

## FENARIMOL (191)

### IDENTITY

ISO common name: fenarimol

Chemical name

IUPAC: (±)-2,4'-dichloro-Æ-(pyrimidin-5-yl)benzhydryl alcohol

CA: (±)-Æ-(2-chlorophenyl)-Æ-(4-chlorophenyl)-5-pyrimidinemethanol

CAS registry no: 60168-88-9 (unstated stereochemistry)

CIPAC No: 380

Synonyms: compound 57322  
development code EL-222

Structural formula:



Molecular formula: C<sub>17</sub>H<sub>12</sub>Cl<sub>2</sub>N<sub>2</sub>O

Molecular weight: 331.2

### Physical and chemical properties

#### Pure active ingredient

Vapour pressure:	6.5 x 10 <sup>-5</sup> Pa at 25°C (99.7% pure) (A 21)	
Hydrolysis (no purity stated): (Dow Elanco Ltd., undated)	pH 3	no hydrolysis
	pH 6	no hydrolysis at 25, 37 and 52°C
	pH 9	no hydrolysis
Following 40 hours reflux at 100°C:	pH 3	30% hydrolysis
	pH 6	no hydrolysis
	pH 9	13% hydrolysis

Photolysis (no purity stated):

Sunlight or simulated sunlight

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half-life in 2 mg/l water solution in summer sun: 12 hours  
half-life in water in laboratory simulated sunlight: <1 hour  
half-life on silica gel plates in sunlight: approx 14 hours (Day, undated)

### Laboratory irradiation apparatus

half-life in distilled water: 0.6 hours  
half-life in 2% acetone/water: 2.0 hours (Mosier and Saunders, 1976)

No information was submitted for the pure active ingredient on melting point, octanol/water partition coefficient, solubility or specific gravity.

### Technical material

Purity: Typically  $\geq 97\%$  with certified limits of 95-101% to allow for assay and production variability.

Impurities <0.5%. except for the 2,2'-, 2,3'- and 4,4'-dichloro isomers of fenarimol (total max. 3%) (Day, 1985)

Colour: off-white to buff (Day, 1984)

Physical state: crystalline solid (Day, 1984)

Odour: slightly aromatic (Day, 1984)

Melting point: 117-119°C (Day, 1984)

Octanol/water partition

coefficient:  $\text{Log } K_{ow} = 3.69$  (Loh, 1976, Day, 1984)

Solubility

(mg/l at 25°C; purity was either 95.4% or unspecified)

water at pH 3	14.6
water at pH 7	13.7
water at pH 10	13.8
acetone	>250
acetonitrile	40-45
benzene	100-125
chloroform	>500
cyclohexanone	>500
ethyl cellosolve	>250
heavy aromatic naphtha	40-45
hexane	1.1
methanol	100-125
methyl cellosolve	>250
xylene	40-45 (Day, 1976, 1984)

Specific gravity:

Packed bulk density: 0.7 - 0.8 kg/m<sup>3</sup>

Loose bulk density: 0.4 kg/m<sup>3</sup> (Hudson, 1987; Day, 1984)

### **Formulations**

Fenarimol is formulated mainly as either WP, EC or SC products.

## METABOLISM AND ENVIRONMENTAL FATE

### Animal metabolism

Rats. [<sup>14</sup>C]fenarimol was extensively metabolized in wistar rats with less than 3% of the dose excreted unchanged in the urine and faeces within 7 days, and with only trace amounts being detected in the bile. More than 40 metabolites, each representing only a small fraction (<10%) of the dose, were detected in the urine and faeces. Some 10 metabolites were tentatively identified by a combination of thin-layer chromatography/autoradiography, mass spectrometry, infrared spectrometry and nuclear magnetic resonance spectrometry. Many metabolites appeared to be common to both the urine and faeces. The proposed major metabolic pathways of fenarimol are oxidation of the carbinol-carbon atom, the chlorophenol rings and the pyrimidine ring, as shown in Figure 1. A proposed minor metabolic pathway involves cyclization between a chlorophenol ring and the pyrimidine ring (Goebel, 1985a; Althaus, 1985a).

Biliary metabolites existed predominantly as glucuronic acid conjugates, with similar metabolite profiles being seen at both the dose levels tested. The main metabolite present in bile after enzymatic hydrolysis was 4-[(2-chlorophenyl)(4-chlorophenyl)hydroxymethyl]-3-pyrazolone (metabolite K, Figure 1). In contrast, most of the radioactivity in the faeces was present as unconjugated compounds indicating that biliary metabolites undergo further metabolism or hydrolysis before being eliminated (Goebel, 1985a).

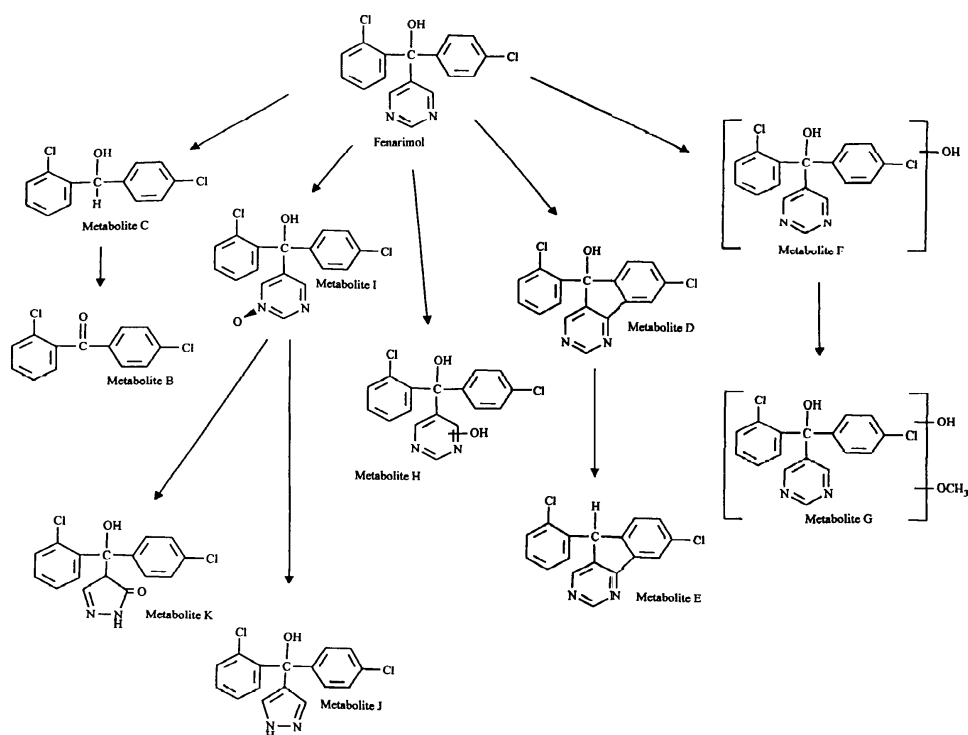
In a further study rats were dosed with a single oral dose of 1 or 13 mg/kg [<sup>14</sup>C]fenarimol. The major radiolabelled constituents identified in the blood and kidneys 1 hour after dosing were unchanged fenarimol and fenarimol *N*-oxide (metabolite I); fenarimol predominated, except in the blood of low-dose males, as shown in Tables 1 and 2. Identification was by thin-layer chromatography. Fenarimol also accounted for most of the radioactivity in the liver 1 h after dosing (Table 3). In addition 3-6% of the radioactivity in the liver was tentatively identified as 4-[(2-chlorophenyl)(4-chlorophenyl)hydroxymethyl]-3-pyrazolone (metabolite K) (Althaus, 1985b).

Table 1. Major compounds in whole blood of male and female rats.

Blood	Dose, mg/kg	% of total <sup>14</sup> C	% of <sup>14</sup> C in blood		
			Fenarimol	Fenarimol <i>N</i> -oxide	Other
Male	1	0.152	19.3	41.3	39.4
Female	1	0.126	49.5	21.8	28.7
Male	13	1.154	40.4	36.7	22.9
Female	13	1.804	72.5	10.9	16.6

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Figure 1. Proposed metabolic pathways of fenarimol in rats.



Metabolite Metabolite F: Three isomers observed. One isomer was hydroxylated in the 4-position of the 2-chlorophenyl ring and was confirmed by synthesis of the authentic model compound. The positions of the ring hydroxyl group in the other two isomers are unknown.

Metabolite G: This compound contains hydroxy and methoxy groups. Their positions are unknown.

Metabolite H: The position of the hydroxyl group on the pyrimidine ring is unknown.

Table 2. Major compounds in kidneys of male and female rats.

Kidneys	Dose, mg/kg	Fenarimol, %	Fenarimol <i>N</i> -oxide, %	Other, %
Male	1	48	19	32
Female	1	66	11	23
Male	13	64	15	21
Female	13	84	5	11

Table 3. Major compounds in liver of male and female rats.

Liver	Dose, mg/kg	Fenarimol, %	Metabolite K, %	Other, %
Male	1	67	6	27
Female	1	82	5	13
Male	13	77	6	17
Female	13	90	3	7

**Goats.** A lactating goat (breed unspecified) was dosed twice daily for 5 days with gelatine capsules containing [carbinol-<sup>14</sup>C]fenarimol at a dose equivalent to 10 ppm in the diet and killed sixteen hours

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after the final dose.

The radioactivity of tissue samples was determined by combustion/LSC. The chromatographic profiles of samples were determined by radio-TLC following preparation which generally involved an acidification and purification on a C18 column eluted with methanol. Flash chromatography was used to prepare some samples. Samples of protease-digested livers were also obtained. Further identification was carried out by HPLC with UV detection and/or GC-MS. Eighty two per cent of the total dose was excreted by the end of the study (urine 28%, faeces 53%, cage wash 0.7%, milk <0.1%). The tissues and gut contents accounted for 16% of the total dose. The maximum plasma concentration occurred 97 hours after the first dose (0.034 mg/l fenarimol equivalents) which coincided with the maximum concentration in whole blood (0.03 mg/l fenarimol equivalents) indicating that binding to red blood cells was not taking place. The maximum concentration in the milk occurred 80 hours after the first dose (0.08 mg/l fenarimol equivalents). The radioactivity in other compartments was distributed as shown in Table 4.

Table 4. Radioactivity in a goat dosed with [<sup>14</sup>C]fenarimol.

Sample	mg/kg fenarimol equivalents	% of total dose
Bile	2.97	0.1
GI tract	0.18	0.82
GI tract contents	0.94	12.2
Carcase	0.02	2.0
Fat - omental	0.03	-
Fat - renal	0.03	-
Fat - subcutaneous	0.03	-
Kidneys	0.14	0.04
Liver	0.42	0.7
Muscle	0.01	0.1

At least 90% of the total radioactivity in muscle and fat samples was extractable. The compounds shown in Table 5 were identified.

Table 5. Extraction efficiency and metabolites detected in goats (% of radioactivity present).

Compounds <sup>1</sup>	Sample						
	Liver		Kidney		Faeces, %	Urine, %	Bile, %
	% <sup>2</sup>	mg/kg <sup>3</sup>	%	mg/kg			
Compound 1 + Compound 2	34	0.14	38	0.05	36	87	93
fenarimol	-		-		9	-	3
fenarimol + 2-chlorobenzoic acid	21	0.09	11	0.02	-	-	-
2-chlorobenzoic acid + 4-chlorobenzoic acid + dehydroxyfenarimol	-		-		9	--	
4-chlorobenzoic acid + dehydroxyfenarimol	-		4		-	-	-
Unidentified	40		43		42	0	3
Numer of unidentified compounds	4		3		3	0	1
Extractable <sup>14</sup> C as % of <sup>14</sup> C in sample	69		94		61	100	85

<sup>1</sup> See Figure 2

<sup>2</sup> Of extracted <sup>14</sup>C in sample

<sup>3</sup> Fenarimol equivalents

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The presence of compounds 1 and 2 in liver, kidney and bile could not be confirmed with a second solvent system but was confirmed in faeces and urine.

Further characterization was attempted using protease-digested liver but no results were obtained owing to the low levels of radioactivity. GC-MS of the liver extract indicated the possible presence of a fenarimol methyl sulphone derivative (which may arise as a result of glutathione conjugation, thio-ether cleavage, methylation and oxidation) (McCorquodale & Prout, 1995).

Pigs. Three cross-bred pigs were dosed twice daily for 5 days by incorporation of labelled fenarimol (>99% radiochemical purity) into the feed at a level of 1 ppm (dry matter). One pig was dosed with [*carbinol*-<sup>14</sup>C], one with [*2-chlorophenyl*]<sup>14</sup>C and the third with [*4-chlorophenyl*-<sup>14</sup>C]fenarimol. The animals were killed 6-7 hours after the final feed. The radioactivity of the samples was determined by combustion and/or LSC. Results are shown in Table 6.

Table 6. Total residues in pig tissues following dosing with [<sup>14</sup>C]fenarimol (all label positions)

Sample	mg/kg fenarimol equivalents	LSC recovery from spiked samples (%)
Liver	0.19-0.24	106, 141
Kidney	0.05-0.06	114, 127
Fat	0.04-0.06	-
Muscle	0.01	105, 140

Liver samples were extracted with methanol and dichloromethane/sodium chloride solution and analysed by TLC with autoradiography following purification by column chromatography (silica gel eluted with toluene/ethyl acetate and methanol). Fat samples were extracted with "hexanes" and acetonitrile, and the <sup>14</sup>C measured by LSC. The distribution of radioactivity in various extracts was as shown in Table 7.

Table 7. Distribution of radioactivity in sample extracts.

Sample/fraction	Position of radiolabel/% of total <sup>14</sup> C in sample		
	carbinol	2-chlorophenyl	4-chlorophenyl
Liver			
unextracted	23	35	20
dichloromethane extract	65	57	68
aqueous extract	13	18	12
Fat			
acetonitrile extract	88	85	90
"hexanes" extract	12	14	10

The major compound in the dichloromethane extracts of liver and the acetonitrile extracts of fat was fenarimol, accounting for 41-43% of the total radioactivity in the liver and 90% of the total in the fat (Althaus *et al.*, 1984).

Chickens. Eight chickens (Hubbard x White Mountain Cross) were fed for 5 days with a diet containing 0.7 or 7 ppm [*carbinol*-<sup>14</sup>C]fenarimol (radiochemical purity 99.8%) and killed within one hour of removing the feed. The radioactivity of the samples was determined by combustion and LSC, with the results shown in Table 8 (Althaus *et al.*, 1982a).

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Table 8. Radioactive residues in chicken tissues following dosing with [<sup>14</sup>C]fenarimol.

Sample	Assay recovery (%)	mg/kg fenarimol equivalents	
		0.7 ppm diet	7 ppm diet
Liver	109	0.01-0.013	0.113-0.12
Kidney	126	0.005-0.006	0.06-0.07
Fat	91	0.001-0.002	0.02-0.05
Skin	90	0.001-0.002	0.02
Muscle	113	0.001	0.003-0.005

In a second study, six Leghorn hens were dosed for 7 days with a feed containing 0.6 ppm [*carbinol*-<sup>14</sup>C]fenarimol (radiochemical purity >99%) and then for a further 23 days with untreated feed. Eggs were collected daily, bulked to form a composite sample and analysed by LSC. Assay recoveries were 86.0-98.6%. The highest level of radioactivity was detected in day 7 samples (0.003 mg/kg fenarimol equivalents). By day 10 (3 days after the final treated feed) the radioactivity had decreased to 0.001 mg/kg, and was equivalent to background levels by day 17 (10 days after withdrawing treated feed) (Althaus, 1982b).

### Plant metabolism

Apples. [*Carbinol*-<sup>14</sup>C]fenarimol (radiochemical purity >99%) was formulated as an emulsifiable concentrate and diluted to give a 40 mg/l aqueous emulsion. This was applied as a spray to apple trees (Jonathan). The location of the trials was unspecified. Applications were made to run-off (2-5 litres aqueous emulsion/tree/application) at 80% full bloom (unlabelled formulation), 80% petal fall and on nine other occasions (radiolabelled formulation) at one- to two-week intervals (equivalent to 80-200g ai/ha based on a planting density of 1000 trees/ha). The total radioactivity was determined by combustion/LSC. The distribution of radioactive residues is shown in Table 9.

Table 9. Distribution of radioactive residues in apples.

Time after spraying	Whole apple	Peel		Pulp	
	mg/kg fenarimol equivalents	% of <sup>14</sup> C in whole apple	mg/kg fenarimol equivalents	% of <sup>14</sup> C in whole apple	mg/kg fenarimol equivalents
6 hours	0.207	92	0.983	9	0.023
29 days	0.108	87	0.477	13	0.019
49 days	0.074	81	0.351	19	0.017

Samples were extracted with methanol/sodium chloride solution and dichloromethane, then analysed by TLC/LSC. The distribution of radioactivity in the extracts and the fenarimol content were as shown in Table 10.

Table 10. Distribution of radioactivity and fenarimol in apple extracts (mean of 2 trees).

Sample	% of <sup>14</sup> C in sample	[ <sup>14</sup> C]fenarimol in sample
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	aqueous phase	dichloromethane extract	unextracted	% of total <sup>14</sup> C	mg/kg sample
6 hour peel	10.8	67.9	21.4	53	0.52
29 day peel	13.9	47.6	38.6	24	0.18
49 day peel	15.7	44.8	39.5	23	0.14
49 day pulp	57.7	32.5	9.9	18	0.003

The authors of the study state that radioactivity other than that from fenarimol, equivalent to 0.06 mg/kg fenarimol on a whole-apple basis in the 49-day peel samples, was "widely distributed between many compounds".

Samples of peel obtained 52 days after the final application were also taken to attempt to identify metabolites. The samples were refluxed with methanol/2N sodium hydroxide solution and then partitioned successively with dichloromethane and butanol. These extracts were analysed by LSC or purified by column chromatography (silica column eluted with methanol/water). Analysis was by TLC with detection by UV and/or autoradiography and comparison with photodegradation products. Following extraction, the radioactivity was distributed as shown in Table 11.



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Table 11. Distribution of radioactive residues in peel fractions.

Fraction	% of peel radioactivity	mg/kg fenarimol equivalents
spent peel (after refluxing)	17.2	0.24
dichloromethane extract	50.9	0.70
butanol extract	26.4	0.36
aqueous phase	5.5	0.08

Several compounds were tentatively identified by comparison with photolysis products (photoproducts A, E, D and H, Figure 2), all at  $\leq 1\%$  of total radioactivity or  $\leq 0.01$  mg/kg fenarimol equivalents. The authors concluded that photochemical degradation occurred on the surface of the apple. Other compounds (including >40 which were very polar) were observed but not identified. They had similar chromatographic characteristics to photodegradation products (Althaus and Bewley, 1978a,b).

In a further study carried out in Chile radiolabelled fenarimol was formulated as emulsifiable concentrates, diluted to give 1000 mg/l aqueous emulsions and applied directly as a mist spray to apples (Starkrimson). Radiolabelling was either at the carbinol carbon or mixed carbinol and both chlorophenyl rings (radiochemical purity 99.5-99.9%).

Individual apples were sprayed with 1 ml of the formulation or to run-off (whichever occurred first). This rate is equivalent to 268 kg ai/ha based on an average yield of 30t/ha and a medium-sized apple weighing 112g. Samples were taken 14 days after application and separated into pulp and peel.

Peel samples were extracted with aqueous methanol and dichloromethane, then refluxed with 2-butanol/water before partitioning between dichloromethane and aqueous methanol. Analysis was by TLC with autoradiography and LSC. The distribution of radioactive residues was as shown in Table 12.

Table 12. Distribution of radioactive residues in apple peel extracts.

Sample	$^{14}\text{C}$ carbinol		mixed label $^{14}\text{C}$	
	% of radioactivity	mg/kg fenarimol equivalents	% of radioactivity	mg/kg fenarimol equivalents
First dichloromethane	84	3.4	86	4.2
First aqueous	3	0.1	5	0.24
Second dichloromethane	3	0.1	3	0.15
Second aqueous	1	0.04	1	0.05
Unextractable	9	0.4	5	0.24
Total	100	4.0	100	4.9

Pulp samples were found to contain *c.* 0.06 mg/kg fenarimol equivalents in both experiments. TLC and LSC of peel samples identified *c.* 65% of the  $^{14}\text{C}$  from both labels as the parent (*c.* 3 mg/kg).

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No differences were detected between the TLC autoradiographs from the two radiolabels. No major degradation product was detected. Individual degradation products accounted for 2% of the total radioactivity, and all those identified in the peel were present as photolysis products. Small amounts of the major photolysis product *o*-chlorobenzoic acid were detected (Althaus, 1984a).

Grapes. A mixture of [*carbinol*-<sup>14</sup>C], [*4-chlorophenyl*-<sup>14</sup>C] and [*2-chlorophenyl*-<sup>14</sup>C]fenarimol was formulated as an emulsifiable concentrate and diluted to give 120 mg/l and 500 mg/l aqueous emulsions. These were applied as foliar sprays to grapes (Ribier) four times at two-week intervals (120 mg/l formulation; total dose equivalent to 0.166 kg ai/ha) or once (500 mg/l formulation; dose unspecified). Samples were collected 0, 15, 30, 45 and 60 days after the final treatment.

Samples from the multiple-treatment study were extracted with methanol and partitioned with dichloromethane. The spent grape residue was extracted with 2-butanol-water by Soxhlet. The distribution of radioactivity was as shown in Tables 13 and 14.

Tables 13 and 14. Distribution of radioactivity in grapes following multiple applications of [<sup>14</sup>C]fenarimol.

Table 13.

Days after final application	Total radioactivity as mg/kg fenarimol	% of total radioactivity			
		Dichloromethane	Aqueous	Butanol	Remainder
0	0.66	67.5	16.8	8.5	7.2
15	0.46	63.6	15.2	11.7	9.5
30	0.33	61.6	16.1	8.1	14.3
45	0.33	59.8	16.8	9.0	14.4
60	0.19	56.4	18.2	11.1	14.3

Table 14.

Days after final application	TLC of dichloromethane fraction					
	Fenarimol		"Metabolite complex"		Unidentified	
	% <sup>1</sup>	mg/kg	% <sup>1</sup>	mg/kg <sup>2</sup>	% <sup>1</sup>	mg/kg <sup>2</sup>
0	46.0	0.305	12.7	0.08	8.8	0.06
15	26.9	0.124	26.5	0.12	10.2	0.05
30	19.3	0.063	29.1	0.10	13.2	0.04
45	17.8	0.058	27.9	0.09	14.1	0.05
60	15.6	0.029	26.5	0.05	14.3	0.03

<sup>1</sup> Of total radioactivity in Table 13

<sup>2</sup> Fenarimol equivalents

Samples taken 60 days after the single application were extracted into acidic water, refluxed with neutral, basic or acidic aqueous methanol, combined with sodium chloride solution, partitioned with dichloromethane, and then further partitioned with neutral, basic or acidic dichloromethane.

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Neutral and acidic dichloromethane extracted 61 and 67% of the total radioactivity respectively. The extracts contained fenarimol and "metabolite complex" (which was not identical in different extracts). The term "metabolite complex" was applied to a group of two major, one minor and several trace components which were "extractable in the non-polar organic solvents , but which possessed polar adsorption chromatographic properties."

After extraction under strongly basic conditions the dichloromethane phase contained 74% of the total radioactivity but did not contain significant amounts of "metabolite complex".

Three compounds were identified: fenarimol (20%), dehydroxyfenarimol (DHF, 22%) and 2,4'-dichlorobenzophenone (DCBP, 8%). The structures of these compounds are shown in Figure 2 below. The "metabolite complex" was thermally degraded when subjected to GLC or MS, degraded by aqueous hydrolysis, and bound strongly during HPLC (Althaus, 1984b).

Further studies were conducted to identify the components of the "metabolite complex". Grape samples were refluxed with methanol/water, the extract was diluted with aqueous NaCl solution and extracted with dichloromethane. After drying, the residue was reconstituted in aqueous methanol and sequentially partitioned with hexane, chloroform/trichloroethane, and dichloromethane. The distribution of radioactivity was as shown in Table 15.

Table 15. Composition of grape extracts after sequential partitioning.

Solvent	% of radioactivity extracted as				
	Fenarimol	"Metabolite complex" <sup>1</sup>			Total
		Zone A	Zone B	Zone C	
Hexane	1-2	0	0	0	2
80:20 Chloroform/trichloroethane	18	3	1	1	27
50:50 Chloroform/trichloroethane	0.5	6	3	2	15
Dichloromethane	<0.5	1	5	2	9
Total	c. 20	10	9	5	53

<sup>1</sup> Zones refer to retention on TLC plate. Zone C most polar, Zone A least polar.

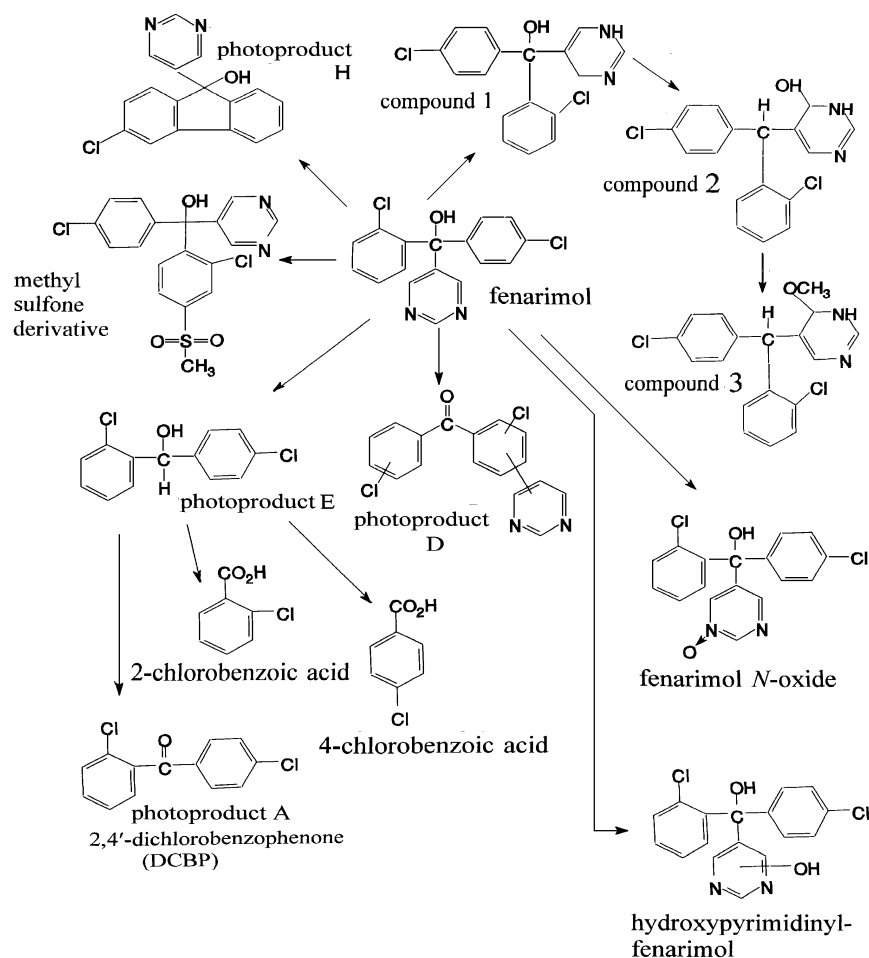
The 50:50 chloroform/trichloroethane and the dichloromethane fractions were subjected to further aqueous/methanolic sodium hydroxide hydrolysis when c. 50% of the extracted radioactivity was attributed to dehydroxyfenarimol (DHF) and 2,4'-dichlorobenzophenone (DCBP). The dehydroxyfenarimol was apparently produced during the hydrolysis.

Further analytical investigations of the "metabolite complex" in the basic extract were carried out using radio-HPLC, NMR and MS.

Compound 3 (Figure 2) was tentatively identified by MS but could not be confirmed by NMR, owing to the small quantity obtained. Compound 1 was tentatively identified by MS. Positions of reduction of the pyrimidine ring were investigated using NMR. Compound 2 was tentatively identified by MS but there was too little for confirmation by NMR. Three isomeric structures could exist (where -H and -OH have been added to the pyrimidine ring). The hypothesis that compound 1 could be converted to compound 2 under acidic conditions and subsequently to compound 3 by methanolysis under acidic conditions was proposed.

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Figure 2. Proposed pathways of metabolism in livestock and plants, and of potodegradation.



In further work to characterize other metabolites in grapes, it was concluded that the unidentified radioactivity was associated with many minor components (34 "zones" were isolated). No individual component accounted for more than 2.9% of the total radioactivity (0.04 mg/kg fenarimol equivalents) (Goebel, 1985b; Rainey, 1987).

**Cucumbers.** [*Carbinol*- $^{14}\text{C}$ ]fenarimol was formulated as an emulsifiable concentrate and diluted to give a 26.5 mg/l aqueous emulsion. It was applied as a spray to field-grown cucumbers (Green Prolific) in the USA. One application was made to run-off at a rate equivalent to 24.7g [ $^{14}\text{C}$ ]fenarimol in 934 litres water/ha. Samples were taken four days after treatment and analysed by combustion and/or LSC. The characterization of metabolites was carried out by radio-TLC.

After extraction by refluxing with methanol and further extraction with dichloromethane the total radioactivity in the crop ranged from 0.003 to 0.042 mg/kg fenarimol equivalents. Approximately 93% of this (0.04 mg/kg fenarimol equivalents) was extracted into dichloromethane and 85% of the extracted radioactivity (0.03 mg/kg fenarimol equivalents) was attributed to fenarimol and 8% (0.003

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mg/kg fenarimol equivalents) remained at the origin. Three other chromatographic bands were separated, each accounting for 3% of the radioactivity (0.001 mg/kg fenarimol equivalents) (Althaus, 1986).

### **Environmental fate in soil and water/sediment systems**

No data were submitted.

### **METHODS OF RESIDUE ANALYSIS**

#### **Analytical methods**

Methods for the analysis of a wide range of samples were supplied. In all of these the final determination is by GLC of a toluene solution, with EC detection. Validation data are shown in Table 16.

Crops and soil. Samples were extracted with ethanol/acetone, partitioned into chloroform, dissolved in toluene and analysed by GLC with an ECD. No validation data were submitted (Dow Elanco Ltd., 1976).

Crops other than cereals. Samples were extracted with methanol, partitioned into dichloromethane and transferred to toluene for analysis. No validation data were submitted (Dow Elanco Ltd., 1977).

Fresh fruit and vegetables, pomace, raisins, juice, bananas and "other crops". Samples were extracted with methanol, methanol/water or dichloromethane, then purified by chromatography on an alumina column which was eluted with 1-chlorobutane/methanol. The extract was evaporated and the residue dissolved in toluene for analysis. The authors state that the procedure "usually gives recoveries in excess of 90%" and has a limit of detection of 0.02 mg/kg except in dry pomace and "other crops" where the limit of detection is 0.01 mg/kg. No other validation data were submitted (Griggs and Decker, 1981).

Animal feeding-stuffs (hay and straw). Samples were extracted with methanol/water then purified by chromatography on an alumina column, which was eluted with 1-chlorobutane/methanol, before transfer to toluene (Griggs and Decker, 1985).

Beer. Samples were combined with sodium hydrogen carbonate solution, and partitioned into toluene for analysis (Butcher, 1992).

Spent yeast. Samples were extracted with methanol and, after dilution with water, partitioned with toluene. The extract was concentrated to dryness and the residue dissolved in 30:70 acetonitrile/water, then cleaned up on a C18 column eluted with 50:50 acetonitrile/water, acidified and partitioned into toluene (Butcher, 1992).

Fresh, dried and spent hops. Samples were extracted with methanol and sodium hydrogen carbonate solution and partitioned into methyl isobutyl ether. The extract was treated with alkaline permanganate, partitioned into toluene, dissolved in 1-chlorobutane, and cleaned up on an alumina column eluted with methanol/1-chlorobutane and on a C18 column eluted with acetonitrile/water. After acidification, the extract was partitioned into toluene for analysis (Butcher and Perkins, 1992).

Grape must, wine, grapes, tomatoes, peaches and melons. Samples were extracted with methanol and sodium hydrogen carbonate solution, partitioned into toluene, transferred to dichloromethane and

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cleaned up on a C18 column eluted with methanol/dichloromethane or on a silica extraction column eluted with methanol/dichloromethane. The solvent was evaporated and the residue dissolved in toluene for analysis by capillary GLC (Butcher and Long, 1993; Butcher, 1994a).

Soil. Samples were extracted with methanol/water and cleaned up by column chromatography on alumina. Elution was with 1-chlorobutane/methanol. The authors state that the procedure "usually gives recoveries in excess of 90%" and has a limit of detection of 0.02 mg/kg. No other validation data were submitted (Griggs and Decker, 1981,1985).

Banana and banana pulp. Samples were ground with liquid nitrogen, then refluxed in methanol/HCl. NaOH was added to the hot solution which was then allowed to cool. The extract was partitioned with hexane and the hexane fraction washed through sodium sulphate, then evaporated to dryness. The residue was redissolved in toluene and analysed on a 2% OV 17 column. The compounds I and II (Figure 2) are also be determined by this method as dehydroxyfenarimol (Turner, 1992).

In a development of this method the methanol from the reflux solution was evaporated after the addition of NaOH. The remaining aqueous solution was extracted with dichloromethane, which was evaporated and the residue reconstituted in aqueous sodium chloride solution and partitioned with diethyl ether. The ether was evaporated and toluene added. The toluene extract was cleaned up on a silica solid-phase extraction column with elution with 10% ethyl acetate in dichloromethane. After evaporation the reconstituted toluene extract was analysed as above (Catta-Preta and Matos, 1993).

Wildlife. Meat and egg samples were extracted with methanol/acetonitrile or methanol and methylene chloride. Fat was extracted with hexane/1-chlorobutane and milk with acetonitrile, which was washed with hexane and partitioned with methylene chloride. Extracts were cleaned up on a Florisil column, eluted with methylene chloride/methanol, and dissolved in toluene (Yordy and Turner, 1982).

Table 16. Validation of analytical methods (treated plants, plant products, foodstuffs and feeding-stuffs).

Substrate	Spike, mg/kg % recovery	Precision-repeatability	Limit of determination, mg/kg	Reference
Whole apple fruit	0.001-0.02 73-98	no data	0.002-0.003	OR 1B
Dried apple pomace	0.005-0.1 65-103	no data	0.01	OR 1B
Whole fresh grapes	0.001-0.02 100-110	SD + 1-10	0.002-0.003	OR 1B
Wine	0.001-0.02 101-123	SD $\pm$ 2-14	0.002-0.003	OR 1B
Wine	0.01-0.1 99-107	RSD 2.5%	0.01	OR 22
Beer	0.01-0.1 90-108	RSD 4.0%	0.01	OR 21
Spent yeast	0.01-0.1 77-105	RSD 9.7%	0.01	OR 21
Dried hops	0.1-5 78-108	RSD 10.1%	0.1	OR 20
Fresh hops	0.1-2 75-94	RSD 7.4%	0.05	OR 20
Spent hops	0.02-0.5 75-102	RSD 8.3%	0.02	OR 20

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Substrate	Spike, mg/kg % recovery	Precision-repeatability	Limit of determination, mg/kg	Reference
Tomatoes	0.01-0.1 86-101	RSD 5.1%	0.01	OR 24
Peach flesh	0.01-0.1 82-117	RSD 9.3%	0.01	OR 24
Melon peel	0.01-0.1 93-109	RSD 5.0%	0.01	OR 24
Melon pulp	0.01-0.1 81-112	RSD 10.2%	0.01	OR 24
Meat	0.01 101	SD $\pm$ 16.5	0.01	OR 19
Liver	0.01 108	SD $\pm$ 11.5	0.01	OR 19
Kidney	0.01 105	SD $\pm$ 13.7	0.01	OR 19
Fat/skin	0.01 87	SD $\pm$ 9.1	0.01	OR 19
Milk	0.001 95	SD $\pm$ 16.4	0.01	OR 19
Eggs	0.01 98	SD $\pm$ 9.0	0.01	OR 19
Banana	0.005-1.0 84-114	no data	0.01	OR 27
Banana pulp	0.005-1.0 82-105	no data	0.01	OR 27
Banana	0.005-1.1 55-114	no data	0.01	OR 28
Banana pulp	0.01-0.53 54-110	no data	0.01	OR 28

**Stability of pesticide residues in stored analytical samples**

Samples of grapes and wine were fortified with 0.1 mg/kg or mg/l fenarimol and stored deep frozen at -10°C to -27°C up to 370 days. Residues following storage and corrected for procedural recoveries were as shown in Table 17 (Butcher, 1994b).

Table 17. Residues in grapes and wine following storage at -20°C.

Storage period (days)	Residues, mg/kg			
	Black grapes	White grapes	Red wine	White wine
0	0.10-0.11	0.10-0.11	0.09-0.10	0.10
86	0.10-0.11	0.10-0.11	0.10-0.11	0.10
370	0.09-0.10	0.09-0.10	0.09-0.10	0.08-0.11

Ground fresh grapes and grape pomace were fortified with fenarimol at 0.05 mg/kg, and ground raisins and raisin waste at 0.2 mg/kg. Following 14 days refrigeration at 4°C, the samples were stored frozen for an additional 50-119 days. Samples were analysed after 0, 1, and 14 days and at the end of the study. Residues following storage and corrected for procedural recoveries were as shown in Table

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18 (Day and Saunders, 1988a).

Table 18. Residues in fresh grapes, wet pomace, raisins and raisin waste following refrigeration and freezer storage.

Storage period, days	Residues, mg/kg			
	Fresh grapes	Wet pomace	Raisins	Raisin waste
0	0.054	0.054	0.20	0.19
1	0.052	0.055	0.18	0.23
14	-	0.049	0.18	0.17
18/19	-	-	0.19	0.21
23	0.050	-	-	-
74/76	-	-	0.19	0.18
131/133	0.052	0.054	-	-



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In a further study, samples of cherries were fortified with 0.1 or 1.0 mg/kg fenarimol and stored for 11 days in a chill room at 4°C, then for 93 days in the freezer at -20°C. Samples were analysed using the method of Griggs and Decker (1981). Recoveries were variable but acceptable. The results, corrected for procedural recoveries, were as shown in Table 19 (Day and Saunders, 1988b).

Table 19. Residues in cherries following storage at -20°C.

Fortification level, mg/kg	Residue, mg/kg			
	Sweet cherry		Sour cherry	
	0.1	1.0	0.1	1.0
Storage period (days)				
0	0.11, 0.11	1.1, 1.1	0.11, 0.11	1.1, 1.1
4	0.09, 0.11	1.1, 1.1	0.10, 0.11	1.1
7	0.12, 0.13	1.1, 1.10	0.13, 0.11	1.1, 1.2
11	0.12, 0.13	1.2, 1.3	0.15, 0.13	1.3, 1.3
30	0.10, 0.10	0.9, 1.0	0.11, 0.10	1.0, 1.0
68	0.10, 0.10	0.9	0.11, 0.10	0.93, 0.91
104	0.11, 0.11	1.1, 1.0	0.10, 0.10	1.2, 1.1

A new study on the stability of fenarimol in fortified peaches, tomatoes and melons under frozen storage conditions was made available, but too late for review (Butcher, 1995g).

### Residue definition

The animal and plant metabolism studies indicate that fenarimol is the major residue in products of both animal and plant origin. The residue is therefore defined as fenarimol.

### USE PATTERN

Fenarimol is a systemic fungicide which has protective, curative and eradicated activity. Most commonly it is applied as a foliar treatment where apoplastic movement occurs through the leaf and towards the leaf tip, but movement from treated to untreated leaves is not sufficient to provide disease control. Application via the roots and seeds leads to translocation to all the aerial parts of the plant.

Fenarimol is registered in a large number of countries. Its uses cover a wide range of fruit and vegetables, hops and wheat. Full details of registered use patterns are given in Tables 20-22. The registered uses are for treatments in the field unless otherwise indicated.

Table 20. Registered uses of fenarimol on fruits and pecans.

Commodity	Country	Form	Application			PHI, days	Ref.	
			Method	Rate kg ai/ha	Spray conc, kg ai/hl			No.
Apples	Australia	EC	airblast	0.043- 0.054	0.0029- 0.0036	1-10	14	1 & 2
	Argentina	EC	mist blower broadcast	0.048- 0.09	0.0024- 0.003	2	20	1

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Commodity	Country	Form	Application				PHI, days	Ref.
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
	Belgium	WP	LV overall	0.03-0.06	-----	3-4	1 month	1
	Brazil	EC	mist blower broadcast	0.038- 0.14	0.0048- 0.0072	2	28	1
	Chile	EC	Gun broadcast med vol	0.038- 0.096	0.0036- 0.0042	2	(a)	1
	Denmark	EC	HV overall	0.060	0.006-0.004	5	14	1 & 11
	Germany (Rubigan EC)	EC	L/HV row	0.0108- 0.054	0.0036	max 7	21	1 & 8
	Germany (Elital)	SC	L/HV overall	0.0108- 0.054	0.0036	max 14	21	1 & 8
	Germany (Rubigan SC)	SC	L/HV row	0.0108- 0.054	0.0036	max 14	21	1 & 8
	Greece	WP	HV overall	0.105	0.0042	3-5	20	1
	Ireland	SC	LV overall	0.04-0.08	-----	up to 14 usually 4-6	14	1
	Italy	EC	HV overall	0.054- 0.072	0.0036- 0.0048	Through-out season	21	1
	Italy	SC	HV overall	0.054- 0.072	0.0036- 0.0048	Through-out season	21	1
	Italy	WP	HV overall	0.054- 0.072	0.0036- 0.0048	Through-out season	21	1
	Japan	WP	airblast	0.09- ~0.14	0.003- ~0.004	1-3	21	1
	Mexico	EC	mist blower	0.054- 0.108	0.0027- 0.0036	2	(b)	1
	Netherlands <sup>1</sup> (country submission)	WP	spraying of the aerial part	0.039- 0.076	0.0039- 0.076	3	21	6
	Netherlands (company submission)	WP	HV overall	0.039- 0.076	0.0026- 0.076	max 10	3 weeks	1
	New Zealand	SC	HV to run-off	0.0067- 0.090	0.003	6	35	5
	Peru <sup>1</sup> (country submission)	-	foliar application	-	0.05	3	30	7
	Peru (company submission)	EC	gun broadcast	0.012- 0.060	0.0015- 0.004	2	(a)	1
	Portugal	EC	HV overall	0.024- 0.054	0.0024- 0.0036	5	21	1
	Spain	EC	low volume spray (500- 1,500 l/ha)	-	0.0042- 0.0048	7-10 days intervals	14	4
	Spain	EC	high volume spray (>1,500 l/ha)	0.060- 0.096	-	7-10 days intervals	14	4
	Spain	SC	HV overall	0.063- 0.072	0.0042- 0.0048	1	14	1
	UK	SC	LV overall	0.04- 0.08	-----	up to 14 usually 4-6	14	1
	Uruguay	EC	broadcast mist blower	0.075- 0.090	0.0024- 0.003	2	20	1
	USA	SC	spray	0.049- 0.098	-	7-14***	30	4
	USA	EC	spray	0.067- 0.101	-	7-10***	30	4

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Commodity	Country	Form	Application				PHI, days	Ref.
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
Bananas	Honduras <sup>1</sup>	EC	Aerial	0.08-0.12	0.0053-0.006	7	0 (c)	1
	Nicaragua <sup>1</sup>	EC	Aerial	0.08-0.12	0.533-0.6	7	0 (c)	1
Currants								
, black	Denmark	EC	HV overall	0.06	-----	3	14	1
, black	Ireland	SC	LV overall	0.04	-----	NR	14	1
	Netherlands <sup>1</sup> (country submission)	EC	spray	0.048-0.058	0.0048	4	21	6
	Netherlands (company submission)	EC	HV overall	0.048-0.058	0.0048	5	3 weeks	1
, black	UK	SC	LV overall	0.04	-----	NR	14	1
Cherry	Denmark	EC	HV overall	0.060	-----	5	14	1
	Japan	WP	airblast	0.16 ~0.2	0.004	1-3	3	1
	USA	EC	spray	0.051-0.101	-	4-8***	up to & after harvest	4
Gooseberries	Ireland	SC	HV overall	0.04	-----	NR	14	1
	Netherlands	EC	spray	0.048-0.058	0.0048	4	21	1
	UK	SC	HV overall	0.04	-----	NR	14	1
Grapes	Argentina	EC	gun individual plant	0.0192-0.036	0.0024	2	30	1
	Australia	EC	airblast	0.012-0.024	0.0012-0.0024	1-7	14	1
	Brazil	EC	gun individual plant	0.0108-0.024	0.0018-0.0024	4	15	1
, table	Chile	EC	gun individual plant	0.005-0.012	0.002-0.003	3	(d)	1
	France	SC	LV overall	0.018	0.0009-0.003	1 to 4	7	1
, wine	Germany <sup>1</sup> (Elital) (country submission)	SC	spray	0.0047-0.0125	0.00078	6	35	8
	Germany (Elital) (company submission)	SC	L/HV overall	0.0047-0.0234	0.00156	max 6*	35	1
	Germany (Rubigan SC)	SC	L/HV row	0.0047-0.0234	0.00156	max 6	35	1
	Greece	WP	HV overall	0.012-0.024	0.0012-0.0024	2-4	30	1
	Ireland	SC	LV overall	0.04	-----	NR	14	1
,table	Italy	WP	HV overall	0.03-0.06			14	1
,table	Italy	SC	HV overall	0.018-0.036	0.0018-0.0036	-----	14	1
, wine	Italy	SC	HV overall	0.014-0.054	0.0018-0.0036	-----	14	1
, wine	Italy	WP	HV overall	0.014-0.036	0.0018-0.0036		14	1
	Mexico	EC	mist blower	0.030-0.054	0.0075-0.0054	4	(e)	1
	New Zealand	SC	HV spray to run-off	0.024-0.048	0.0024	4	30	5
	Peru <sup>1</sup> (country	-	foliar	-	0.02	4	30	7

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Commodity	Country	Form	Application				PHI, days	Ref.
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
	submission)		application					
	Peru (company submission)	EC	gun broadcast	0.012-0.060	0.0012-0.005	3	(d)	1
	Portugal	EC	HV overall	0.011-0.03	0.0018-0.0030	3	7	1
	Spain	EC	MV-HV overall	0.0099-0.05	0.0033-0.0036	1 (wine) 3(table)	28 (wine) 14 (table)	1
	Spain	SC	MV-HV overall	0.009-0.05	0.003-0.0036	1 (wine) 3(table)	28 (wine) 14 (table)	1
	UK	SC	spray	0.04	-----	NR	14	1 & 4
	Uruguay	EC	gun application individual plant	0.019-0.036	0.0024	2	30	1
	USA	EC	spray	0.017-0.051	-	3-9***	30	4
	USA	SC	spray	0.024-0.049	-	2-7***	30	4
Peaches	Argentina	EC	mist blower	0.048-0.072	0.0024	2	20	1
	Greece	WP	HV overall	0.12	0.0048	2-4	20	1
	Italy	EC	HV overall	0.072	0.0042-0.0048	2-3	14	1 & 12
	Italy	SC	HV overall	0.072	0.0042-0.0048	2-3	14	1 & 12
	Japan	WP	airblast	0.12--0.2	0.004	1-3	1	1
	Spain	EC	HV overall	-	0.0042-0.0048	1	7	4
	Spain	SC	HV overall	-	0.0042-0.0048	1	7	4
	Uruguay	EC	broadcast mist blower	0.048-0.072	0.0024	2	20	1
Pears	Argentina	EC	mist blower broadcast	0.048-0.09	0.0024-0.003	2	20	1
	Australia	EC	airblast	0.043-0.054	0.029-0.0036	1-10	14	1 & 2
, Japanese	Australia	EC	airblast	0.036-0.054	0.0024-0.0036	1-10	14	1 & 2
	Belgium	WP	LV overall	0.03-0.06	-----	3-4	1 month	1
	Chile	EC	Gun broadcast med. vol	0.038-0.096	0.0036-0.0042	2	(a)	1
	Denmark	EC	HV overall	0.060	-----	5	14	1
	Germany (Elital)	SC	L/HV overall	0.0108-0.054	0.0036	max 14	21	1 & 8
	Italy	EC	HV overall	-----	0.0036-0.0048	**	14	1
	Italy	SC	HV overall	-----	0.0036-0.0048	**	14	1
	Italy	WP	HV overall	0.054-0.072	0.0036-0.0048	**	14	1

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Commodity	Country	Form	Application				PHI, days	Ref.
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
	Japan	WP	airblast	0.09- ~0.12	0.003- ~0.004	1-3	21	1
	Mexico	EC	mist blower	0.054- 0.108	0.0027- 0.0036	2	(b)	1
	Netherlands <sup>1</sup> (country submission)	WP	spraying of the aerial part	0.039- 0.076	0.0039- 0.076	3	21	6
	Netherlands (company submission)	WP	HV overall	0.039- 0.076	0.0026- 0.0076	max 10	3 weeks	1
	New Zealand	SC	HV to run-off	0.0067- 0.090	0.003	6	35	5
	Portugal	EC	HV overall	0.024- 0.054	0.0024- 0.0036	5	21	1
	Spain	EC	HV overall	0.063- 0.072	0.0042- 0.0048	1	14	1
	Spain	SC	HV overall	0.063- 0.072	0.0042- 0.0048	1	14	1
	Uruguay	EC	broadcast mist blower	0.075- 0.090	0.0024- 0.003	2	20	1
	USA	SC	spray	0.049- 0.098	-	7-14***	30	4
	USA	EC	spray	0.067- 0.101	-	7-10***	30	4
Pecans	Mexico	EC	mist blower	0.054- 0.108	0.0028- 0.0057	2	(f)	1
	USA	SC	applied to run-off	0.073- 0.098	-	7-9***	30	4
Persimmon, Japanese	Japan	WP	airblast	0.2	0.004	1-3	21	1
Raspberry	UK	SC	LV overall	0.04	-----	3	14	1
	Ireland	SC	LV overall	0.04	-----	3	14	1
Strawberry	Denmark	EC	HV overall	0.084	-----	3	14	1
	Ireland	SC	LV overall	0.04	-----	NR	14	1
	Italy	EC	HV overall	-----	0.0042- 0.0048	3	7	1
	Italy	SC	HV overall	-----	0.0042- 0.0048	3	7	1
	Italy	WP	HV overall	0.034- 0.038	0.0042- 0.0048	3	7	1
	Japan	WP	mist spray <sup>2</sup>	0.03	0.003	1-3	1	1 & 10
	Netherlands <sup>1</sup> (country submission)	EC	spray <sup>2</sup>	0.036- 0.084 (depend. on variety)	0.006- 0.0084	4	treatment before flowering or after harvest	6
	Netherlands (company submission)	EC	HV overall	0.03- 0.05	0.005- 0.01	5	treatment before flowering or after harvest	1
	Spain	EC	HV overall		0.0042- 0.0048	4	3	1
	Spain	SC	HV overall		0.0036- 0.0048	4	3	1

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Commodity	Country	Form	Application				PHI, days	Ref.
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
	UK	SC	LV overall	0.04	-----	NR	14	1

<sup>1</sup> No product label submitted

<sup>2</sup> Glasshouse and Field use

NR No restriction restriction, typically 2-4

\* max 4 between flowering and benning of ripening

\*\* Application throughout season

\*\*\* the maximum number of treatments is controlled by a maximum total dose

Notes (a) to (f) refer to growth stage at last treatment:

(a) immature fruit (b) early fruit

(c) from disease onset (d) mature fruit

(e) fruit initiation (f) pre-flowering

Table 21. Registered uses of fenarimol on vegetables.

Crop	Country	Form	Application				PHI, days	Reference
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
Artichokes	Italy	EC	HV overall	-----	0.0048	3	7	1
	Italy	SC	HV overall	-----	0.0048	3	7	1
	Italy	WP	HV overall	0.038	0.0048	3	7	1
Aubergines	Italy	EC	HV overall	-----	0.0048	3	7	1
	Italy	SC	HV overall	-----	0.0048	3	7	1
	Italy	WP	HV overall	0.038	0.0048	3	7	1
Courgettes	Japan	WP	mist spray	0.024 ~0.04	0.0012 ~0.002	1-3	1	1
	Netherlands <sup>1</sup> (country submission)	EC	spray <sup>2</sup>	0.012- 0.036	0.0024	6	3	6
	Netherlands <sup>1</sup> (country submission)	EC	spray (field only)	0.0096- 0.024	0.0024	6	3	6
Cucumbers	Brazil	EC	knapsack individ. plant	0.038- 0.072	0.0048- 0.0072	4	4	1
	Denmark	EC	HV overall <sup>3</sup>	0.024- 0.036	0.0024	4-8	2	1
	Ireland	SC	LV overall	-----	0.001- 0.002	NR	2	1
	Japan	WP	mist spray	0.024	0.0012	1-3	1	1
	Netherlands	EC	spray <sup>2</sup>	0.012- 0.036	0.0024	6	3	1
	UK	SC	LV overall <sup>3</sup>	-----	0.001- 0.002	NR	2	1
	Uruguay	EC	knapsack individ. plant	0.014- 0.024	0.0012- 0.0024	4	4	1
Cucurbits	Australia	EC	Boom	0.024	0.004	1-10	3	1
	Greece	WP	HV overall	0.018- 0.024	0.0018- 0.0024	as requir ed	1	1
	Italy	EC	HV overall	-----	0.0024- 0.003	3	7	1
	Italy	SC	HV overall	-----	0.0024- 0.003	3	7	1
	Italy	WP	HV overall	0.020-	0.0024-	3	7	1

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Crop	Country	Form	Application				PHI, days	Refer- ence
			Method	Rate kg ai/ha	Spray conc., kg ai/hl	No.		
				0.024	0.003			
	Spain	EC	HV overall	0.01- 0.019	0.0036- 0.0048	2	7	1
	Spain	SC	HV overall	0.013- 0.019	0.0042- 0.0048	2	7	1
Egg plants, see Aubergines								
Gherkins	Netherlands <sup>1</sup> (country submission)	EC	spray <sup>2</sup>	0.012- 0.036	0.0024	6	3	6
	Netherlands <sup>1</sup> (country submission)	EC	spray (field only)	0.0096- 0.024	0.0024	6	3	6
Melons	Japan	WP	mist spray	0.024	0.0012	1-4	1	1
	Netherlands	EC	spray <sup>2</sup>	0.012- 0.036	0.0024	6	3	1
	Portugal	EC	HV overall	0.024- 0.036	0.0024- 0.0036	5	3	1
Musk-melons	Brazil	EC	knapsack individ. plant	0.014- 0.024	0.0018- 0.0024	4	4	1
Peas	Italy	EC	HV overall	-----	0.0024- 0.003	3	7	1
	Italy	SC	HV overall	-----	0.0024- 0.003	3	7	1
	Italy	WP	HV overall	0.02- 0.024	0.0024- 0.003	3	7	1
Peas, Immature	Japan	WP	mist spray	0.024	0.0012	1-5	1	1
Peppers	Italy	EC	HV overall	-----	0.0048	3	7	1
	Italy	SC	HV overall	-----	0.0048	3	7	1
	Italy	WP	HV overall	0.038	0.0048	3	7	1
	Netherlands <sup>1</sup> (country submission)	EC	spray <sup>2</sup>	0.012- 0.036	0.0024	6	3	6
	Japan	WP	mist spray	0.024	0.0012	1-4	1	1
	Spain	EC	HV overall	0.048- 0.072	0.0048- 0.006	3	7	1
	Spain	SC	HV overall	0.048- 0.072	0.0048- 0.006	3	7	1
	UK	SC	overall spray <sup>2</sup>	0.054	0.002	3	7	9
Pumpkins	Brazil	EC	knapsack individ. plant	0.014- 0.024	0.0018- 0.0024	4	4	1
	Japan	WP	mist spray	0.012	0.0012	1-4	3	1
	Peru	EC	gun individ. plant	0.012- 0.060	0.0015- 0.004	4	4	1
Squash, small	Argentina	EC	gun individ. plant	0.0096- 0.024	0.0012- 0.0024	4	4	1
Squash	Uruguay	EC	knapsack individ. plant	0.014- 0.024	0.0012- 0.0024	4	4	1
Squash, summer	Netherlands	EC	spray <sup>2</sup>	0.012- 0.036	0.0024	6	3	1
Tomatoes	Denmark	EC	HV overall <sup>3</sup>	0.024- 0.036	0.0024	4-8	2	1
	Italy	EC	HV overall	-----	0.0048	3	7	1
	Italy	SC	HV overall	-----	0.0048	3	7	1

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Crop	Country	Form	Application				PHI, days	Reference
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
	Italy	WP	HV overall	0.038	0.0048	3	7	1
	Japan	WP	mist spray	0.04	0.002	1-3	1	1
	Netherlands <sup>1</sup> (country submission)	EC	spray <sup>2</sup>	0.024-0.072	0.0048	3	3	6
	Netherlands (company submission)	EC	HV overall	0.024-0.072	0.0048	5	3	1
	Spain	EC	HV overall	0.028-0.057	0.0048	3	7	1
	Spain	SC	HV overall	0.028-0.057	0.0048	3	7	1
	UK	SC	overall spray <sup>2</sup>	0.054	0.002	3	7	9
Watermelons	Brazil	EC	knapsack individ. plant	0.014-0.024	0.0018-0.0024	4	4	1
	Japan	WP	mist spray	0.012	0.0012	1-4	3	1
	Uruguay	EC	knapsack individ. plant	0.0096-0.0024	0.0012-0.0024	4	4	1
Vegetables	Netherlands	EC	HV overall	0.012-0.036	0.0024	5	3	1

<sup>1</sup> No product label submitted

<sup>2</sup> Glasshouse use only

<sup>3</sup> Glasshouse and field use

Table 22. Registered uses of fenarimol on hops and cereals.

Crop	Country	Form	Application				PHI, days	Ref.
			Method	Rate, kg ai/ha	Spray conc., kg ai/hl	No.		
Hops	Germany	WP	HV row	0.06	0.0015	max 4	10	1 & 8
	Spain	EC	HV overall		0.0042-0.0048		-----	1
	Spain	SC	HV overall		0.0042-0.0048		-----	1
Wheat	Japan	WP	Boom	0.04-0.06	0.004	1-2	14	1

Uses of fenarimol were also reported in Algeria, Austria, "Belarus", Bulgaria, China, "CR/SR", Croatia, Egypt, Hungary, India, Indonesia, Iraq, Korea, Lebanon, Libya, Macedonia, Morocco, Pakistan, Poland, Romania, Russia, Slovenia, Slovakia, Switzerland, Syria, Taiwan and Tunisia, but insufficient information was submitted for inclusion in the Tables.

## RESIDUES RESULTING FROM SUPERVISED TRIALS

The residue trials are summarized in the following Tables. Trials were carried out under field conditions unless stated otherwise. Unless indicated in the notes, trials were reported in sufficient detail and acceptable analytical information was supplied. Analytical recoveries outside the range 70-120% and/or storage of samples for longer than 6 months are also indicated in the notes. Analytical results have been rounded to one significant figure if <0.1 mg/kg except where processing information is given.

Apples. Information on GAP was reported for many countries world-wide. The maximum



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application rates are 0.054-0.14 kg ai/ha with PHIs of 14-35 days.

Residue trials data were available from Belgium, Germany, the UK, Canada, the USA, Chile, Brazil, New Zealand and The Netherlands. Residues in 16 Northern European trials according to German GAP (0.0036 kg ai/hl, 21-day PHI) were 0.02-0.21 mg/kg. Three further trials which reflected German GAP showed residues of 0.06, 0.1 and 0.1 mg/kg but only a summary was submitted. Eight Northern European trials complied with GAP in Denmark, the UK and Ireland in which there is a shorter PHI of 14 days (maximum rates 0.06-0.08 kg ai/ha, concentration not specified) with residue levels of 0.02-0.18 mg/kg. A further 6 Dutch trials were within GAP in The Netherlands (0.0039-0.076kg ai/hl, 21-day PHI) with residues of 0.01-0.34 mg/kg in samples taken 21 days after the final treatment. However, these Dutch trials were submitted in summary form only. In 5 replicated US trials according to GAP (ca 0.1 kg ai/ha, 30-day PHI) residue levels were 0.002-0.3 mg/kg. In three New Zealand trials according to GAP (maximum 0.09 kg ai/ha, 0.003 kg ai/hl, 35-day PHI) residues were 0.008-0.03 mg/kg.

Table 23. European supervised residue trials on apples.

Location, year	Application				PHI, days	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl			
Ramecroix, Belgium, 1976 <sup>1</sup>	EC	11	0.034	0.004	0	0.12	NF 13 B76-001
					7	0.07	
					14	0.05	
					21	<u>0.06</u>	
					28	0.04	
					85	0.01	
Giessen, Germany, 1977 <sup>1</sup>	EC	10	0.036	0.003	55	<0.01	NF 15 D76-302
			0.048	0.004	55	<0.01	
Giessen, Germany, 1978 <sup>2,3,5</sup>	EC	14	0.054	0.0036	0	0.13	NF 08 D78-311
					3	0.12	
					7	0.10	
					10	0.11	
					14	<u>0.07</u>	
					21	0.06	
					28	0.08	
36	0.07						
Giessen, Germany, 1981 <sup>3,5</sup>	SC	14	0.054	0.0036	0	0.16	NF 20 D81-302
					4	0.06	
					13	<u>0.05</u>	
					20	<u>0.07</u>	
					27	0.04	
					33	0.06	
Uberlingen, Germany, 1981 <sup>3,4,5</sup>	SC	14	0.054	0.0036	0	0.29	NF 20 D81-353
					4	0.34	
					7	0.02	
					14	<u>0.02</u>	
					21	<u>0.02</u>	
Wulfsdorf, Germany, 1981 <sup>3,5</sup>	SC	13	0.054	0.0036	0	0.36	NF 20 D81-350
					7	0.23	
					14	<u>0.18</u>	
					22	<u>0.06</u>	

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Location, year	Application				PHI, days	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl			
					28	0.05	
					35	0.05	
Wittlich, Germany, 1981 <sup>3,4,5</sup>	SC	10	0.06	0.00396	0	0.37	NF 20 D81-351
					7	0.19	
					14	<u>0.15</u>	
					21	<u>0.15</u>	
					28	0.09	
					63	0.01	
Kriftel, Germany, 1982 <sup>3,5</sup>	EC	13	0.036	0.0036	0	0.06	NF 21 D82-304
					8	0.05	
					14	0.04	
					17	<u>0.04</u>	
	SC	13	0.036	0.0036	0	0.1	
					8	0.09	
					14	0.07	
					17	<u>0.04</u>	
Kriftel, Germany, 1982 <sup>3,5,6</sup>	EC	13	0.036	0.0036	0	0.09	NF 21 D82-305
					8	0.08	
					14	0.06	
					21	<u>0.05</u>	
					30	0.03	
	SC	13	0.036	0.0036	0	0.21	
					8	0.17	
					14	0.04	
					21	<u>0.11</u>	
					30	0.05	
Marbach, Germany, 1982 <sup>3,5</sup>	EC	14	0.036	0.0036	0	0.37	NF 21
					7	0.24	
					13	0.22	
					20	<u>0.21</u>	
					27	0.14	
Marbach, Germany, 1982 <sup>3,5</sup>	EC	14	0.036	0.0036	0	0.18	NF 21 D82-307
					7	0.11	
					13	0.15	
					20	<u>0.14</u>	
					27	0.09	
Giessen, Germany, 1982 <sup>3,5,6</sup>	EC	14	0.036	0.0036	0	0.17	NF 21 D82-301
					5	0.08	
					13	0.05	
					19	<u>0.03</u>	
					26	0.04	
					35	0.01	
	SC	14	0.036	0.0036	0	0.19	
					5	0.11	
					13	0.08	
					19	<u>0.07</u>	
					26	0.04	

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Location, year	Application				PHI, days	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl			
					35	0.02	
Giessen, Germany, 1982 <sup>3,5</sup>	SC	14	0.036	0.0036	0	0.10	NF 21 D82-302
					5	0.12	
					13	0.06	
					19	<u>0.04</u>	
					26	0.04	
					35	0.03	
	EC	14	0.036	0.0036	0	0.10	
					5	0.07	
					13	0.03	
					19	<u>0.03</u>	
					26	0.01	
					35	0.02	
Giessen, Germany, 1982 <sup>3,5,6</sup>	EC	14	0.036	0.0036	0	0.06	NF 21 D82-303
					8	0.03	
					14	0.03	
					21	<u>0.02</u>	
					30	0.01	
	SC	14	0.036	0.0036	0	0.10	
					8	0.09	
					14	0.01	
					21	<u>0.03</u>	
					30	0.01	
Bonn, Germany, 1982 <sup>1</sup>	EC	12	0.05	0.004	0	0.1	8
					7	0.1	
					14	0.1	
					21	<u>0.1</u>	
					28	0.04	
Dossenheim, Germany, 1982 <sup>1</sup>	EC	14	0.05	0.004	0	0.1	8
					10	0.1	
					14	0.04	
Frankfurt, Germany, 1982 <sup>1</sup>	EC	14	0.05	0.004	0	0.1	8
					10	0.1	
					14	0.1	
					21	<u>0.1</u>	
					28	0.02	
Oudenbosch, Netherlands, 1977 <sup>5,7</sup>	WP	1		0.005	7	0.14	6
						0.14	
						0.22	
						0.17	
					14	0.1	
						0.14	
						0.15	
						0.09	
					21	0.09*	
						0.01*	

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Location, year	Application				PHI, days	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl			
						0.11*	
						0.06*	
Berlicum, Netherlands, 1977 <sup>5,7</sup>	WP	1		0.005	7	0.33	6
						0.41	
						0.3	
						0.37	
					14	0.21	
						0.46	
						0.35	
						0.24	
					21	0.28*	
						0.21*	
						0.26*	
						0.34*	
Breskens, Netherlands, 1977 <sup>5,7</sup>	WP	1		0.005	7	0.27	6
						0.34	
						0.22	
						0.19	
					14	0.16	
						0.12	
						0.13	
						0.15	
					21	0.22*	
						0.22*	
						0.18*	
						0.14*	
Knuiningen, Netherlands, 1978 <sup>5,7</sup>	WP	1		0.005	8	0.09	6
					15	0.11	
					22	0.06*	
Knuiningen, Netherlands, 1978 <sup>5,7</sup>	WP	1		0.005	9	0.09	6
					15	0.06	
					22	0.03*	
Knuiningen, Netherlands, 1978 <sup>5,7</sup>	WP	1		0.005	7	0.14	6
					14	0.11	
					21	0.13*	
Surrey, UK, 1981 <sup>3,5</sup>	SC	13	0.06	0.003 x 11 0.002 x 2	0	0.17	NF 20 FF81-002-01
					7	0.12	
					14	<u>0.04</u>	
					21	0.07	
Surrey, UK, 1981 <sup>3,5</sup>	SC	13	0.06	0.003 x 11 0.002 x 2	0	0.30	NF 20 FF81-002-02
					7	0.18	
					14	<u>0.10</u>	
					21	0.09	

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Location, year	Application				PHI, days	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl			
Surrey, UK, 1981 <sup>3,5</sup>	SC	13	0.06	0.003 x 11 0.002 x 2	0	0.31	NF 20 FF81-002-03
					7	0.19	
					14	<u>0.14</u>	
					21	0.13	

Underlined residues are from treatments according to GAP in Germany; those underlined twice from treatments according to GAP in Denmark, Ireland and the UK.

\* According to GAP in The Netherlands.

<sup>1</sup> No detailed report submitted

<sup>2</sup> No weather data submitted

<sup>3</sup> Method of analysis unspecified

<sup>4</sup> Crops stored for 7 (NF20 D81-351) or 8 months (NF20 D81-353) before analysis

<sup>5</sup> No example chromatograms submitted

<sup>6</sup> High associated recoveries (NF21: D82-305 113-126%; D82-301 102-126%; D82-303 110-127%)

<sup>7</sup> Report not in English

Table 24. Non-European supervised residue trials on apples (including US processing trials).

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
Ontario, Canada, 1975 <sup>1,2,7</sup>	EC	13	0.025	0.002	42	fruit	0.01	NF 25 MFM 5-1
			0.05	0.004		fruit	0.02	
			0.075	0.008		fruit	0.04	
Ontario, Canada, 1975 <sup>1,2,7</sup>	EC	13	0.025	0.002	42	fruit	0.02	NF 25 MFM 6-1
			0.03	0.004		fruit	0.02	
			0.05	0.004		fruit	0.02	
			0.075	0.008		fruit	0.06	
Ontario, Canada, 1976 <sup>1,2,7</sup>	EC	12	0.097	0.002	34	fruit	0.01	NF 25 MFM 6-3
			0.134	0.004		fruit	0.02	
			0.270	0.004		fruit	0.06	
		11	0.16 x 4 0.08 x 7	0.004 x 4 0.002 x 7		fruit	0.04	
Meaford, ONT, Canada, 1977 <sup>1,2,7,9</sup>	EC	6	0.016			fruit	0.007	NF 26 MFM 7-12
		6			15	fruit	0.05	
Bowmanville, ONT, Canada, 1977 <sup>1,2,7,9</sup>	EC	5	0.016			fruit	0.17	NF 26 MFM 7-14
London, ONT, Canada, 1977 <sup>1,2,7,9</sup>	EC	8	0.012		28	fruit	0.02	NF 26 MFM 7-28
Simcoe, ONT, Canada, 1977 <sup>1,2,7,9</sup>	EC	8	0.012		84	fruit	0.03	NF 26 MFM 7-29
Simcoe, ONT, Canada, 1977 <sup>1,2,7,9</sup>	EC	10	0.016 x 8 0.08 x 2			fruit	0.03	NF 26 MFM 7-31
		10	8 x 0.141 or 0.016 2 x 0.069 or			fruit	0.03	

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Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
			0.08					
Nattawa, ONT, Canada, 1977 <sup>1,2,7,9</sup>	EC	6	0.016		83	fruit	0.007	NF 26 MFM 7-34
		6	0.016		83	fruit	0.003	
Meaford, ONT, Canada, 1977 <sup>1,7</sup>	EC	6	0.142		15	fruit	0.07	NF 27 MFM 7-12
		6	0.142			fruit	0.05	
Bowmanville, ONT, Canada, 1977 <sup>1,7</sup>	EC	5	0.142		69	fruit	0.02	NF 27 MFM 7-14
London, ONT, Canada, 1977 <sup>1,7</sup>	EC	8	0.1		28	fruit	0.02	NF 27 MFM 7-38
Simcoe, ONT, Canada, 1977 <sup>1,7</sup>	EC	8	0.1		86	fruit	0.03	NF 27 MFM 7-29
Simcoe, ONT, Canada, 1977 <sup>1,7</sup>	EC	8	6 x 0.142 2 x 0.071		45	fruit	0.03	NF 27 MFM 7-33
Simcoe, ONT, Canada, 1977 <sup>1,7</sup>	EC	6	0.142		90	fruit	0.003	NF 27 MFM 7-34
Nottawa, ONT, Canada, 1977 <sup>1,7</sup>	EC	6	0.142		90	fruit	0.007	NF 27 MFM 7-34
Oyamba, BC, Canada, 1980 <sup>1,7</sup>	EC	3	0.101		131	fruit	0.003	NF 27 K Ellison
					95	fruit	0.004	
Kelowna, BC, Canada, 1980 <sup>1,7</sup>	EC	3	0.101		121	fruit	<0.002	NF 27 E. Star
West Bank, BC, Canada, 1980 <sup>1,7</sup>	EC	3	0.101		121	fruit	0.03 <0.002	NF 27 M. Janse
Campinas, Brazil, 1985 <sup>1,6,7</sup>	EC	9		0.018	28	fruit	0.01	NB 29
				0.036		fruit	0.04	
Curico, Chile, 1980 <sup>1,3,7,12</sup>	EC	9	0.06		100	fruit	0.09 0.09	NF 28
	SC					fruit	0.06	
San Fernando, Chile, 1980 <sup>1,3,7,12</sup>	EC	6	0.06		113	fruit	0.08	
			0.048			fruit	0.003	
Albany, NZ, 1976 <sup>1</sup>	EC	10	0.132	0.002-0.004	2	fruit	0.07	NF 29 NZ 75-19
					6	fruit	0.05	
					12	fruit	0.04	
			0.099	0.0015-0.003	2	fruit	0.07	
					6	fruit	0.05	
					7	fruit	0.07	
					21	fruit	0.06	
					35	fruit	<u>0.02</u>	
Hastings, NZ, 1979 <sup>1</sup>	WP	12	0.061	0.0025	52	fruit	0.008	NF 29 NZ 78-2
			0.061	0.003		fruit	0.006	

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Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
Hamilton, NZ, 1980 <sup>1</sup>	WP	1	0.048		120	fruit	<0.002	NF 29 NZ 80-6
Hamilton, NZ, 1980 <sup>1</sup>	WP	8	0.081		1	fruit	0.02	NF 29 NZ 80-5
					8	fruit	0.02	
					15	fruit	0.01	
					29	fruit	<u>0.008</u>	
Christchurch, NZ, 1981 <sup>1</sup>	WP	14		0.003	31	fruit	0.03	NF 29 T Holland
					38	fruit	<u>0.03</u>	
					45	fruit	0.01	
Geneva, NY, USA, 1981 <sup>1,2,4</sup>	EC	6	0.0445		107	fruit	<0.002	NF 18 Cornel
						juice	<0.002	
						sauce	<0.002	
						wet pomace from sauce	0.003	
						dry pomace	0.025	
		3	0.0445		107	fruit	0.002	
		3	0.0223					
						juice	<0.002	
						sauce	<0.002	
						wet pomace from sauce	0.002	
						dry pomace	0.014	
Biglerville, PA, USA, 1981 <sup>1,2,4,9</sup>	EC	11	0.1038		42	fruit	<u>0.037</u>	NF 18 Penn. Univ.
						juice	0.003	
						sauce	0.009	
						wet pomace from sauce	0.20	
						dry pomace	0.67	
		4	0.1038		42	fruit	0.017	
		7	0.0519					
						juice	<0.002	
						sauce	0.004	
						wet pomace from sauce	0.079	
						dry pomace	0.20	
Winchester, VA, USA, 1981 <sup>1,2,4,9</sup>	EC	10	0.1038		34	fruit	<u>0.059</u>	NF 18 Winchester
						juice	0.002	
						sauce	0.015	
						wet pomace from sauce	0.14	
						dry pomace	0.31	
		3	0.1038			fruit	0.057	
		7	0.0519					

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Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
						juice	0.002	
						sauce	0.01	
						wet pomace from sauce	0.015	
						dry pomace	0.36	
Sodus, NY, USA, 1982 <sup>1,2,3,4,9,12</sup>	EC	1 10	0.316 0.105		41	juice	0.002	NF 18 CMR 82-9
						wet pomace from juice	0.049	
						sauce	<0.002	
						dry pomace	0.11	
		1 10	0.316 0.105		41	juice	<0.002	
						wet pomace from juice	0.061	
						sauce	<0.002	
						dry pomace	0.13	
Sodus, NY, USA, 1982 <sup>1,2</sup>	EC	8	0.105		63	fruit	0.014	NF 18 CMR 8-10
						juice	0.002	
						wet pomace from juice	0.073	
						sauce	<0.002	
						dry pomace	0.12	
		8	0.105		63	fruit	0.008	
						juice	0.002	
						wet pomace from juice	0.072	
						sauce	<0.002	
						dry pomace	0.16	
Sodus, NY, USA, 1982 <sup>1,2</sup>	EC	8	0.079		83	fruit	<0.002	NF 18 CMR 82-11
						juice	<0.002	
						wet pomace from juice	0.006	
						sauce	<0.002	
						dry pomace	0.012	
		8	0.079		83	fruit	<0.002	
						juice	0.002	
						wet pomace from juice	0.003	
						sauce	<0.002	
						dry pomace	0.013	
Sodus, NY, USA, 1982 <sup>1,2</sup>	EC	10	0.0789		53	fruit	0.007	NF 18 CMR 82-16
						juice	<0.002	
						sauce	<0.002	



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Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
						wet pomace from sauce	0.068	
						dry pomace	0.12	
		10	0.0789		53	fruit	0.007	
						juice	<0.002	
						sauce	<0.002	
						wet pomace from sauce	0.079	
						dry pomace	0.098	
Daleville, VA, USA, 1982 <sup>1,2,4</sup>	EC	8	0.1052		33	fruit	<u>0.002</u>	NF 18 DAA 82-6
						juice	<0.002	
						wet pomace from juice	0.013	
		11	0.1052		33	fruit	<u>0.002</u>	
						juice	<0.002	
						wet pomace from juice	0.009	
Tehachapi, CA, USA, 1982 <sup>1,2,9</sup>	EC	4	0.2105		118	fruit	<0.002	NF 18 DHF 82-12
						juice	<0.002	
						wet pomace from juice	0.009	
Gardners, PA, USA, 1982 <sup>1,2,11</sup>	EC	8	0.0526		136	fruit	<0.002	NF 18 PEB 82-5
						juice	<0.002	
						sauce	<0.002	
						wet pomace from sauce	<0.002	
Thurmont, MD, USA, 1982 <sup>1,2</sup>		10	0.1052		70	fruit	0.02	NF 18 PEB 82-6
						juice	0.002	
						sauce	0.003	
						wet pomace from sauce	0.036	
Gettysburgh, PA, USA, 1982 <sup>1,2,11</sup>		10	0.0526		75	fruit	0.021	NF 18 PEB 82-14
						juice	0.003	
						sauce	<0.002	
						wet pomace from sauce	0.054	
Watsonville, CA, USA, 1982 <sup>1,2,9</sup>		4	0.1052		104	fruit	0.005	NF 18 RAH 82-1
						juice	0.002	
						wet pomace from juice	0.018	
		4	0.2105		104	fruit	0.013	
						juice	0.003	

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Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
						wet pomace from juice	0.043	
Snelling, CA, USA, 1982 <sup>1,2,9</sup>		4	0.1052		93	fruit	0.008	NF 18 RAH 82-2
						juice	0.002	
						wet pomace from juice	0.021	
		4	0.2105		93	fruit	0.011	
						juice	0.002	
						wet pomace from juice	0.029	
Moxee, WA, USA, 1982 <sup>1,2</sup>		1 3	0.084 0.104		122	fruit	0.002	NF 18 WTC 82-4
						juice	<0.002	
						wet pomace from juice	0.005	
		1 3	0.104 0.132		122	fruit	0.002	
						juice	<0.002	
						wet pomace from juice	0.004	
Orondo, WA, USA, 1982 <sup>1,2</sup>		2 2	0.105 0.132		147	fruit	0.007	NF 18 WTC 82-8
						juice	<0.002	
						wet pomace from juice	0.015	
Covert, MI, USA, 1982 <sup>1,2,9</sup>		10	0.1052		147	fruit	0.019	NF 18 DG 082-10
						juice	<0.002	
						wet pomace from juice	0.14	
						sauce	0.003	
						wet pomace from sauce	0.33	
Sodus, NY, USA, 1976 <sup>1,2</sup>		10	0.1075		62	fruit	0.004	NF 18 CDC 6-16
						juice	<0.002	
						wet pomace from juice	0.022	
						dry pomace	0.068	
Reedley, CA, USA, 1988	EC	7	0.105		30	fruit	<u>0.03</u>	NF 31 DHF88-02
		7	0.105		30	fruit	<u>0.02</u>	NF 31 DHF 88-03
Sunnyside, WA, USA, 1988	EC	7	0.105		29	fruit	<u>0.01</u>	NF 31 BJB88-01
		7	0.105		29	fruit	<u>0.01</u>	NF 31 BJB88-02
		7	0.105		29	fruit	<u>0.02</u>	NF 31

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Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
								BJB88-03

Underlined residues are from treatments according to GAP in the USA; those underlined twice from treatments according to GAP in New Zealand

<sup>1</sup> No weather data submitted

<sup>2</sup> Method of analysis unspecified. Stated to be GLC for studies NF 20, 25 & 26 but no further details

<sup>3</sup> No control plot data submitted

<sup>4</sup> Crops stored for 8-15 months before analysis

<sup>6</sup> No example chromatograms submitted

<sup>7</sup> Duration of sample storage unspecified

<sup>9</sup> High associated recoveries (NF26: MFM 7-12 98-140%, NF 18 dry pomace 132%; juice 121-128%

<sup>11</sup> Half sprayed - one side of row only

<sup>12</sup> System recoveries only submitted (i.e control extract or extraction solvent, not the commodity, was fortified)

Pears. GAP was reported for many countries world-wide and was generally the same as that reported for apples.

A few trials were available which complied with GAP (the same as for apples) in Germany (one trial), Italy (one trial) or the USA (4 trials with replicates), but the recoveries associated with the German (0.13 mg/kg) and Italian trials (0.09 mg/kg) were low at 67 and 63% respectively. Residues in the US trials were 0.01-0.04 mg/kg.

Table 25. Supervised residue trials on pears.

Location, year	Application				PHI, days	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl			
Australia, 1985 <sup>1,5,6</sup>				0.0036	14	0.03	NB 30 AUS 78-314
				0.0072		0.04	
Giessen, Germany, 1978 <sup>1-4,6</sup>	EC	14	0.054		0	0.1	NF 03 D78-312
					3	0.08	
					10	0.07	
					13	0.08	
					17	0.08	
					20	0.09*	
					24	0.03	
					31	0.06	
Baricella, Italy, 1981 <sup>1-4</sup>	SC	17		0.004	20	<u>0.13</u>	NF 06 181 211
Hood River, OR, USA, 1983 <sup>1,5</sup>	EC	3	0.143		112	0.003	NF 33 WTC83-2
Medford, OR, USA, 1983 <sup>1,5</sup>	EC	2	0.143		120	<0.001	NF 33 830R12
					144	<0.001	
Hood River, OR, USA, 1984 <sup>1,5</sup>	EC	3	0.092		120	<0.001	NF 33 840R4
			0.143		123	<0.001	
Medford, OR, USA, 1985 <sup>1,5</sup>	EC	2	0.092 0.071		147	<0.001	NF 33 840R5
			0.143 0.109			<0.001	
Clayton, NC, USA, 1986 <sup>1,5</sup>	SC	7	0.1		30	<u>0.01</u>	NF 33 DAA86-13
		7	0.1			<u>0.02</u>	
Reedley, CA, USA, 1986	SC	7	0.1		30	<u>0.03</u>	NF 33 DHF86-5

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Location, year	Application				PHI, days	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl			
	EC					<u>0.01</u>	
Parlier, CA, USA, 1986 <sup>1,5</sup>	EC	7	0.1		29	<u>0.04</u>	NF 33 DHF86-6
Mesa, WA, USA, 1986 <sup>1,5</sup>	EC	7	0.1		28	<u>0.02</u>	NF 33 DHF86-8
	SC					0.08	

Underlined residues are from treatments according to GAP in the USA; those underlined twice from treatments according to GAP in Italy

\* according to GAP in Germany

<sup>1</sup> No weather data submitted

<sup>2</sup> Method of analysis unspecified

<sup>3</sup> Low associated recoveries (NF03 D78-312 67%; NF06 181-211 63%)

<sup>4</sup> No example chromatograms submitted

<sup>5</sup> Duration of sample storage unspecified

<sup>6</sup> Crop variety unspecified

Peaches. GAP was reported for Uruguay, Argentina, Japan, Greece, Italy and Spain. No GAP was reported for apricots or nectarines, although some trials data were submitted. The maximum application rates are 0.036-0.2 kg ai/ha (0.0024-0.0048 kg ai/hl) with a PHI of 1-20 days.

Residue trials were available only from Spain, Italy and France. The critical European GAP for peaches was the Spanish (0.0048 kg ai/hl, PHI 7 days) for which there were 5 trials (one of them replicated) with residues of 0.03-0.3 mg/kg. In two of these trials the volume of spray per hectare was not specified. A further Spanish trial on apricots in 1988 where the use pattern was the same as the Spanish GAP for peaches with a residue of 0.36 mg/kg at 7 days provided supporting information. A single Chilean trial on nectarines reflected the Argentinian GAP for peaches (0.072 kg ai/ha, PHI 20 days) with no residue detected. No data on supervised trials were available for Japanese GAP in which there is a 1-day PHI.

Table 26. Supervised residue trials on peaches, apricots and nectarines.

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
Fronton, S. France, 1993 <sup>1</sup>	EC	3	0.04	0.0078	0	pulp	0.13	NG 07 R93-46
					6		<u>0.04</u>	
					10		0.06	
					13		0.04	
Fronton, France, 1994	EC	5	0.04	0.008	8	pulp	0.03	NG 11 GHE-P-4062
Follonica, Italy, 1977 <sup>2-6</sup>	WP	8		0.0042	34	fruit	<0.01	NG 01 I77-212A
Puntone, Italy, 1977 <sup>2-6</sup>	WP	4		0.0042	20	fruit	0.02	NG 02 I77-213
Follonica, Italy, 1977 <sup>2-6</sup>	WP	6	0.24	0.0042	16	fruit	<0.01	NG 03 I77-214
S. Biagio, Italy, 1993 <sup>1</sup>	SC	5	0.09	0.0042	0	pulp	0.44	NG 08 R93-45
					7		<u>0.13</u>	
					10		0.08	
					14		0.08	
							0.1	
					7		<u>0.15</u>	
					10		0.15	

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Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
					14		0.16	
Francolino, Italy, 1994	SC	4	0.066 0.069 0.071 0.072	0.0048 x 4	13	pulp	0.05	NG 10 GHE-P-4014
Luchente, Spain, 1988 <sup>2,3,5,6,7</sup>	EC	1	0.18	0.0048	0	fruit	0.41	ref. 13
					3		0.38	
					7		<u>0.30</u>	
					14		0.12	
					21		0.10	
Pobla del Duc, Spain, 1992 <sup>2,3,5,6,7</sup>	EC	1		0.0036	0	fruit	0.18	ref. 13
					7		<u>0.08</u>	
					14		0.03	
					21		0.02	
Pobla del Duc, Spain, 1993 <sup>2,3,5,6,7</sup>	EC	1		0.0036	0	fruit	0.07	ref. 13
					7		<u>0.03</u>	
					14		0.02	
					21		0.01	
NECTARINE								
Chile <sup>2,5,7</sup>	EC		0.072	0.0036	0	fruit	0.03	NG 09
					6		<0.01	
					16		ND	
					24		<u>ND</u>	
APRICOT								
Luchente, Spain, 1988 <sup>2,3,5,6,7</sup>	EC	1	0.18	0.0048	0	fruit	0.45	ref. 13
					3		0.44	
					7		0.36	
					14		0.14	
					21		0.08	

Underlined residues are from treatments according to GAP in Spain

Results underlined twice reflect GAP in Argentina

ND - not detected

<sup>1</sup> Crops stored for 11 months before analysis

<sup>2</sup> No weather data submitted

<sup>3</sup> Method of analysis unspecified (reports 2, 3, 4 & 5 in Spanish)

<sup>4</sup> Low associated recoveries (NG01 69%; NG02 68%; NG03 59%)

<sup>5</sup> No example chromatograms submitted

<sup>6</sup> Duration of sample storage unspecified

<sup>7</sup> No English translation provided

**Cherries.** GAP was reported for Denmark, Japan and the USA. The maximum application rates reported were 0.06 to about 0.2 kg ai/ha with PHIs of 0-14 days.

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All 15 trials submitted were from the USA with samples being taken at 0 and 1 day after the final treatment. In all these trials no account was taken of the weights of the stones. US GAP (0.101 kg ai/ha) allows treatment 'up to and after harvest' and residues in the 9 trials (3 of which were replicated) complying with it were 0.06-0.89 mg/kg.

Table 27. Supervised residue trials on cherries in the USA.

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference		
	Form	No.	kg ai/ha	kg ai/hl						
Traverse City, MI, 1987 <sup>1,2</sup>	EC	6	0.053		0	fruit pulp	0.21	NG 04 87MI1		
					1		0.24			
Geneva, NY, 1987 <sup>1,2</sup>	EC	5	0.095		0	pulp	0.07	NG 04 87NY1		
					1		<u>0.10</u>			
Biglerville, PA, 1987 <sup>1,2</sup>	EC	5	0.089		0	pulp	0.10	NG 04 87PA1		
					1		<u>0.11</u>			
Hart, MI, 1987 <sup>1,2</sup>	EC	5	0.053		0	fruit	0.16	NG 04 WWH87-2		
					1		0.17			
Hart, MI, 1987 <sup>1,2</sup>	EC	5	0.053		0	pulp	0.18	NG 04 WWH87-3		
					1		0.13			
Sutton Bay, MI, 1987 <sup>1,2</sup>	EC	5	0.053		0	pulp	0.28	NG 04 WWH87-5		
					1		0.26			
Sutton Bay, MI, 1987 <sup>1,2</sup>	EC	6	0.053		0	pulp	0.20	NG 04 WWH87-6		
					1		0.10			
Sutton Bay, MI, 1987 <sup>1,2</sup>	EC	5	0.053		0	pulp	0.17	NG 04 WWH87-7		
					1		0.16			
Vantage Bay, WA, 1987 <sup>1,2</sup>	EC	4	0.105		0	pulp	<u>0.06</u>	NG 04 WTC87-3		
					1		0.05			
Malago, WA, 1987 <sup>1,2</sup>	EC	4	0.105		0	pulp	<u>0.44</u>	NG 04 WTC87-6		
					1		0.41			
Othello, WA, 1987 <sup>1,2</sup>	EC	4	0.105		0	pulp	<u>0.17</u>	NG 04 WTC87-7		
					1		0.15			
Corvallis, MI, 1987 <sup>1,2</sup>	EC	4	0.105		0	pulp	0.63	NG 04 WTC87-8		
					1		<u>0.64</u>			
Linden, CA, 1989	EC	4	0.106		0	fruit	<u>0.89</u>	NG 05 LES89-05		
					1		0.49			
			0.106	0.0056	0	fruit	<u>0.77</u>			
					1		0.63			
Grevais, OR, 1989	EC	4	0.106	0.0056	0	fruit	0.22	NG 05 LR89-01		
					1		<u>0.28</u>			
			SC	4	0.106	0.0056	0		fruit	<u>0.1</u>
							1			0.1
Westley, CA, 1989	EC	4	0.106	0.0056	0	fruit	0.4	NG 05 LES89-04		
					1		<u>0.88</u>			
					SC		4		0.106	0.0056
1	0.25									

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Underlined residues are from treatments according to GAP in the USA

<sup>1</sup> No weather data submitted

<sup>2</sup> Duration of sample storage unspecified

Currants. GAP for blackcurrants was reported for Denmark, Ireland and the UK, and for all currants for The Netherlands. The application rates were 0.04-0.06 kg ai/ha or 0.0048 kg ai/hl with PHIs of 14 or 21 days.

Data were available only from 5 trials in The Netherlands. Residues were 0.04-0.74 mg/kg 15 days after the final treatment but with a variety of application rates with only one trial according to the reported GAP.

Gooseberries. GAP in Ireland and The Netherlands is the same as for currants. Only one trial in The Netherlands was reported with a residue of 0.05 mg/kg at 10 days and this trial was submitted in summary form only.

Table 28. Supervised residue trials on currants and gooseberries in The Netherlands in 1980. All EC applications. All reference 6.

Crop	Application			PHI, days	Residues, mg/kg
	No.	kg ai/ha	kg ai/hl		
Blackcurrant <sup>1,2</sup>					
	8		40ppm	2	0.1
				10	0.07
				14	0.04
				22	<u>0.05</u>
				29	0.06
	1	6-	60 ppm	13	0.47
	1		80 ppm	13	0.45
	?	0.06		50	0.10
	?	0.08		13	0.74
Redcurrant <sup>1,2</sup>					
	3	0.048		25	0.07
					0.14
					0.06
					0.08
Gooseberry <sup>1,2</sup>					
	8		40ppm	2	0.07
				10	0.05

Underlined residues are from treatments according to GAP in The Netherlands

<sup>1</sup> No example chromatograms submitted

<sup>2</sup> No English translation provided

Grapes. GAP was reported for many countries world-wide. The maximum application rates were 0.012-0.06 kg ai/ha with PHIs of 7-35 days. [CLICK HERE to continue](#)