. HOE-9239, Az.96674/92. Unpublished.

Wyss-Benz, M. 1993a. Storage stability of ^{14}C-fenpyroximate (NNI-850) [pyrazole-labeled] in apples. RCC, Switzerland. Rep. No.RCC-358683. Unpublished.

Wyss-Benz, M. 1993b. Storage stability of ^{14}C-fenpyroximate (NNI-850) [pyrazole-labeled] in grapes. RCC, Switzerland. Rep. No.RCC-360000. Unpublished.

Wyss-Benz, M. and Mamouni, A. 1992a. 14C-fenpyroximate (NNI-850) [benzyl-labeled]: Plant metabolism study in field grown apples. RCC, Switzerland. Rep. No.RCC-274948. Unpublished.

Wyss-Benz, M. and Mamouni, A. 1992b. 14C-fenpyroximate (NNI-850) [pyrazole-labeled]: Plant metabolism study in field grown grape. RCC, Switzerland. Rep. No.RCC-274950. Unpublished.

Wyss-Benz, M. and Mamouni, A. 1992c. 14C-fenpyroximate (NNI-850) [pyrazole-labeled]: Plant metabolism study in field grown grape. RCC, Switzerland. Rep. No.RCC-274937. Unpublished.

Reports on residues from supervised trials

R-01. Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080102, Unpublished.

R-02. Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080103, Unpublished.

R-03. Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080202, Unpublished.

R-04. Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080203, Unpublished.

R-05. Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080302, Unpublished.

R-06. Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080303, Unpublished.

R-07. Iawamato, T. and Matano, O. 1993a. Residue determination of fenpyroximate in or on Satsuma mandarin treated with fenpyroximate 5% SC at 50 ppm (ai). Japan Plant Protection Association, Japan and The

Institute of Environmental Toxicology, Japan. Rep. No-4056, Unpublished.

R-08. Hoechst, 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90BRA004000102, Unpublished.

R-09. Hoechst, 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90BRA004000202, Unpublished.

R-10. Hoechst, 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90BRA004000302, Unpublished.

R-11. Hoechst, 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90BRA004000402, Unpublished.

R-12. Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER92GRC002000102, Unpublished.

R-13. Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER92GRC002000103, Unpublished.

R-14. Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA008080102, Unpublished.

R-15. Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA008080202, Unpublished.

R-16. Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA008080302, Unpublished.

R-17. Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA009080102, Unpublished.

R-18. Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA009080202, Unpublished.

R-19. Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA009080302, Unpublished.

R-20. Bull, M.S. and Holding, R.K. 1992. Residues of fenpyroximate and its metabolites (M1 & 12) in pome fruit following application of NNI-850. Ciba-Geigy, Australia. Rep. No. 92/12/1378, Unpublished.

R-21. Benet, F. and Decraecke, H. 1992. Recherche de residus de fenpyroximate et de ses deux metabolites dans des pommes. ICI, France. Rep. No.RE-9205-H, Unpublished.

R-22. Benet, F. and Massenot, F. 1991a. Recherche de residus de fenpyroximate dans des pommes. ICI, France. Rep. No. RE-9109-H, Unpublished.

R-23. Benet, F. and Massenot, F. 1991b. Recherche de residus de fenpyroximate et de ses deux metabolites dans les pommes. ICI, France. Rep. No. RE-9117-H, Unpublished.

R-24. Burstell, H. Raquet, H. and Werner, H. 1991a. Investigation of residues in apples following application of Hoe 094552 for the control of spider mites. Hoechst AG, Germany. Rep No. DEU89I801, Unpublished.

R-25. Burstell, H. Raquet, H. and Werner, H. 1991b. Investigation of residues in apples following application of Hoe 094552 for the control of spider mites. Hoechst AG, Germany. Rep No. DEU89I811, Unpublished.

R-26. Burstell, H. Raquet, H. and Werner, H. 1992a. Investigation of residues in apples following a single application of Hoe 094552. Hoechst AG, Germany. Rep No. ERDEU90DEU812, Unpublished.

R-27. Burstell, H. Raquet, H. and Werner, H. 1992b. Investigation of residues in processed apples following two applications of Hoe 094552. Hoechst AG, Germany. Rep No. ERDEU90DEU801, Unpublished.

R-28. Iawamoto, T. and Matano, O. 1993b. Residue determination of fenpyroximate in or on apples treated with fenpyroximate 5% SC at 50 ppm (ai). Japan Plant Protection Association, and The Institute of Environmental Toxicology, Japan. Rep. No.R-4058, Unpublished.

R-29. Patterson, T.M., 1992. The analysis of apple for fenpyroximate residues. Ciba-Geigy New Zealand Limited, New Zealand. Rep. No.91/35B, Unpublished.

R-30. Patterson, T.M., 1994. The analysis of apple for fenpyroximate residues. Ciba-Geigy New Zealand Limited, New Zealand. Rep. No.93/35B, Unpublished.

R-31. Benet, F. and Massenot, F. 1992. Recherche de residus de fenpyroximate et de ses deux metabolites dans du raisin et du vin. ICI, France. Rep. No. RE-9206-H, Unpublished.

R-32. Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU813020102, Unpublished.

R-33. Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU813020202, Unpublished.

R-34. Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU803020102, Unpublished.

R-35. Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU813020202, Unpublished.

R-36. Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU805020102, Unpublished.

R-37. Hoechst. 1991. Report on plant residue trial.

Hoechst AG, Germany. Rep. No.ER89DEU805020202, Unpublished.

R-38. Raquet, H. Werner, H.J. and Burstell, H 1994. Fenpyroximate (50 g/l) water miscible suspension concentrate. Investigation of residues in grapes following two applications of Hoe 094552. Hoechst Schering AgroEvo GmbH, Germany. Rep. No. ER91DEU814, Unpublished.

R-39. Sochor, H. 1994. Investigation of residues in vine grapes following one application of Hoe 094552. Hoechst, Germany. Rep. No.ER91ITA004, Unpublished.

R-40. Hoechst. 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA104080102, Unpublished.

R-41. Hoechst. 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA104080103, Unpublished.

R-42. Iawamoto, T. and Matano, O. 1993c. Residue determination of fenpyroximate in or on grapes treated with fenpyroximate 5% SC at 50 ppm (ai)-Ishikawa- Japan Plant Protection Association, and The Institute of Environmental Toxicology, Japan. Rep. No.R-4059, Unpublished.

R-43. Iawamoto, T. and Matano, O. 1993d. Residue determination of fenpyroximate in or on grapes treated with fenpyroximate 5% SC at 50 ppm (ai)-Fukui- Japan Plant Protection Association, and The Institute of Environmental Toxicology, Japan. Rep. No.R-4060, Unpublished.

R-44. Hoechst. 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU804030102, Unpublished.

R-45. Hoechst. 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU804030202, Unpublished.

R-46. Hoechst. 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU804030302, Unpublished.

R-47. Hoechst. 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU804030402, Unpublished.

R-48. Sochor, A. 1994. Fenpyroximate, water miscible suspension 50 g/l. Investigation of residues in processed and no processed hops following one application. Hoechst, Germany. Rep. No. ER90DEU804, Unpublished.

R-49. Sochor, A. 1994. Fenpyroximate, water miscible suspension 50 g/l. Investigation of residues in processed and no processed hops following one application. Hoechst, Germany. Rep. No. ER91DEU804, Unpublished.