DINOCAP (087)

EXPLANATION

Dinocap is a contact fungicide used to control powdery mildew on many crops and is also used as a non-systemic acaricide. It has been evaluated several times by the JMPR. In 1992 the JMPR recommended withdrawal of the temporary MRLs and in 1993 the CAC agreed to delete dinocap from the Codex list. In the present evaluation dinocap is therefore considered as a new compound.

The manufacturer has provided residue data on grapes, apples, cucurbits, strawberries, peppers, peaches, apricots and tomatoes for review by the present Meeting.

IDENTITY

ISO common name: dinocap

Chemical name

IUPAC: 2,6-dinitro-4-octylphenyl crotonates and 2,4-dinitro-6-octylphenyl crotonates in which "octyl" is a mixture of 1-methylheptyl, 1-ethylhexyl and 1-propylpentyl groups.

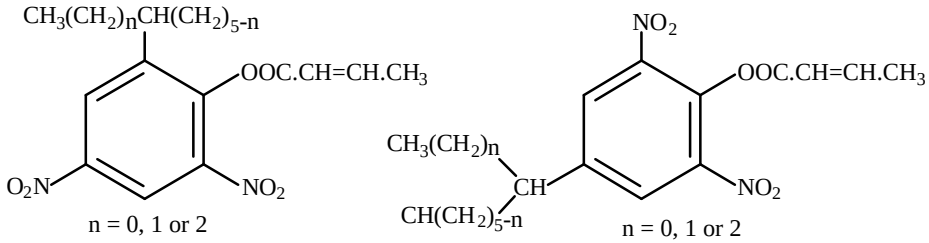
CA: 2-butenoic acid, 2-isooctyl-4,6-dinitrophenyl ester and 2-butenoic acid, 4-isooctyl-2,6-dinitrophenyl ester.

CAS No.: [39300-45-3] (for isomer mixture)

CIPAC No.: 98

Synonyms: RH-23,004, DNOPC

Structural formula:



2,4-dinitro-6-octyl (2,4-DNOPC)

2,6-dinitro-4-octyl (2,6-DNOPC)

Molecular formula: $C_{18}H_{24}N_2O_6$

Molecular weight: 364.18

Physical and chemical properties

Technical material

Technical dinocap consists of a mixture of the 2,4-dinitro-6-octyl isomers and 2,6-dinitro-4-octyl isomers (2,4-DNOPC and 2,6-DNOPC) in a ratio of about 2,6:1.

Vapour Pressure:

Temperature (°C)	Vapour pressure (Pa)
20	5.64×10^{-7}
25	3.33×10^{-6}
30	8.29×10^{-6}

Purity: 92% (minimum)

Melting point: >-25ºC (freezing point -6.5ºC)

Octanol/water partition coefficient at 20.5ºC (Betteley, 1997a):
log P_{ow}: 6.55 and 6.45 for the 2,4-dinitro and 2,6-dinitro isomers respectively.
log P_{ow}: 3.85 and 3.93 for the corresponding phenols.

Solubility: dinocap is soluble in most organic solvents in water at 20ºC (Betteley, 1994):
1.5×10^{-4} g/l for 2,4-dinitro isomer
1.15×10^{-4} g/l for 2,6-dinitro isomer

Hydrolysis (Winwick, 1998a):

pH	Test substance	Half-life, days	
		20ºC	30ºC
4	2,4-DNOPC	447	91.4
	2,6-DNOPC	114	55
7	2,4-DNOPC	30.4	30.5
	2,6-DNOPC	16.2	14.8
9	2,4-DNOPC	9.25	2.34
	2,6-DNOPC	3.65	1.01

Relative density: 1.13

Photolysis (Winwick, 1998b): The 2,4- and 2,6-isomer mixtures had half-lives in aqueous buffer solutions at PH 4 of 0.63 and 0.73 days respectively

Formulations

Dinocap is available as an emulsion concentrate containing 350 g ai/l and a wettable powder containing 185 g ai/kg. Other formulations have been developed in which dinocap is mixed with other fungicides.

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Rats and mice. In a rat feeding study in 1970 one adult male and one adult female were dosed daily for seven days with 11.7 mg [^{14}C]2,4-DNOPC (the main component of commercial dinocap). The rats were killed 6 hours after the final dose. Dinocap residues were rapidly eliminated in the faeces and urine of both the male and female, the excreted radioactivity being 72.9% and 71.9% of the dose in the male and female respectively. Residues did not appear to accumulate in any tissues except in the digestive tract, which contained 7.6% and 11.3% of the administered dose in the male and female respectively (Honeycutt and Garstka, 1976a).

Table 1. Distribution of radioactivity in rats (Honeycutt and Garstka, 1976a).

Sample	^{14}C, % of administered dose	
	Male	Female
Urine	14.9	19.9
Faeces	58.0	52.0
All tissues except digestive tract	2.9	3.8
Unwashed digestive tissue	7.6	11.3
Exhaled CO_2	0.02	0.02
Cage washing	11.1	5.7
Total	94.5	92.7

The urine and faeces were analysed to identify the main metabolites, using GLC, mass spectrometry and nuclear magnetic resonance. The two main extractable metabolites of 2,4-DNOPC in rat urine were identified as 2,4-dinitro-6-(1-methyl-7carboxyheptyl)phenol (27% of the total ^{14}C in the urine) and 2,4-dinitro-6-(1-methyl-5-hydroxyheptyl)phenol (37%). Two minor metabolites in the faeces were identified as 2,4-dinitro-6-(2-octyl)phenol (2,4-DNOP, 5% of the total ^{14}C in the faeces) and 2,4-dinitro-6-(1-methyl-5-hydroxyheptyl)phenol (4%) (Honeycutt and Garstka, 1976b).

Another study of pharmacokinetics and metabolism was conducted with male mice and rats dosed with [^{14}C]2,4-DNOPC, the mice at 0.5, 3, and 25 mg/kg and the rats at 3, 50, and 100 mg/kg. Urine and faeces were collected for 24 hours after dosing and analysed by HPLC with UV spectrometric detection (Udinsky *et al.,* 1986). The metabolic profiles in mice and rats were different. In mice, three metabolite peaks dominated the chromatograms and at least five other compounds were present in significant amounts, whereas rat urine showed only two major metabolite peaks. Incubation of urine from each species with three types of glucuronidase and arylsulfatase had little effect on the HPLC profile, suggesting that conjugation did not contribute significantly to producing the main metabolites in the urine.

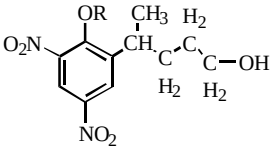
Most of the metabolites in mouse urine were substituted at the phenolic group, whereas the main metabolites in the rat urine were free phenols. In the mouse urine, the radioactivity decreased from 61% to 24% of the dose as the dose increased from 0.5 to 25 mg/kg. By contrast, no significant dose-related trends were evident in the excretion of total radioactivity or individual metabolites in rat urine.

In another study to elucidate the metabolism of dinocap in rats and mice after oral exposure, Potter (1996) treated six male rats and 15 male mice with single gavage doses, of 2,4-DNOPC labelled with ^{13}C and ^{14}C, the rats at 100 mg/kg and mice at 25 mg/kg. The 2-4-dinitro mixture was selected because it is the main component of the technical material and is representative of dinocap metabolism. Urine was collected for 24-hour periods ending at 24, 48, 72 and 96 hours after dosing. The metabolites were identified by HPLC and mass spectrometry and the radioactivity was quantified by LSC.

Only the urinary metabolites were examined since they appear to be a more complex mixture than those in the faeces. DNOPC was rapidly metabolized and excreted into the urine of both rats and mice. Approximately 30.9% of the administered DNOPC was excreted in rat urine and 58.3% in mouse urine. In both more than 90% of the urinary ^{14}C was excreted within 24 hours after administration, so only the 0-24 h urine was analysed.

Twelve urinary metabolites from rats and thirteen from mice were identified and quantified, accounting for 99% of the ^{14}C in rats and approximately 89% of that in mice. The structures of the identified metabolites are shown in Figures 1 and 2.

Figure 1. Urinary metabolites of DNOPC in mice.



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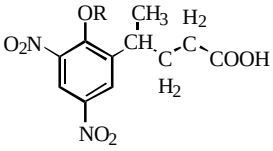

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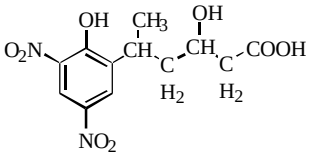

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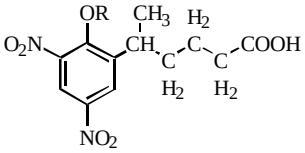

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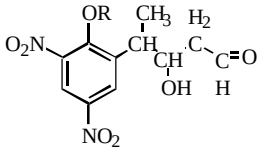

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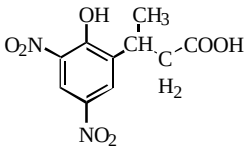

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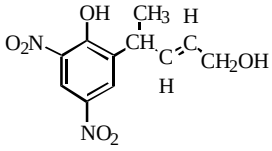

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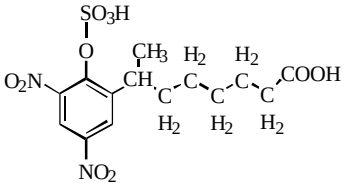

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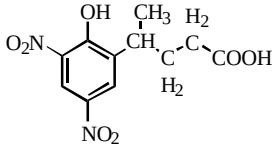

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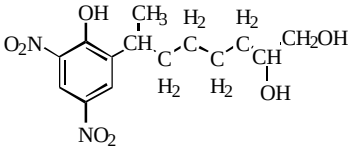

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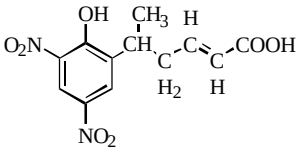

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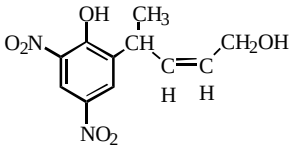

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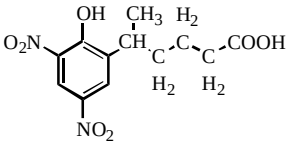

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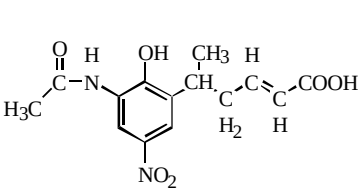
Figure 2. Urinary metabolites of DNOPC in rats.



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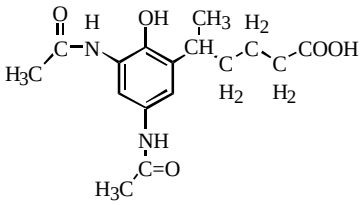

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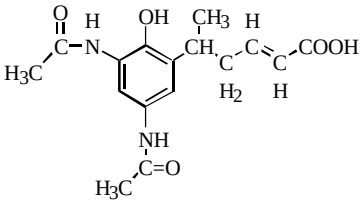

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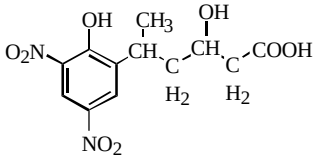

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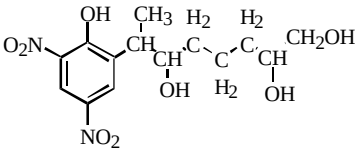

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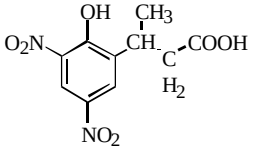

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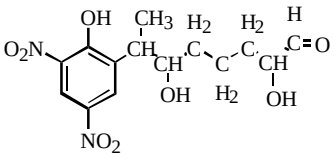

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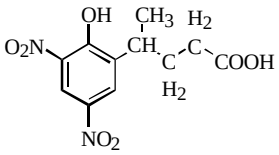

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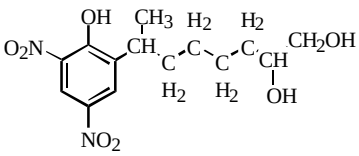

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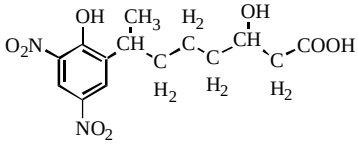

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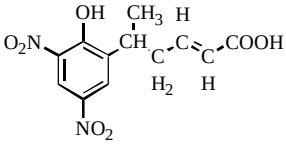

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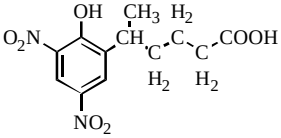

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MW = 298

The metabolites appear to be produced by following processes.

1. Fatty acid β-oxidation: 5 metabolites in rats (67.3% of the ^{14}C); 5 metabolites in mice (45%).
2. Fatty acid β-oxidation: 1 metabolite in rats (18% of the ^{14}C); 3 metabolites in mice (28%).
3. In rats only, fatty acid β-oxidation followed by reduction of the nitro groups and *N*-acetylation: 3 metabolites (4.5%).
4. In mice only, fatty acid α- and β-oxidation followed by conjugation: 4 metabolites (6.5%), one a sulfate conjugate.
5. Multiple mono-oxygenation: 3 metabolites in rats (4.37%); 1 metabolite in mice (1.13%).

The proposed schemes for DNOPC metabolism in rats and mice are shown in Figures 3 and 4 respectively.

Table 2. DNOPC metabolites identified in rat and mouse urine.

Metabolite	% of total rat urinary metabolites	% of total mouse urinary metabolites
5-(3-acetamido-2-hydroxy-5-nitrophenyl)hex-2-enoic acid	2.12	
5-(3,5-diacetamido-2-hydroxyphenyl)hexanoic acid	2.39	
4-(2-hydroxy-3,5-dinitrophenyl)pentanol, phenolic conjugate		1.73
4-(2-hydroxy-3,5-dinitrophenyl)pentanoic acid, phenolic conjugate		1.73
5-(2-hydroxy-3,5-dinitrophenyl)-3-hydroxyhexanoic acid	4.21	8.09
5-(2-hydroxy-3,5-dinitrophenyl)hexanoic acid, phenolic conjugate		1.56%
7-(2-hydroxy-3,5-dinitrophenyl)octane-1,2,6-triol	1.26	
4-(2-hydroxy-3,5-dinitrophenyl)-3-hydroxypentanal		1.49
3-(2-hydroxy-3,5-dinitrophenyl)butanoic acid	1.83	6.0
7-(2-hydroxy-3,5-dinitrophenyl)-2,6-dihydroxyoctanal	1.56	
4-(2-hydroxy-3,5-dinitrophenyl)pent-2-enol		1.24
7-(2-hydroxy-3,5-dinitrophenyl)octanoic acid, phenolic sulfate		1.23
4-(2-hydroxy-3,5-dinitrophenyl)pentanoic acid	17.97	23.9
7-(2-hydroxy-3,5-dinitrophenyl)octane-1,2-diol	1.55	1.13
7-(2-hydroxy-3,5-dinitrophenyl)-3-hydroxyoctanoic acid	0.42	
5-(2-hydroxy-3,5-dinitrophenyl)hex-2-enoic acid	2.66	8.95
4-(2-hydroxy-3,5-dinitrophenyl)pent-2-enol		2.78
5-(2-hydroxy-3,5-dinitrophenyl)hexanoic acid	58.2	21.92
Total	94.17	81,75

Figure 3. Proposed metabolic pathways of dinocap in rats.

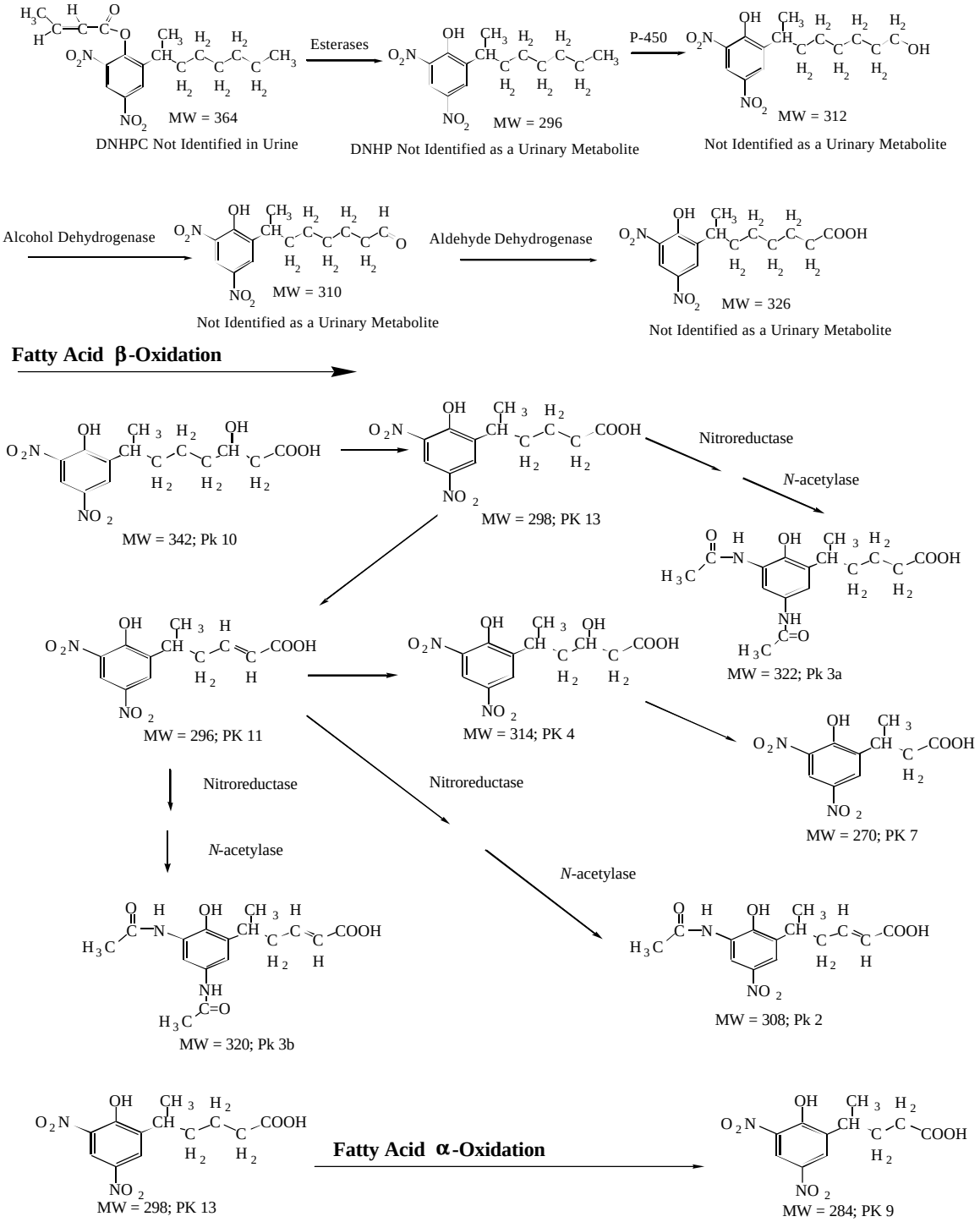
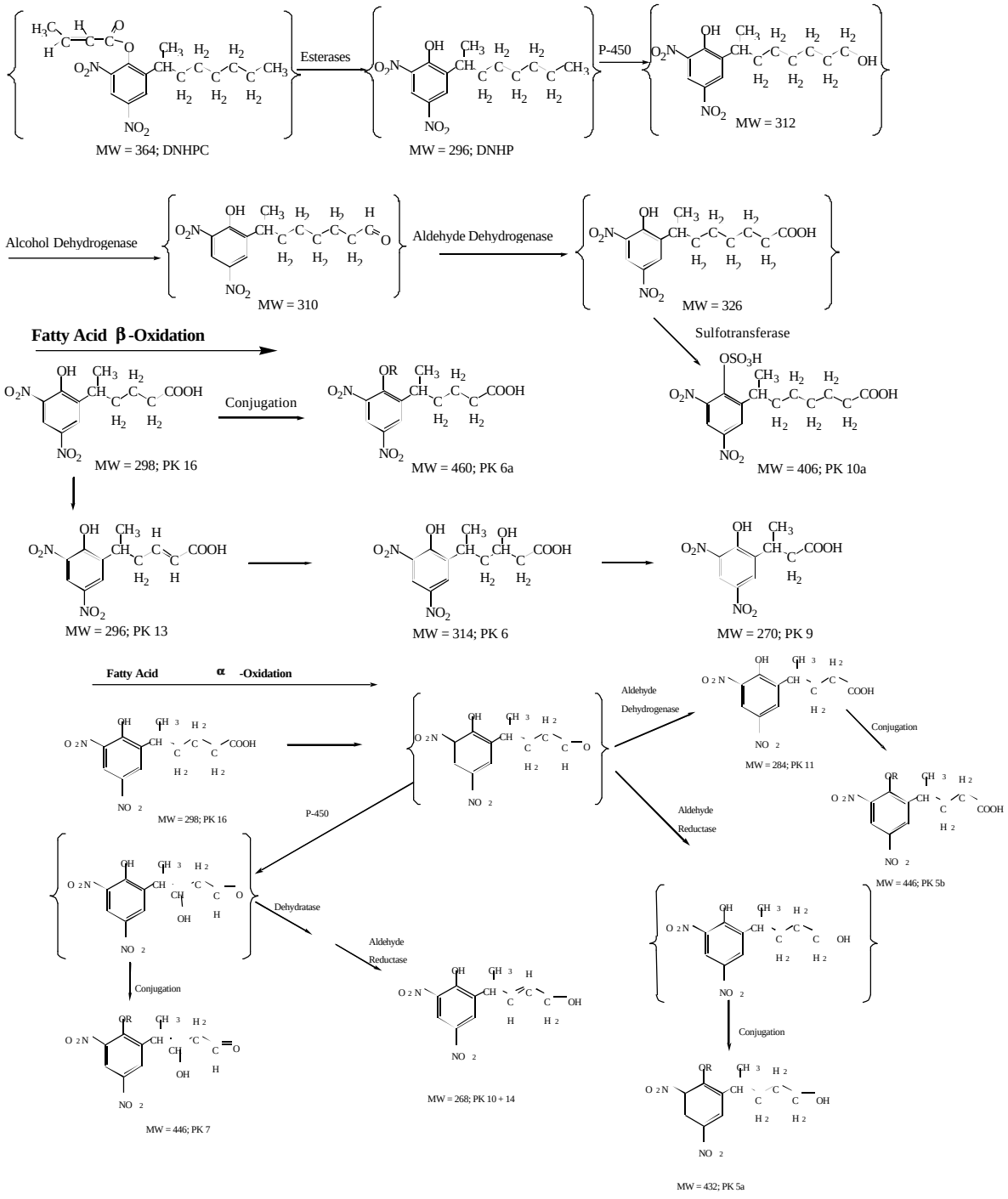


Figure 4. Proposed metabolic pathways of dinocap in mice.



Cows. Three cows were dosed by gelatine capsule containing sugar cane with dinocap technical uniformly labelled with ^{14}C in the phenyl ring. The five-week study was divided into three periods, one week with all cows dosed with control capsules, the next two weeks with the three cows dosed at a level equivalent to 0.1 ppm in the diet and the final two weeks during which the cows were dosed at 0, 0.03 and 1.0 ppm (Graham and Bornak, 1972). The dose regimen is shown in Table 3.

Table 3. Cows, dose regimen.

Week	Dose equivalent, ppm in the diet			
	Control	Cow 1	Cow 2	Cow 3
1	0	0	0	0
2	0	0.1	0.1	0.1
3	0	0.1	0.1	0.1
4	0	0	0.3	1.0
5	0	0	0.3	1.0

Samples of urine and faeces were taken for 24-hour periods during the second week of each test period. Milk samples were collected daily. Cows 2 and 3 were slaughtered at the end of the study and cow 1 at the end of week 3. Aliquots of milk and urine were radio-assayed and the ^{14}C in the organs and tissues was measured by combustion and LSC. No activity was detectable in any muscle, kidney, liver, fat or milk samples (LOD 0.04 mg/kg, except fat 0.08 mg/kg).

The main route of elimination was in the faeces with small amounts in the urine. Table 4 shows the dinocap residues in the faeces and urine at 23 and 37 days.

Table 4. Dinocap residues in urine and faeces of dosed cows.

Day	Cow	^{14}C, mg/kg as dinocap and % of TRR				Urine + faeces, % of TRR
		Urine		Faeces		
		mg/kg	% of TRR	mg/kg	% of TRR	
23	1	0.008	1.5	0.072	130	131.5
	2	ND		0.073	100	100
	3	0.015	7.9	0.041	62	69.9
37	2	0.02	4.4	0.2	105	109.4
	3	0.06	3.1	0.47	69	72.1

Samples were refrigerated rather than frozen before analysis and the specific activity of the test mixture was low (0.75 mCi/g).

Bioaccumulation in fish. The uptake and bioconcentration of [^{14}C]2,4-DNOPC by bluegill sunfish were studied in a flow-through system for 28 days of exposure at levels of 0.2 µg/l and 1 µg/l, followed by 14 days depuration. Concentrations of 2,4-DNOPC in the water were measured by LSC. Fish were taken for analysis at 0, 1, 3, 7, 14, 21 and 28 days during the exposure phase and 1, 3, 7, 10 and 14 days during the depuration phase. Total radioactive residues were determined in edible and inedible tissues and in whole fish, and the uptakes and bioconcentration factors determined. Radioactive residues increased within 1 to 3 days to steady levels which were maintained throughout the exposure period at both concentrations (Corden, 1998).

The ^{14}C residues and the calculated bioconcentration factors (BCFs) at the low and high concentrations are shown in Tables 5 and 6.

Table 5. Residues and bioconcentrations factors in fish exposed to 0.2 µg dinocap/l (Corden, 1998).

Day	Water, µg/l	Edible, µg/g	Edible, BCF	Inedible, µg/g	Inedible, BCF	Whole fish, µg/g	Whole fish, BCF
Exposure phase							
1	0.19	0.016	84	0.25	1320	0.15	790
3	0.22	0.027	120	0.27	1200	0.18	820
7	0.21	0.014	67	0.39	1900	0.2	950
14	0.2	0.027	140	0.33	1700	0.19	950
21	0.19	0.034	180	0.24	1300	0.13	680
28	0.2	0.033	170	0.43	2200	0.22	1100
Depuration phase							
1	nd	0.014		0.14		0.079	
3	nd	0.009		0.033		0.02	
7	nd	0.006		0.02		0.014	
10	nd	0.006		0.018		0.012	
14	nd	0.004		0.015		0.009	

nd: <0.004 µg/l

Table 6. Residues and bioconcentrations factors in fish exposed to 1.0 µg dinocap/l (Corden, 1998).

Day	Water, µg/l	Edible, µg/g	Edible, BCF	Inedible, µg/g	Inedible, BCF	Whole fish, µg/g	Whole fish, BCF
Exposure phase							
1	1.07	0.18	170	0.98	920	0.54	510
3	1.04	0.22	210	1.01	970	0.65	630
7	0.96	0.08	83	1.31	1400	0.69	720
14	0.97	0.17	180	1.19	1200	0.74	760
21	0.99	0.12	120	1.2	1200	0.65	660
28	0.98	0.24	250	1.63	1700	0.94	960
Depuration phase							
1	nd	0.1		0.87		0.48	
3	nd	0.049		0.16		0.1	
7	nd	0.043		0.11		0.073	
10	nd	0.03		0.092		0.059	
14	nd	0.028		0.07		0.048	

nd: <0.004 µg/l

The elimination half-lives calculated for edible and inedible tissues and whole fish were as follows.

	Elimination half-life, days		
	Edible tissue	Inedible tissue	Whole fish
Low dose	0.7	0.7	0.6
High dose	0.6	0.9	0.9

Plant metabolism

Metabolism studies with [^{14}C]2,4-DNOPC were conducted on apples, cucumbers and squash.

Apples. An apple tree was treated with a single foliar application of an EC formulation containing 45.6% ai at a rate equivalent to 1.96 kg ai/ha, four times the normal maximum application (0.49 kg ai/ha). Two untreated trees were used as control (Dohmeier, 1993).

Apples and leaves were harvested from treated and control trees on the day of application, both before and after treatment, and after 7, 14, and 21 days. The samples were stored frozen for one year before analysis. Half of each fruit sample was analysed as whole fruit, and the other half peeled and the peel and pulp analysed separately. The total radioactivity in the samples was determined by radiocombustion with the results shown in Table 7.

Table 7. Radioactivity in apples treated with dinocap.

PHI	^{14}C, mg/kg as dinocap				
	Whole fruit	Pulp	Peel	Pulp + peel	Leaves
0	1.37	0.25	16.7	2.9	195
7	2.38	0.13	12.8	2.3	113
14	1.67	0.15	12.97	2.2	76.3
21	1.57	0.12	10.1	1.57	70.6

More than 92% of the radioactivity at each PHI was associated with the peel. The samples were extracted with methanol which extracted more than 90% of the radioactivity from the day 0 samples and 40-60 % from the aged samples. When the residues extracted by methanol were partitioned with hexane and ethyl acetate most of the radioactivity (80-90%) passed into the hexane. An additional 30-45% of the total radioactivity in the aged fruit samples could be released with 0.1 M NaOH in methanol. After adjusting the pH of the extract 80-95% of this radioactivity could be partitioned into ethyl acetate. The total radioactivity recovered in the neutral and alkaline methanolic extracts was more than 80% in all cases. The results are shown in Table 8.

Table 8. Distribution of radioactivity in extracts of apple peel and whole apples.

Fraction/ extract	% of total radioactivity							
	0 days		7 days		14 days		21 days	
	Peel	whole fruit	Peel	Whole fruit	Peel	Whole fruit	Peel	Whole fruit
Hexane/MeOH	88.1	91.8	41.6	46.2	26.3	25.7	20.2	25.2
EtOAc/MeOH	8.2		14.1	10.2	12.1	11.8	11.3	10.3
Aqueous/MeOH	0.4	0.4	3.8	5.3	6.3	5.4	8.3	9.6
EtOAc/MeOH NaOH	_	_	31.7	19.0	41.1	40.1	45.1	32.5
Aqueous/MeOH/ NaOH .	_	_	1.3	2.0	2.1	2.3	2.3	8.1
Post-extraction solid	3.3	2.8	7.5	9.1	12.1	14.3	12.8	13.2

Peel samples were analysed six months after the whole fruit, showing that the nature of the residues did not change dramatically during storage.

The parent 2,4-DNOPC and the metabolite 2,4-DNOP were identified in the hexane and ethyl acetate fractions of the fruit extracts by TLC and reverse phase HPLC. The parent decreased from 73% of the total radioactivity at day 0 to 23% at day 7, 11% at 14 and 8% at 21 days.

Table 9. Residues of 2,4-DNOPC and 2,4-DNOP in fruit.

PHI, days	^{14}C, mg/kg as 2,4-DNOPC	
	2,4-DNOPC	2,4-DNOP
0	2.12	0.06
7	0.52	0.08
14	0.25	0.05
21	0.12	0.03

The half-life of 2,4-DNOPC was 5.2 days, showing that it was rapidly degraded on the fruit surface. The phenol metabolite was present at low concentrations, 2-4% of the total radioactivity at all sampling intervals, and appeared to be quickly metabolized to many polar compounds, none of them individually accounting for more than 7% of the total radioactivity. They could not be identified.

An additional study was conducted to provide information on the identity of the unidentified metabolites of 2,4-DNOPC in apples (Dohmeier, 1994). The test substance was 2,4-DNOPC, uniformly labelled with ^{13}C and ^{14}C in the phenyl ring, applied to a single apple tree as an EC formulation at a rate of 1.96 kg ai/ha.

Apple peel samples were extracted three times with MeOH in a blender and the extract was partitioned with hexane. The post-extraction solids were treated with methanolic NaOH solution to release additional radioactivity. After acidification, the methanolic base extract was partitioned with ethyl acetate.

The hexane fraction was cleaned up by silica gel chromatography and the residues eluted with increasing concentrations of methanol in methylene chloride. Fractions containing radioactivity but not 2,4-DNOPC or 2,4-DNOP were methylated and fractionated by TLC and HPLC and the purified components analysed by GC-MS. The resulting mass spectra allowed tentative structures to be proposed.

The methanolic base extracts were evaporated, and the solutes redissolved in ethyl ether and chromatographed on silica gel. The residues were eluted with increasing concentrations of ethyl acetate in ethyl ether followed by increasing concentrations of methanol in ethyl acetate. Individual fractions were analysed by normal and reverse-phase TLC.

As photolysis was identified as a possible degradation pathway for 2,4-DNOPC on the apple surface, a mixture of ^{14}C- and ^{13}C-labelled 2,4-DNOPC was irradiated with a Hanau “Sun test” lamp for 26 hours. The photolysis products were methylated and cleaned up on Florisil columns and by TLC and HPLC. The isolated products were analysed by GC-MS, and their spectra compared with the spectra of the metabolites isolated from apple peel.

Photolysis appears to be a significant pathway for the degradation of 2,4-DNOPC in plants: two metabolites identified in apple peel were also identified as photoproducts.

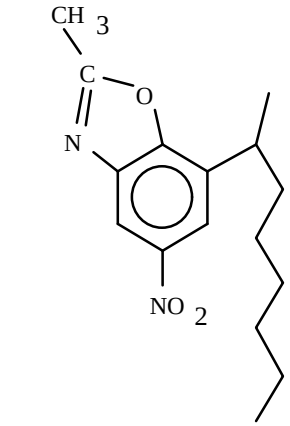
The structures of five metabolites identified by GC-MS are shown in Figure 5.

The proposed pathway for their formation involves reduction of a nitro group to the amine and hydrolysis of the crotonyl ester to the phenol. Metabolites are then formed by reaction of the amine with formic or acetic acid to form amides, or by intramolecular transfer of the crotonyl group to form the crotonamide. Ring closure of the amides then forms benzoxazoles. The fraction containing most radioactivity was the ethyl acetate extract of the alkaline methanol extract. Individual metabolites could not be isolated. The influence of pH on the partitioning of the radioactivity in this fraction indicated that one or both nitro groups had been reduced to the corresponding amine. The amines could readily form conjugates with acids to form amides. Hydrolysis of the fraction with NaOH produced more polar radioactive residues, consistent with hydrolysis of amides to amines.

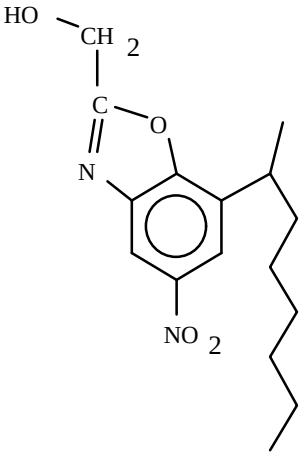
Table 10. Metabolites isolated from hexane fraction from MeOH extract of apple peel.

Metabolite	Conc., mg/kg as dinocap	% of total radioactivity
A	0.006	0.3
B	0.001	0.1
C	0.002	0.1
D	0.007	0.4
E	0.001	0.1

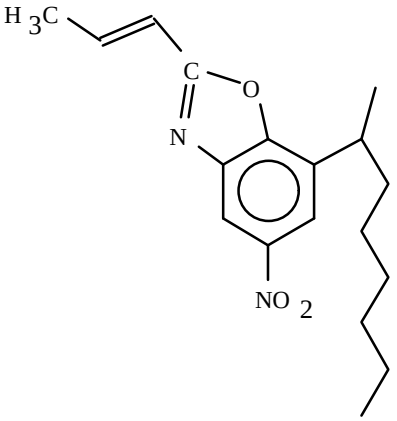
Figure 5. Metabolites identified in apples (Dohmeier, 1994).



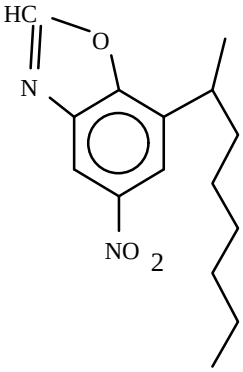
2-methyl-5-nitro-7-(2-octyl) benzoxazole



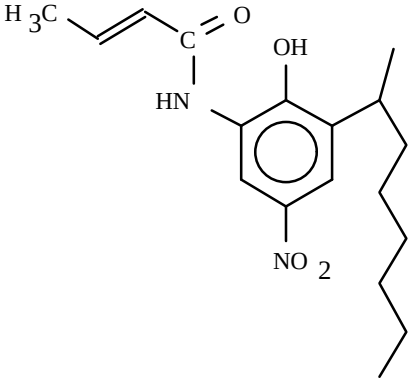
2-(hydroxymethyl)-5-nitro-7-(2-octyl) benzoxazole



2-(1-propenyl)-5-nitro-7-(2-octyl) benzoxazole



5-nitro-7-(2-octyl) benzoxazole



2-hydroxy-5-nitro-3-(2-octyl)-phenyl crotonamide

Cucumbers. The distribution and rate of decrease of residues after a single treatment with [^{14}C]2,4-DNOPC at 0.56 kg ai/ha were studied. Samples of leaves, stems and soil were taken 0, 8, 21, 34, 48, and 63 days after treatment, and of fruits at 21, 48 and 63 days. The samples were assayed by combustion and LSC (Honeycutt, 1976a).

Table 11. Residues in cucumbers treated with [^{14}C]2,4-DNOPC.

PHI	Residues, mg/kg as DNOPC						
	Leaves	Stems	Flowers	Immature fruit	Mature Fruit		
					Peel	Pulp	Whole
0	38.2	3.6	-	-			
8	28.9	3.9	5.4	-			
21	4.1	0.7	1.0	1.0			
34	2.5	0.6	0.5	-			
48	1.1	0.4		0.2	0.15	0.11	0.16
63	1.4	0.5					0.09

The ^{14}C residues dissipated rapidly from the cucumber leaves and stems, with half-lives of 11.8 and 18.8 days respectively. The residues in the soil in which the cucumbers were grown dissipated at a much lower rate (0.45 mg/kg at day 0 and 0.31 mg/kg at final harvest in the top 2.5 cm).

Cucumber leaves from day 8 were analysed by TLC for metabolites. Twenty eight metabolites were detected but only the parent compound and DNOP were identified.

Table 12. Relative levels of dinocap and metabolites in cucumber leaves after 8 days.

Metabolite	% of extractable residue	% of total residue
Two unidentified	0.9	0.4
2,4-DNOPC	0.7	0.3
2,4-DNOP	5.7	2.4
Unidentified	19.4	8.2
Unidentified	3.9	1.6
Unidentified	3.1	1.3
12 polar metabolites	66.1	27.8
Unextractable	-	58.0

Cucumbers harvested at 48 and 63 days were extracted with acetone and the post-extraction solid analysed by combustion and radio-assay. The acetone extract was redissolved in acetone/water and partitioned twice with methylene chloride. The organic phases were combined and concentrated to dryness, and the residue redissolved in petroleum ether/methylene chloride. The concentrated extract was analysed by TLC and radioactive bands quantified by LSC (Honeycutt, 1976a). The results are shown in Table 13.

Table 13. Relative levels of dinocap and metabolites in cucumbers after 48 and 63 days (Honeycutt, 1976a)

Compound or fraction	% of total ^{14}C	
	48 days	63 days
2,4-DNOPC	0.7	3.5
2,4-DNOP	0.6	4.5

Compound or fraction	% of total ^{14}C	
	48 days	63 days
Unidentified	0.9	1.3
Unidentified	0.6	0
Unidentified	0.4	1.5
Unidentified	0.6	2.3
Unidentified	0.9	3.3
Unidentified	1.1	3.8
Polar metabolites	1.4	5
Aqueous fraction	40	35
Unextractable	52	40

Squash. Formulated [^{14}C]2,4-DNOPC was applied three times at a rate of 0.56 kg ai/ha to two rows of squash (Early Straight Neck variety). The squash plants were in bloom at the time of the first treatment. Whole plants were sampled 0, 7, 17, 25, 32, 40, 53, 66 and 80 days after the first application (0, 8, 15, 23, 36, 49 and 63 days after the final application). Fruit samples were taken from 15 days after the final application. Soil cores taken at three different places in the plot at each sampling were sectioned in 0-2.5, 2.5-7.6, and 7.6-15.2 cm depths and the three sections at each depth pooled.

Samples were assayed for radioactivity by combustion and LSC (Honeycutt and Garstka, 1976d). The results are shown in Table 14.

Table 14. Residues in squash treated three times post-emergence with [^{14}C]2,4-DNOPC.

Days after 1st treatment	^{14}C, mg/kg as dinocap					
	Leaves	Root and stems	Immature whole fruit	Mature fruit		
				Peel	Pulp	Whole
0	4.2					0.14
7 (after 2nd treatment)	44.0	8.2				0.36
17 (after 3rd treatment)	34.8	3.1				0.11
25	17.5	3.3				0.35
32	12.2	1.9		0.58	0.15	0.25
40	11.9	1.8		0.19	0.08	0.21
53	4.2	1.5	0.02	0.70	0.19	0.09
66	2.7	0.7	0.04	0.15	0.06	0.18
80	1.7	0.7	0.06			

The half-life of the radioactivity in the leaves was 8 days. The leaves sampled at this time were extracted twice with benzene and the fruit twice with acetone. The fruit extract was partitioned 3 times with petroleum ether/methylene chloride, and the organic phases combined and dried with sodium sulfate. The organic and aqueous phases from the fruit extraction were radio-assayed. The organic extracts from the leaves and fruit were concentrated and analysed by TLC. Radioactive bands on the TLC plates were visualized by autoradiography. The radioactivity was eluted from each band with acetone or methanol and the eluates radio-assayed.

Table 15. Extractable radioactivity in fractions from extracts of squash leaves and fruit 8 days after last of 3 applications of [^{14}C]2,4-DNOPC.

Fraction	Sample	% of TRR
Benzene extract	leaves	14
Unextractable	leaves	86
Acetone extract	fruit	42
Unextractable	fruit	58
Organic phase[1]		45
Aqueous phase[1]		44

[1] From partition of acetone extract

2,4-DNOP was the main metabolite in the leaves and was also found in the fruit. About 6 unidentified metabolites were found in the fruit and 10 in the leaves, none of which individually accounted for more than 10% of the TRR.

The distribution of radioactivity in the fruit and leaves 8 days after the last treatment is shown in Table 16.

Table 16. Radioactive residues in extracts of squash fruit and leaves, 8 days after last application of [^{14}C]2,4-DNOPC.

Sample	Compound	% ^{14}C	% of ^{14}C
Fruit	2,4-DNOP	3	1.3
	2,4-DNOPC	14	5.9
	Unidentified	1	0.4
	Unidentified	1	0.4
	Unidentified	2	0.8
	Two unidentified	13	5.5
	Organosoluble polar metabolites	13	5.5
	Water-soluble polar metabolites	50	21
	Unextractable	-	57.6
Leaves	2,4-DNOP	34	4.8
	2,4-DNOPC	23	3.2
	Unidentified	4	0.6
	Unidentified	2	0.3
	Unidentified	2	0.3
	Unidentified	2	0.3
	Two unidentified	7	1.0
	Two unidentified	3	0.4
	Unidentified	4	0.6
	Organosoluble polar metabolites	12	1.7
	Unextractable	-	86.0

The ^{14}C residues in the top section of the soil (0-2.5 cm) decreased from 0.43 mg/kg after the last treatment to 0.40 mg/kg 63 days later. The ^{14}C residues in the other sections were low.

A comparative TLC study of metabolites of [^{14}C]2,4-DNOPC from rat urine and faeces, cucumbers and squash was conducted to determine whether any metabolites not found in either rat urine or faeces were among the metabolites in squash or cucumbers (Honeycutt, and Garstka, 1976c). The metabolites from cucumbers and squash were very similar in their TLC behaviour. The metabolites from

rat faeces were closer in their TLC behaviour to those from cucumber and squash than to those from rat urine. The urine metabolites were the most polar of any from the four sources tested. ^{14}C photoproducts of DNOPC from squash leaf surfaces were similar in polarity to cucumber, squash and faeces metabolites.

Environmental fate in soil

A study in 1971 determined the rate of dissipation of dinocap in silt loam soil, the effect of a higher than normal application rate on overall microbial activity and the activity of dinocap *in vitro* against selected soil micro-organisms. The study was not according to FAO Guidelines, but showed that after 170 days 34.7% of the initial radioactivity was trapped as $^{14}C0_2$ and 53.3% was accounted for in the soil. The rate of degradation of dinocap gradually decreased with time, which was attributed to the depletion of substrate and the depressed rate of microbial activity (Fisher, 1971).

To measure the decline of ^{14}C-dinocap from greenhouse-aged soil and to characterize the bound ^{14}C residues, sandy loam and silt loam soils were fortified at 5 and 10 mg/kg in open containers in the greenhouse (24-32ºC) and sampled at frequent intervals for 270 days. A portion of the silt loam soil was transferred at 30 days from aerobic to anaerobic conditions for an additional 60 days to compare aerobic and anaerobic degradation. Soil samples were analysed by TLC, and bound ^{14}C residues characterized as associated with the fulvic or humic acid components of the soil organic matter (Honeycutt *et al.*, 1976). The characteristics of the soils are shown in Table 17 and the residues in Table 18.

Table 17. Physical properties of soils.

	Sandy loam	Silt loam
Organic matter, %	2.59	3.83
pH	5.5	5.5
Sand, %	71.0	13.0
Silt, %	22	65
Clay, %	7	22
CEC meq/100g	7	10.1
Moisture capacity, %	12.5	15.6

Table 18. Residues in soils fortified at 5 and 10 mg/kg (Honeycutt *et al.*, 1976).

Day	^{14}C, mg/kg as dinocap		
	Silt loam, 5 mg/kg	Sandy loam, 5 mg/kg	Sandy loam, 10 mg/kg
0	4.4	4.6	8.8
15	5.1	3.9	7.7
30	4.1	4.3	8.0
60	3.7	4.2	7.1
90	2.8	2.8	4.0
120	2.5	2.5	4.8
187	1.9	2.6	4.7
270	2.5	2.5	5.0

The half-lives for the disappearance of the radioactivity from the silt loam and sandy loam treated with 5 mg/kg were 134 and 199 days respectively. A number of unidentified polar and non-polar degradation products were detected by TLC.

In another study the degradation of ring-labelled [^{14}C]dinocap was investigated in standard German soils 2.2 (Neuhofen Neu) and 2.3 (Hatzenbuhl) and in one German agricultural soil (Eschweiller) under laboratory conditions at a concentration of 9 mg ai/kg soil. In soil 2.2, the influence of an organic fertiliser in the form of alfalfa meal was examined. The soils were incubated at 15 and 25ºC in the dark for 100 days (Mittelstädt and Fuhr, 1982). Table 19 shows the characteristics of the soils.

Table 19. Soil characteristics.

	Soil 2.2, Neuhofen Neu	Soil 2.3, Hatzenbuhl	Eschweiller agricultural soil
pH	6.8	4.7	5.9
Organic matter, %	2.1	1.7	1.4
Total N, %	0.24	0.12	0.12
Clay, %	8.3	6.9	12.0
Silt	6.3	13.6	28.4
Fine sand	73.8	38.6	58.3
Coarse sand	11.6	40.9	1.4
Ca (meq/100g)	12.8	2.1	11.8
Total sorption capacity, meq/100 g	15.3	6.3	11.2
Exchangeable cations, meq/100 g	14.1	3.6	12.8

Moist CO_2-free air was passed over the soils, and the CO_2 produced was absorbed in 1N NaOH. Samples of the soils were exhaustively extracted after 30 and 100 days incubation and the extracts were examined by HPLC and TLC. Total radioactivity in the soil was determined by combustion and LSC. Recovery of the total radioactivity was in the range 83-102.2% of the applied material. The results are shown in Table 20.

Table 20. Degradation of ^{14}C-Dinocap in German Soils, $^{14}CO_2$ evolution and total radioactivity.

Days, sample	^{14}C, % of applied					
	Soil 2.2, 25ºC	Soil 2.2 + alfalfa, 25ºC	Soil 2.2 15ºC	Soil 2.3, 25ºC	Soil 2.3, 15ºC	Agricultural soil, 25ºC
1, CO_2 trap	0.02	0.02	0.02	0.01	0.01	0.1
11, CO_2 trap	0.43	0.96	0.08	0.1	0.03	3.9
30, CO_2 trap	1.75	2.4	0.32	0.59	0.08	15.6
100, CO_2 trap	4.99	5.14	1.41	3.34	0.57	32.3
100, soil	93.9	90.5	81.6	98.9	100.8	55.3
Total ^{14}C recovery	98.9	95.6	83	102.2	101.3	87.6

Mineralization in the agricultural soil was much greater, with 15.6 and 32.3% of the applied radioactivity evolved as CO_2 after 30 and 100 days respectively. The quantity of organoextractable radioactivity decreased during the study. In standard soil 2.3 70% of the applied radioactivity was organosoluble after 100 days incubation at 25ºC with up to 22% bound in the soil. The only major degradation product identified was 2,4-DNOP. Several others were detected but individually these accounted for no more than 2% of the applied radioactivity, and after 100 days less than 1%.

Lewis (1995) determined the rate and route of [^{14}C]dinocap degradation in sandy loam, silty loamy sand, loamy sand and clay loam soils. The soil characteristics are shown in the Table 21.

Table 21. Characteristics of the test soils.

	Sandy loam	Silty loamy sand	Loamy sand	Clay loam
Organic carbon, %	2.3	1.9	1.2	3.0
Organic matter, %	4.0	3.3	2.1	5.2
CEC,[1] meq/100g soil	15.6	16.0	10.2	28.2
Sand, %	54	49	70	30
Silt, %	36	40	16	37
Clay, %	10	11	14	33
PH (1:2.5 in 1M KCl)	5.5	6.7	4.8	7.1
Water holding capacity (% w/w) -0.33 bar -0.001 bar	27.00 68.4	18.8 57.7	13.0 49.6	35.8 87.5
Microbial biomass (µg C/g soil): Pre-study Post-study, 20ºC Post-study, 10ºC	 447.6 328.6 322.74	 186.24 257.45 NA	 59.9 42.47 NA	 1023.59 1085.56 NA

NA: not applicable
[1] Cation-exchange capacity

To study routes of degradation in the sandy loam soil over a 123-day period, soil samples (50 g dry weight equivalent) in a common chamber in the dark were maintained at 20ºC (the sandy loam also separately at 10ºC). Moistened CO_2-free air was drawn through the chamber and the effluent air passed through a series of traps. After a pre-incubation period of three days, [^{14}C]2,4-DNOPC was applied to each unit at a rate of 2.6 kg ai/ha, approximately five times the highest use rate of 0.52 kg ai/ha. Duplicate incubation units were removed for analysis at 0, 1, 3, 8, 14, 30, 60, 91 and 123 days after application.

The rate of degradation was measured in the four soils at 20ºC and in the sandy loam soil also at 10ºC. After a pre-incubation period of 3 days in the dark at 20ºC, [^{14}C]2,4-DNOPC was applied to each soil at a rate of 1 kg ai/ha. Duplicate samples were removed on days 0, 1, 3, 8, 14, 30, and either 60 or 100 days depending upon the soil.

The soil samples were extracted with neutral, acidic and basic methanol and the extracts assayed for radioactivity by LSC. Samples from the route study taken on day 60 were fractionated into fulvic acid, humic acid and humin, and assayed by LSC to determine the bound residues. Controls were used to determine the microbial biomass. The degradation rates in the four soils are given in Table 22.

Table 22. Degradation rates of 2,4-DNOPC in soil.

Soil	Temp., ºC	Application rate, kg ai/ha	DT-50, days	DT-90, days
Sandy loam	20	2.6	14.9	49.4
Sandy loam	10	1.0	31.2	103.7
Silty loamy sand	20	1.0	8.2	27.4
Loamy sand	20	1.0	24	79.8
Clay loam	20	1.0	4.1	13.5

The results of HPLC analysis of the sandy loam soil treated with 2,4-DNOPC at a rate of 2.6 kg ai/ha and 20ºC are shown in Table 23.

Table 23. HPLC analysis of sandy loam soil (Lewis, 1995).

Days	% of applied radioactivity			
	DNOPC	DNOP	Unknown	Unresolved background
0	92.34	1.69	0.87	1.40
1	87.0	5.88	ND	1.01
3	79.77	8.08	ND	1.96
8	60.92	11.63	0.24	2.0
14	45.11	13.47	ND	0.7
30	16.47	5.59	2.53	0.13
60	6.11	1.47	0.84	0.06

ND: not detected

The main degradation product was DNOP. Degradation was more rapid in the two soils of pH 6.7 and 7.1 than in those of pH 4.8 and 5.5, indicating that chemical hydrolysis to DNOP is a main route of degradation in soil. 2,4-DNOPC was degraded rapidly in all the soils, at a lower rate at 10ºC than at 20ºC.

The fate of labelled 2,4-DNOPC and 2,6-DNOPC was investigated separately in a sandy loam soil (pH 5.8 and 1.8% organic carbon) under aerobic conditions at an application rate of 0.52 kg ai/ha. The soil was allowed to acclimatise in darkness for 7 days before adding the test substances, then incubated in darkness at 20 ± 2ºC for 120 days. The microbial biomass was determined at the beginning (285 µgC/g) and end (255 µgC/g) of the incubation period (Whittle, 1998).

Duplicate samples taken immediately after application of the test substance and after 1, 3, 7, 14, 30, 59, 90 and 120 days incubation were analysed by LSC, HPLC and TLC. 2,4-DNOP and 2,6-DNOPC were quantified by reverse-phase HPLC. The results are shown in Table 24.

Table 24. Degradation of 2,4- and 2,6-DNOPC in sandy loam soil (Whittle, 1998).

Time after application, days	% of applied radioactivity	
	2,4-DNOPC	2,6-DNOPC
0	97.6	98.4
1	93.3	90.6
3	78.6	67.4
7	59.2	31.8
14	39.4	14.1
30	29.9	4.2
59	17.7	1.8
90	15	1.6
120	7.8	1.9

Calculated DT-50 and DT-90 values for 2,4-DNOPC were 10.0 and 112.9 days respectively. 2,6-DNOPC was degraded more rapidly with DT-50 and DT-90 values of 4.5 days and 16.4 days.

The principal route of degradation was hydrolysis to 2,4-DNOP or 2,6-DNOP with subsequent incorporation into bound residues. In both cases the polar material and minor components remained unidentified. At 120 days, significant mineralization of both isomers to $^{14}CO_2$ was observed (22.4% and 36.7% of the AR for 2,4-DNOPC and 2,6-DNOPC respectively).

Adsorption and desorption

The adsorption and desorption of dinocap were investigated in four agricultural soils, sandy loam, loam, loamy sand and clay loam in aerobic conditions (Hawkins *et al*., 1992b). The characteristics of the soils are shown in Table 25.

Table 25. Soil characteristics.

	Sandy loam	Loam	Loamy sand	Clay loam
Sand, %	58	46	84	36
Silt, %	26	43	12	33
Clay, %	15	11	3	31
Organic Carbon, %	1.57	3.66	0.87	2.15
pH	7.4	6.8	7.2	7.7
CEC (meq/100g)	13.2	24.2	5.7	22

Sieved samples of the soils (1g dry weight) were mixed with 20 ml of 0.01 M $CaCl_2$. Solutions of ring-labelled [^{14}C]2,4-DNOPC were added to triplicate soil samples to give final dinocap concentrations of 0.1, 0.05, 0.025 and 0.01 mg/l. Test samples were shaken for 2 hours in the dark at 25ºC. After centrifugation the supernatant was decanted, the volume recorded and duplicate aliquots were analysed for radioactivity by LSC.

Desorption was determined with the same samples. Fresh 0.01 M $CaCl_2$ (20 ml) was added and the soil samples shaken for a further two hours in the dark at 25ºC. Soil and solutions were separated by centrifugation and analysed as before. A second desorption step followed. The radioactivity remaining in the soils was determined by combustion and LSC and the dinocap in the soils and solutions by HPLC. The results are shown in Tables26-28.

Table 26. Recovery of radioactivity in the aqueous solutions, soil extracts and extracted soils after 2 hours equilibration.

	% of applied radioactivity			
	Sandy loam	Loam	Loamy sand	Clay loam
Aqueous solution	13.0	10.5	18.0	8.2
Soil extracts	84.8	88.9	80.9	94.7
Unextractable	2.0	3.8	1.2	4.1
Total recovered	99.8	103.2	100.1	107

Table 27. Recovery of radioactivity in the aqueous solutions, soil extracts and extracted soils after adsorption and two desorption equilibrations.

	% of applied radioactivity			
	Sandy loam	Loam	Loamy sand	Clay loam
Adsorption solution	15.5	7.7	18.2	10.0
Desorption solution 1	5.9	2.8	7.8	4.5
Desorption solution 2	5.3	2.4	5.1	4.2
Soil extract	66.8	82.5	62.1	72.2
Unextractable	2.6	4.0	1.1	8.7
Total	96.1	99.4	94.3	99.6

Table 28. Proportions of 2,4-DNOPC and other radioactive components in aqueous solutions and soil extracts after adsorption and two desorption equilibrations.

Radioactive components	% of radioactivity in solution			
	Sandy loam	Loam	Loamy sand	Clay loam
Soil extract				
2,4-DNOPC	82.8	82.8	89.9	70.8
Others	17.2	17.2	10.1	29.2
Aqueous solution				
2,4-DNOPC	39.6	26.4	53.2	20.9
Others	60.4	73.6	46.8	79.1

Freundlich adsorption and desorption coefficients were calculated from the results.

Table 29. Adsorption coefficients of 2,4-DNOPC in soils.

Soil	OC %	K_a	K_{oc}
Sandy loam	1.57	114	7260
Loam	3.66	206	5630
Loamy sand	0.87	133	15300
Clay sand	2.15	176	8190

OC: organic carbon
K_a: Freundlich adsorption coefficient
K_{oc}: adsorption coefficient per unit organic carbon

Dinocap was strongly adsorbed by the soils studied and can be classified as having low mobility in soil. Adsorption was greater than would have been expected in the low organic carbon soil indicating that other factors are also important in the adsorption to soil. Dinocap was more strongly adsorbed than its degradation products.

Leaching

A laboratory study was carried out on five soils classified as clay, clay loam, silt loam, sandy loam and silty clay loam (Graham, 1971). [^{14}C]dinocap was mixed with the soils at a rate of approximately 156 mg/kg (to simulate the application of 0.227 kg ai/ha), and applied to the top of duplicate soil columns (25.5 cm). The columns were saturated with water and the equivalent of 2.5 cm rain per week was allowed to percolate through them over a period of nine weeks. Leachates and column segments were analysed. In all five soils, the radioactivity in the top segment was 70% or more of the total radioactivity

recovered, which ranged from 74% of that applied in silt loam to 96% in clay loam. In only silt loam and clay loam was radioactivity detectable in the leach water. It can be concluded that dinocap and/or its degradation products are not leached extensively in a range of different soils.

In another laboratory leaching study sandy loam soil fortified with ^{14}C-dinocap at a rate of 5 mg/kg was aged in a greenhouse for a period of 30 days before addition to the 30 cm test column (Fisher, 1975). Leachates were collected daily for 44 days and radio-assayed. After 44 days the column was disassembled into 5 cm segments for the top 15 cm and 7.5 cm for the bottom 15 cm, and all the segments were radio-assayed.

No appreciable ^{14}C was detected in the leachates collected throughout the period, and combustion assays of the soil indicated that all the radioactivity was in the first and second segments, showing that soil-aged dinocap residues are not leached in a sandy loam soil.

A similar study was carried out with a silt loam soil (OM 2%, pH 6.1) aged in a greenhouse for 102 days. Additional columns were prepared using untreated soil as a control and soil freshly fortified with [*phenyl*-^{14}C]2,4-D as a reference (Streelman, 1980). Duplicate 30 cm glass columns were filled with silt loam soil, and 7.6 cm layers of untreated soil and soil fortified with labelled dinocap or 2,4-D at 5 mg/kg were added to the tops of the columns. On each working day for the next 46 days, 55 ml of water (equivalent to 1.3 cm of rainfall) was added dropwise to each column. No dinocap or 2,4-D was found in the leachate for the first two weeks and thereafter the radioactivity was only slightly above the limit of determination (1 µg/l). The total radioactivity found in the eluate was on average 0.28% of the applied dinocap and 0.05 % of the 2,4-D.

Radio-assay of the soil immediately after fortification with dinocap gave a value of 5.14 mg/kg. After ageing for 102 days the level was 2.8 mg/kg. Radioactivity was also recovered from the pot in which the soil was aged (13% of the applied ^{14}C). The remaining radioactivity was assumed to have been lost as volatile degradation products. In the dinocap-treated soils a mean of 83.4% of the radioactivity applied to the columns was recovered from the soils, and more than 90% of the recovered radioactivity was found in the top 5 cm of the soil columns. The distribution of radioactivity is shown in Table 30.

Table 30. Distribution of radioactivity in aged soil columns (Streelman, 1980).

Soil depth, cm	Column 1		Column 2	
	mg/kg as dinocap	% of recovered ^{14}C	mg/kg as dinocap	% of recovered ^{14}C
0-5	0.766	99	0.69	91.6
5 -10 cm	0.007	1	0.027	3.6
10-15	ND		0.24	3.2
15-22.5	ND		0.006	0.8
22.5-30	ND		0.006	0.8

The greater movement of the radioactivity in the second column was considered to be due the activity of an earthworm later observed in this column. It can be concluded that aged dinocap residues will not be leached from a silt loam soil even under exaggerated laboratory conditions.

Environmental fate in water/sediment systems

The solubility of dinocap in water at 20ºC was determined in two studies by a column elution method. In the first only 2,4-DNOPC was determined (Betteley, 1994). In the second the solubilities of [^{14}C]2,4-DNOPC and [^{14}C]2,6-DNOPC and the corresponding phenols were determined at flow rates of 300 and 600 ml/hr, in water buffered at pH 5 (Betteley, 1997b). The results are shown in Table 31.

Table 31. Solubilities of dinocap and dinocap phenols in water (Betteley, 1997b).

Isomer mixture	Water solubility at 20ºC, g/l	
	Flow rate 300 ml/hr	Flow rate 600 ml/hr
2,4-DNOPC	1.46×10^{-4}	3.3×10^{-4}
2,6-DNOPC	1.15×10^{-4}	1.19×10^{-4}
2,4-DNOP	2.87×10^{-5}	3.0×10^{-5}
2,6-DNOP	8.17×10^{-4}	5.31×10^{-4}

The octanol/water partition coefficients of 2,4-DNOPC, 2,6-DNOPC and the phenols were determined by an HPLC method (Betteley , 1997a) with the following results.

	log P_{ow} (20.5ºC)
2,4-DNOPC	6.55 ± 0.33
2,6-DNOPC	6.45 ± 0.33
2,4-DNOP	3.85 ± 0.33
2,6-DNOP	3.93 ± 0.33

The hydrolysis of dinocap was determined in buffered solutions at pH 5, 7 and 9 by Streelman (1981). Who concluded that the hydrolysis was base-catalysed, occurring rapidly at pH 9 and quite slowly at pH 5.

The hydrolysis of 2,4- and 2,6-DNOPC and DNOP in aqueous buffer solutions pH 4, 7 and 9 was determined by Winwick (1998a). [^{14}C]DNOPC and [^{14}C]DNOP were added separately to buffer solutions at a concentration of 50 µg/l (about half the reported water solubility of DNOPC) and incubated at 20ºC and 30ºC. The rate of hydrolysis was monitored by HPLC with the following results.

Test substance	pH	Half-life, days	
		20ºC	30ºC
2,4-DNOPC	4	447	91.4
	7	30.4	30.5
	9	9.25	2.34
2,6-DNOPC	4	114	55
	7	16.2	14.8
	9	3.65	1.01

The only major degradation product of DNOPC in all the solutions was the phenol, DNOP. There was no significant degradation of DNOP at any pH at 20ºC or 30ºC.

The photolysis of labelled dinocap was investigated in a 0.1 mg/l aqueous pH 5 buffer solution at 25ºC. Test samples were irradiated continuously with a Xenon arc for 367 hours, equivalent to 82.84 days of summer sunlight at 30º N. Duplicate samples of both irradiated and control solutions were taken at approximately 1, 2, 4, 6 and 24 hours and 5 and 15 days. The radioactivity was measured by LSC, and TLC and HPLC were used to identify and quantify degradation products (Hawkins *et al.*, 1992a).

The photolytic degradation of 2,4-DNOPC was found to be biphasic with initial and terminal half-lives equivalent to 4.9 and 57.2 hours of summer sunlight at 30º N respectively. The main degradation product was $^{14}CO_2$, accounting for approximately 55% of the applied radioactivity after 367 hours of irradiation. 2,4-DNOP was an important product during the first 120 hours, accounting for 19.4% of the applied radioactivity, but declined to a level of 1.6% at 367 hours. The dark control samples showed no significant degradation until 120 hours of irradiation, and contained 76.4% of the applied radioactivity at 367 hours.

Another study was conducted to investigate the aqueous photolysis of 2,4- and 2,6-DNOPC and DNOP uniformly labelled in the phenyl ring ^{14}C- DNOPC and DNOP were added separately to sterile, aqueous pH 4 buffer solutions at a concentration of 50 µg/l. The test samples were irradiated continuously with a xenon arc for periods up to 10 hours, equivalent to 2.1 days of summer sunlight at 40º N, and maintained at 25 ± 1ºC . Control samples were incubated in the dark. Solutions containing DNOP were irradiated for periods of up to 96.1 hours equivalent to 19.3 days of summer sunlight at 40º N (Winwick, T. 1998b). Volatile radioactivity was trapped and solutions were analysed by HPLC.

The half-lives of the test substances were as follows.

Test Substance	Half-life, days
2,4-DNOPC	0.63
2,6-DNOPC	0.73
2,4-DNOP	8.71
2,6-DNOP	20.82

Two photodegradation products of DNOPC were identified as DNOP and CO_2. The cumulative amounts of $^{14}CO_2$ accounted for 5.2 and 5.1% of the applied radioactivity from 2,4-DNOPC and 2,6-DNOPC respectively. DNOP could not be quantified because it had a similar retention time to other photodegradation products. The only identified photodegradation product of DNOP was CO_2. Other products were not resolved by HPLC.

The aerobic aquatic degradation of dinocap was studied in two water/sediment systems containing sandy loam from two sites in the UK (BCH: Brown Carrick Hill and HB: Hinchigbrooke). The systems were incubated in the dark with 0.01 mg/l of [^{14}C]2,4-DNOPC at 20 ± 1ºC for periods up to 100 days with a humidified air flow maintained above the water but both sediments remaining anaerobic (Elsom *et al.*, 1993). The characteristics of the two systems are shown in Table 32.

Table 32. Water/sediment characteristics.

	BCH sandy loam system		HB sandy loam system	
	soil	water	soil	water
Sand, %	70.4		52.4	
Silt, %	24.0		38.4	
Clay, %	5.6		9.2	
OM, %	2.3		18.2	
CEC meq/100g	12.3		53.6	
Microbial biomass µgC/g	43 (a) 36 (b)		220 (a) 274 (b)	
pH	6.2	7.7	7.4	7.3
O_2, %				

	BCH sandy loam system		HB sandy loam system	
	soil	water	soil	water
under surface 5 cm above surface		98 95		66 58
Water source		ditch carrying hill catchment flow		pond

(a) at application (b) at the end of the study

Duplicate samples were taken at intervals and assayed for radioactivity by LSC. The aqueous phases were extracted with diethyl ether and the sediments successively with acetonitrile, methanol and dioxane before drying and treatment with NaOH to separate fulvic and humic acid fractions. The extracts were analysed by TLC. Volatile degradation products were collected. The results are shown in Table 33.

Table 33. Distribution of radioactivity in two sandy loam systems (Elsom *et al.*,1993).

Days incubation	% of applied radioactivity							
	BCH system				HB system			
	Water	Sediment	Traps	Total	Water	Sediment	Traps	Total
0	101.2 101.5	<LOD <LOD	-	101.2 101.5	99.9 100.3	0.3 0.6		100.2 100.9
1	87.6 91.3	9.6 5.1	<LOD	97.2 96.4	93.1 82.7	5.5 16.2	<LOD	98.6 98.9
2	94.1 92.5	5.1 1.5	<LOD	99.2 94.0	88.0 87.7	10.2 6.8	<LOD	98.2 94.5
7	72.4 55.8	19.8 26.5	<LOD 0.6	92.2 82.9	54.1 47.8	29.0 29.7	<LOD	83.1 77.5
14	48.4 56.9	30.4 26.0	1.3 0.4	80.1 83.3	32.5 30.4	56.6 55.1	0.4 1.4	89.5 86.9
21	41.0 57.7	30.4 30.0	1.6 1.3	73.0 89.0	44.4 52.0	43.9 43.4	2.0 0.9	90.3 96.3
30	43.0 46.9	41.2 45.1	1.1 0.6	85.3 92.6	18.2 13.9	63.2 81.3	2.2 2.7	83.6 97.9
61	14.2 13.2	47.4 65.0	8.2 8.7	69.8 86.9	7.1 15.9	82.9 57.0	4.4 5.2	94.4 78.1
100	11.8 9.2	40.7 47.5	13.3 13.5	65.8 70.2	6.5 6.4	78.4 68.0	5.0 8.6	89.9 83.0

No significant quantities of volatile radioactivity were recovered during the first 30 days of the study and no dinocap was detected at 60 or 100 days after treatment in either system. TLC analysis of the water samples indicated that dinocap was hydrolysed to DNOP and this was followed by binding of other water-soluble degradation products to the sediments. Approximate half-lives were calculated to be 7.3 and 4.1 days in the BCH and HB systems respectively.

Residues in rotational crops

Beans, oats and turnips were grown in soil plots which had been used the previous year for residue decline studies with [^{14}C]2,4-DNOPC on cucumbers (0.56 kg ai/ha) and squash (3 application at 0.56 kg ai/ha). Approximately 200 days after the application of [^{14}C]2,4-DNOPC to the cucumber and squash plots, they were rototilled and oats and turnips were sown. Beans were planted 250 days after the application of the DNOPC. All the rotational crops were allowed to grow to maturity. Samples were taken at various times during the growing season and at final harvest (Honeycutt and Garstka, 1976e).

Radioactive residues in all the samples were [0.02 mg/kg and in the final harvest samples [0.01 mg/kg.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Dinocap is a mixture of six dinitro-octylphenyl crotonates, three of 2,4-DNOPC and three of 2,6 isomers of 2,6-DNOPC. In each group the octyl substituents are mixtures of 1-methylheptyl, 1-ethylhexyl and 1-proylpentyl.

Crops. Methods have been developed for apples, grapes, cucumbers, peppers, peaches and melons, and processed commodities derived from them. All are similar: the crotonate isomers are converted to the corresponding phenols which are methylated. The analytical standards are 2,4-DNOPMe and 2,6-DNOPMe.

Samples are extracted with methanol by Soxhlet or maceration and hydrolysed with 1 N NaOH to convert the dinocap isomers to phenols. The methanolic solution is partitioned with hexane, the hexane fraction is discarded, and the methanol phase acidified with HCl and partitioned again with hexane. After solvent evaporation the residue is taken up in diethyl ether, methylated with diazomethane, and cleaned up by silica gel column chromatography. Quantification is by programmed temperature GLC with an ECD or NPD. The six peaks are measured separately and then combined to give a total peak height or area. The method was first described for apples (Brackett, 1991).

A confirmatory method for apples was validated using both EC and NP detectors. Modification included homogenization rather than Soxhlet extraction and scaled-down methylation with diazald rather than diazomethane. Samples were fortified with 0.05, 0.1, and 1.0 mg/kg of 2,4- and 2,6- dinocap. The LOD was 0.05 mg/kg. Recoveries by the ECD were 69 to 98% and by the NPD 60 to 101% (Howie, 1997).

In another validation study with various crops (Lees, 1997) a limit of determination of 0.05 mg/kg was achieved for grapes, wine and grape juice, apple purée and juice, strawberry preserve and jam, cucumbers and peppers. Recoveries from samples fortified at 0.05, 0.1 and 1 mg/kg with 2,4-DNOPC and 2,6-DNOPC were >70% in all the commodities at all fortification levels.

Another study was conducted in 1997 to evaluate the method for melons, peaches, tomatoes, canned tomatoes, tomato purée, ketchup and juice, peach preserve and juice, and apple pomace. Quantification was by GLC on a DB 608 capillary column with an ECD. The LOD in all the commodities was 0.05 mg/kg. Recoveries from samples fortified at 0.05, 0.1 and 1 mg/kg ranged from 71 to 109% (Lees, 1998i).

Water. Dinocap residues are extracted with methylene chloride. The crotonates are hydrolysed with 1 N NaOH, and the hydrolysate is neutralized with HCl, partitioned with ethyl acetate/hexane (1:1) and cleaned up on a silica gel column. Quantification is by HPLC on a C-18 column with UV detection at 265 nm. The reported LOD was 1 µg/l. The mean recovery from various types of water was 80.6 ± 6.0% at fortification levels of 1 to 10 µg/l (Burton, 1995a).

Soil. Dinocap residues are extracted from soil samples for one hour with acetone/methanol/4 N HCl (100:10:5). After adding NaCl and more HCl the extract is partitioned with hexane. The dinocap isomers

are converted to the phenols by hydrolysis in 4 N NaOH, the solution is neutralized and partitioned with hexane/ethyl acetate and cleaned up on a silica gel column. The phenol residues are determined by HPLC as above. The reported LOD was 0.1 mg/kg and the mean recovery at fortification levels of 0.1 and 1 mg/kg was 78% (Burton, 1995b).

Stability of residues in stored analytical samples

Grape and apple samples fortified with a mixture of 2,4-DNOPC and 2,6-DNOPC standard at 1 mg/kg . were stored at approximately -20ºC for 24 months in the dark, together with untreated controls. Analysis was by the method of Brackett (1991) with minor modifications. At intervals three stored control samples, two stored fortified samples and two freshly fortified control samples were analysed (Gillis, 1995). The results are shown in Table 34.

Table 34. Stability of dinocap in grapes and apples stored at –20 ± 5ºC (Gillis, 1995).

Days, storage	0	30	99	218	370	551	769
GRAPES							
Analytical recovery %	95.5	90	90	98	96.5	88.5	103
Residue remaining %	88.5	87.5	89.5	96.5	108	77	81.5
APPLES							
Analytical recovery %	93.5	90	93.5	97	71.5	81.5	102
Residue remaining %	87	85.5	72	68	58	68.5	60

There was only a very slight decrease of the residues in grapes after 24 months storage at -20ºC, but a more marked decrease in apples.

The stability of dinocap at levels of 1 mg/kg in cucumbers, tomatoes, peaches, apples and strawberries stored for 9 months in the dark at approximately -20ºC was determined. It was reported that the study would be continued for 24 months of storage (Lees, 1998j). The analytical method for apples was modified slightly by increasing the extraction solvent volumes to improve the extraction efficiency. The results, uncorrected for procedural recoveries are given in Table 35.

Table 35. Stability of dinocap in apples, cucumbers, peaches, tomatoes and strawberries.

Days storage	0-1	30-37	106-113	181-190	271-273
APPLES					
Analytical recovery %	82	91	87	91	93
Residue remaining %	81	89	81	107	105
CUCUMBERS					
Analytical recovery %	101	81	94	94	89
Residue remaining %	95	94	102	105	101
PEACHES					
Analytical recovery %	99	87	95	90	92
Residue remaining %	96	92	96	98	105
TOMATOES					
Analytical recovery %	102	85	93	72	86
Residue remaining %	94	96	107	82	97
STRAWBERRIES					

Days storage	0-1	30-37	106-113	181-190	271-273
Analytical recovery %	99	81	76	91	92
Residue remaining %	96	83	81	108	104

Definition of the residue

The results of metabolism studies showed that the dinocap isomers are readily hydrolysed to the corresponding phenols. The analytical methods used in residue trials quantify the residues of dinocap and their phenol metabolites as the methylated phenols and express the results as dinocap. The Meeting concluded that the residues should be defined as the sum of the dinocap isomers and dinocap phenols, expressed as dinocap, both for compliance with MRLs and for the estimation of dietary intake.

USE PATTERN

Dinocap is a contact fungicide used to control powdery mildew (*Unicicula neactor, Podosphaera or Sphaerotheca spp., Leveillula taurica and Erysphe cichoracearum*) on many crops, and is also used as a non-systemic acaricide. The printed labels indicate multiple applications but do not specify a maximum. It was reported to the Meeting that proposed changes in the PHIs are pending for stone fruits in Italy, Portugal and Spain, and for strawberries in Portugal and Spain. The registered uses are shown in Table 36 are those whose labels were submitted to the Meeting.

Table 36. Registered uses of dinocap.

Crop	Country	Form.	Application				PHI, days
			Field or greenhouse	kg ai/ha	kg ai/hl	No.	
Apples	Austria	WP	F	<0.27	0.022		21
	Austria	EC	F	<0.26	0.018		21
	Belgium	WP	F	<0.2-0.33	0.009-0.011		21
	Bulgaria	EC	F	0.18-0.26	0.018		21
	Czech Rep.	EC	F	0.26	0.018		35
	France	WP	F	0.18-0.27	0.018		28
	France	EC	F	0.17-0.26	0.0175		
	Greece	WP	F	0.33-0.42	0.016-0.021		20
	Greece	EC	F	0.35	0.018		20
	Hungary	EC	F	0.11-0.32	0.011-0.021		30
	Hungary	WP	F	0.11-0.32	0.011-0.022		30
	Israel	EC	F		0.007-0.014		21
	Italy	WP	F	0.35-0.42	0.018-0.021	3-6	20
	Italy	EC	F	0.35-0.42	0.018-0.021		20
	Morocco	WP	F		0.015-0.021		21
	Morocco	EC	F	0.16	0.018		21
	Poland	WP	F	0.41	0.04-0.08		21
	Portugal	EC	F	0.18	0.018		21
	Portugal	WP	F	0.18-0.22	0.018-0.021		21
	Rumania	EC	F	0.18-0.26	0.018		21
	Slovenia	EC	F	0.25-0.34	0.017-0.023		28
	Slovenia	WP	F	0.27-0.33	0.018-0.022		28
	Spain	WP	F	0.21-0.32	0.021		21
	Spain	EC	F	0.21-0.32	0.021		21
	UK	EC	F	0.39-0.49		<10	14

Crop	Country	Form.	Application				PHI, days
			Field or greenhouse	kg ai/ha	kg ai/hl	No.	
Apricot	France	WP	F	0.18-0.27	0.018		7
	France	EC	F	0.17-0.26	0.017		7
	Greece	WP	F	0.22-0.27	0.015-0.018		20
	Greece	EC	F	0.26-0.31	0.018-0.021		20
	Italy	WP	F	0.21-0.31	0.015-0.021		20
	Italy	EC	F	0.21-0.26	0.014-0.018		20
	Morocco	EC	F	0.26	0.018		21
	Morocco	WP	F	0.33	0.015-0.022		21
	Portugal	WP	F	0.15-0.18	0.015-0.018		21
	Spain	WP	F	0.21-<0.32	0.021		21
	Spain	EC	F	<0.32	0.021		21
Cucumbers	Belgium	WP	G	<0.2-0.33	0.013-0.022		
	Czech Rep	EC	F/G	0.21	0.014		7
	France	WP	F/G	0.18	0.018		3
	France	EC	F/G	0.17	0.018		3
	Greece	EC	F/G	<0.12-0.17	0.012-0.018		7
	Greece	WP	F/G	<0.1-0.18	0.01-0.018		7
	Hungary	EC	F/G	0.06-0.14	0.011-0.018		3 G 7 F
	Hungary	WP	F/G	0.05-0.14	0.009-0.018		3 G 7 F
	Israel	EC	F/G	0.26			7
	Italy	WP	F/G	0.1-0.18	0.01-0.018		7
	Italy	EC	F/G	0.12-0.18	0.012-0.018		7
	Morocco	EC	F/G	0.18	0.018		21
	Morocco	WP	F/G	0.073	0.014		21
	Poland	WP	F	0.11	0.018-0.02		4
	Portugal	WP	F/G	<0.09-0.15	0.009-0.015		7
	Portugal	EC	F/G	0.07-0.32	0.011-0.014		7
	Rumania	EC	F	0.11-0.14	0.018		7
	Slovakia	EC		0.21	0.014		7
	Slovenia	WP		0.15-0.18	0.015-0.018		42
	Spain	EC	F/G	0.21-0.63	0.011		7
	Spain	WP	F/G	0.11			7
Grapes	Austria	WP	F	<0.29	0.018		21
	Austria	EC	F	<0.28	0.018		21
	Czech Rep	EC	F	0.26	0.018		35
	France	WP	F	0.21	0.018		21
	France	EC	F	0.21	0.011-0.021		21
	Greece	WP	F	<0.1-0.18	0.01-0.018		20
	Greece	EC	F	<0.14-0.17	0.014-0.017		20
	Hungary	EC	F	0.18-0.28	0.018-0.028		30
	Hungary	WP	F	0.18	0.018		30
	Israel	EC	F	0.07-0.14	0.007-0.014		35
	Italy	WP	F	0.16-0.32	0.016-0.021		20
	Italy	EC	F	0.15-0.21	0.015-0.021		20
	Morocco	WP	F	0.11	0.015-0.021		
	Portugal	EC	F	0.18	0.0175		21
	Portugal	WP	F	<0.18-0.21	0.018-0.021		21
	Rumania	EC	F	0.18	0.018		21
	Slovakia	EC	F	0.26	0.018		35
	Slovenia	EC	F	0.15-0.19	0.015-0.019		42
	Spain	WP	F	0.21			21

Crop	Country	Form.	Application				PHI, days
			Field or greenhouse	kg ai/ha	kg ai/hl	No.	
	Spain	EC	F	0.21			21
Melons	Belgium	WP	G	<0.2-0.33	0.013-0.022		
	France	WP	F/G	0.18	0.018		3
	France	EC	F/G	0.16-0.17	0.017		3
	Greece	WP	F/G	<0.1-0.18	0.01-0.018		7
	Greece	EC	F/G	<0.12-0.17	0.012-0.018		7
	Italy	EC	F/G	0.18	0.011-0.018		7
	Italy	WP	F/G	0.18	0.011-0.018		7
	Morocco	EC	F	0.16	0.016		10
	Portugal	EC	F/G	0.07-0.32	0.007-0.011		7
	Portugal	WP	F/G	0.09-0.44	0.009-0.015		7
	Spain	EC	F/G	0.21-0.63	0.011		7
Nectarines	Greece	WP	F	<0.22-0.27	0.015-0.018		20
	Greece	EC	F	<0.26-0.31	0.018-0.021		20
	Italy	WP	F	0.21-0.31	0.015-0.021		20
	Italy	EC	F	0.21-0.26	0.014-0.018		20
	Spain	WP	F	0.32	0.021		21
	Spain	EC	F	<0.32	0.021		21
Peaches	France	WP	F	0.18	0.018		7
	France	EC	F	0.17-0.26	0.018		7
	Greece	WP	F	<0.22-0.27	0.015-0.018		20
	Greece	EC	F	<0.26-0.31	0.018-0.021		20
	Italy	WP	F	0.21-0.31	0.015-0.021		20
	Italy	EC	F	0.21-0.32	0.014-0.018		20
	Morocco	EC	F	0.26	0.018		
	Morocco	WP	F	0.33	0.015-0.021		
	Portugal	WP	F	0.15-0.18	0.015-0.018		21
	Portugal	EC	F	0.11-0.14	0.011-0.014		21
	Slovenia	EC		0.23-0.29	0.015-0.019		42
	Slovenia	WP		0.17-0.27	0.011-0.018		42
	Spain	WP	F	<0.32	0.021-0.026		21
	Spain	EC	F	<0.32	0.021-0.026		21
Peppers	Greece	EC	F/G	<0.12-0.17	0.012-0.018		7 G 20 F
	Morocco	WP	F/G	0.073	0.014-0.021		
	Morocco	EC	F/G	0.18	0.018		
	Portugal	WP	F/G	0.09-0.45	0.009-0.015		21
	Portugal	EC	F/G	0.07-0.32	0.007-0.011		21
	Spain	WP	F/G	0.11			7
	Spain	EC	F/G	0.21-0.32	0.011		7
Summer squash	Belgium	WP	G	<0.2-033	0.013-0.022		
	France	WP	F/G	0.18	0.018		3
	France	EC	F/G	0.17	0.017		3
	Israel	EC	F/G	0.26	0.014		7
	Italy	WP	F/G	0.1-0.18	0.01-0.018		7
	Italy	EC	F/G	0.12-0.18	0.012-0.018		7
	Morocco	EC	F	0.16	0.016		10
	Portugal	WP	F/G	0.09-0.15	0.009-0.015		7
	Spain	EC	F/G	0.21-0.63	0.011		7
Strawberries	Belgium	WP	F/G	0.2-0.33	0.013-0.022		21
	France	EC	F	0.16	0.016		3
	Morocco	EC	F	0.16	0.016		10
	Poland	WP	F	0.68	0.03		21

Crop	Country	Form.	Application				PHI, days
			Field or greenhouse	kg ai/ha	kg ai/hl	No.	
	Portugal	EC	F/G	0.09-0.11	0.009-0.011		21
	Spain	EC	F	0.32	0.021		7
	UK	EC	F	0.39	0.019	5	7
Tomatoes	Greece	EC	F/G	0.12-0.18	0.012-0.018		7 G 20 F
	Morocco	EC	F/G	0.18	0.018		14
	Morocco	WP	F/G	0.073	0.014-0.021		14
	Poland	WP	F	0.11	0.018-0.02		4
	Portugal	WP	F/G	0.09-0.44	0.009-0.015		21
	Portugal	EC	F/G	0.07-0.32	0.007-0.011		21
	Spain	EC	F/G	0.21-0.32	0.011		7
	Spain	WP	F/G	0.11			7

RESIDUES RESULTING FROM SUPERVISED TRIALS

Trials were carried out in Europe on a number of crops. The samples were analysed by the GLC method of Brackett (1991), with a reported LOD of 0.05 mg/kg. The results were not corrected for analytical recoveries unless noted. Analytical recoveries were generally >80%, so using corrected or uncorrected results should not significantly influence the interpretation.

Residues were generally quantified as the sum of the heights or areas of all six isomer peaks, but owing to interfering peaks present in some samples the sum of four or five peaks was used. Where the sum of the three 2,4- or 2,6-DNOPC peaks is below 0.05 mg/kg the residue of that group of isomers is recorded as <0.05 mg/kg irrespective of the total residue measured by summing the six peaks.

Apples. Trials were conducted on several varieties of apples in France, Greece, Italy and the UK from 1990 to 1997.

Two field trials were carried out on Golden Delicious and Red Chief apples at two locations in France in 1996. Dinocap was used at a rate of 0.021 kg ai/hl, with application intervals of 10 days and spray volume of 700-800 and 1500-2700 l/ha. Samples were stored frozen for 202-294 days before analysis (Lees, 1998c). The samples taken 14 days after the last application were processed into apple juice and apple purée. No dinocap residues were found in the processed commodities.

Summary information from four field trials in Italy, two in 1991 and two in 1993, was submitted. In the 1993 trials dinocap was applied 4 times to plots of 16 trees in spray volumes of 1500 l/ha at intervals of 21-28 days. The reported LOD was 0.04 mg/kg and recoveries were 70-102%.

In two other trials in Italy in 1996, dinocap EC was applied at the GAP rate, but with a higher number of applications. Each plot of 6 trees was sprayed at 2000 l/ha at intervals of 13-15 days. The sampling-to-analysis interval (SAI) ranged from 210 to 266 days. Recoveries were 77-88%.

In trials in Greece and Italy in 1997 (Sutcliffe, 1998a) the EC (350 g/l) or WP (18%) was sprayed 6 times on plots of 6 trees at intervals of 10-14 days and with spray volume of 1500 l/ha in Greece and 1150-1450 l/ha in Italy.

Several trials were conducted at various locations in the UK from 1990 to 1997. In four trials in 1990 the EC formulation was applied with an airblast or knapsack sprayer at a rate of 0.49 kg ai/ha, 3 to 7 applications at 12- to 24-day intervals. Samples were stored at -20ºC for 400 to 500 days before analysis. Residues decreased from 0.25-0.59 mg/kg on day 0 to [0.05 mg/kg at 14 days.

In six trials according to GAP in 1991, two on small plots and four on plots of 0.5-2 ha, 3 to 8 applications of the EC formulation were made at intervals of 6 to 21 days. Samples were stored at -20ºC for 60 days before analysis. In the two small-plot trials a normal xylene-based and a xylene-free formulation were compared. The xylene-based formulation was applied at the GAP rate of 0.49 kg ai/ha, the xylene-free formulation at 0.49 and 0.98 kg ai/ha. There was essentially no difference between the residue levels.

In two field trials in 1992 on plots of 4 trees the EC formulation was applied 11 or 12 times with a motorised knapsack sprayer at the GAP rate with spray volumes of 2000 l/ha, spraying to run-off, at intervals of 12-14 days. The final applications were made at 7-day intervals to fruit at a growth stage of 8-9 cm. Residues were quantified as the sum of the first four isomer peaks. Recoveries were 73-88%. The SAI was 10 days.

In 1997 the EC and WP formulations were each sprayed 10 times at 10-14 day intervals with a motorised knapsack sprayer. In trials T1 and T2 the spray volume was 1500 l/ha and in T3 and T4 500 l/ha. Samples were stored frozen before analysis for 58 to 194 days (Lees, 1998h). At day 0 the 2,4-DNOPC residues were higher than the 2,6-; at the GAP PHI of 14 days both groups were <0.05 mg/kg. Samples from two locations at 14 days PHI were processed to purée, juice and pomace.

The results of all the trials are shown in Table 37.

Table 37. Residues of dinocap in apples. Underlined residues are from treatments according to GAP.

Country, Location, Year	Application				PHI, days	Dinocap, mg/kg[1]			Ref.
	Form.	No	kg ai/ha	kg ai/hl		2,4 -	2,6 -	Total	
France 1996	EC	6	0.16-0.19	0.021	0	<0.05	<0.05	0.06	Lees, 1998c
					14	<0.05	<0.05	<0.05	
					21	n.d	n.d	<u><0.05</u>	
France 1996	EC	6	0.31-0.58	0.021	0	0.20	0.09	0.29	Lees, 1998c
					14	0.06	<0.05	0.09	
					21	<0.05	<0.05	<u><0.05</u>	
Greece, 1997	EC	6	0.31	0.021	0	0.35	0.17	0.52	Sutcliffe, 1998a
					14	<0.05	<0.05	<0.05	
					21	<0.05	<0.05	<u><0.05</u>	
Greece 1997	WP	6	0.32	0.021	0	0.32	0.12	0.45	
					14	<0.05	<0.05	0.07	
					21	<0.05	<0.05	<u><0.05</u>	
Italy 1991	EC	2	0.38	0.021	0	0.17	0.09	0.26	Pessina, 1993a
					18	<0.05	<0.05	<u><0.05</u>	
Italy 1991	EC	2	0.25	0.021	0	0.1	0.07	0.13	
					18	<0.05	<0.05	<u><0.05</u>	
Italy 1993	EC	4	<0.32	0.021	0			0.06	Pessina, 1993f
					20			<u><0.04</u>	
Italy 1993	EC	4	0.15-0.26	0.021	0			0.05	
					20			<u><0.04</u>	
Italy 1997	EC	6	0.31-0.42	0.021	0	0.21	0.10	0.31	Lees, 1998c

Country, Location, Year	Application				PHI, days	Dinocap, mg/kg[1]			Ref.
	Form.	No	kg ai/ha	kg ai/hl		2,4 -	2,6 -	Total	
					14	0.07	<0.05	0.11	
					21	0.07	<0.05	0.09	
Italy 1997	EC	6	0.31-0.42	0.021	0	0.26	0.11	0.37	
					14	0.05	<0.05	0.08	
					21	<0.05	<0.05	<0.05	
Italy 1997	EC	6	0.24-0.31	0.021	0	0.1	<0.05	0.15	Sutcliffe, 1998a
					14	n.d	n.d	<0.05	
					21	n.d	n.d	<0.05	
Italy 1997	WP	6	0.24-0.31	0.021	0	0.07	<0.05	0.1	
					14	<0.05	<0.05	<0.05	
					21	n.d.	n.d	n.d	
UK Cambs 1990	EC	4	0.49	0.088	0			0.43	Murray, 1992a
					5			0.24	
					7			0.2	
					10			0.21	
					17			<0.05	
UK Cambs. 1990	EC	7	<0.49	0.025	0			0.25	
					3			0.11	
					5			0.05	
					9			<0.05	
					14			<0.05[2]	
UK Essex 1990	EC	4	0.49	0.088	0			0.59	Murray, 1992a
					5			0.05	
					10			0.05	
					14			<0.05	
UK Essex 1990	EC	3	0.49	0.039	0			0.49	
					5			0.09	
					10			0.08	
					14			0.05	
UK Oxford 1991	EC	8	0.49	0.025	0			0.44	Murray, 1992c
					7			0.11	
					14			0.08	
			0.49	0.025	0			0.58	
					7			0.17	
					14			<0.05	
			<0.98	0.049	14			<0.05	
UK 1991	EC	6	0.49	0.088	0			0.31	Murray, 1992c
					14			<0.05	
UK 1991	EC	3	0.49	0.088	0			0.17	
					15			<0.05	
UK 1991	EC	8	<0.49	0.025	0			0.35	Murray, 1992c
					7			<0.05	with xylene
					14			<0.05	
			<0.49	0.025	0			0.37	Murray, 1992c
					7			0.06	without xylene.
					14			<0.05	
			<0.98	0.049	14			<0.05	
UK 1991	EC	5	0.25	0.29	4			0.14	

Country, Location, Year	Application				PHI, days	Dinocap, mg/kg[1]			Ref.
	Form.	No	kg ai/ha	kg ai/hl		2,4 -	2,6 -	Total	
					12			0.06	
UK 1991	EC	4	0.18	0.063	0			0.67	Murray, 1992c
					15			0.08	
UK 1992	EC	11	<0.49	0.025	0			0.13[3]	Murray, 1993
					14			<0.05[3]	
UK 1992	EC	12	<0.49	0.025	0			0.34[3]	
					14			0.11[3]	
UK Nottingham	EC	10	0.36-0.38	0.025	0	0.19	0.08	0.27	Lees, 1998h
1997 T 1					7	<0.05	<0.05	0.07	
					14	<0.05	<0.05	0.06	
	WP	10	0.36-0.38	0.025	0	0.15	0.06	0.21	
					7	0.08	<0.05	0.11	
					14	<0.05	<0.05	<0.05	
UK Kent	EC	10	0.37-0.38	0.025	0	0.18	0.09	0.27	Lees, 1998h
1997 T 2					7	<0.05	<0.05	<0.05	
					14	<0.05	<0.05	0.08	
	WP	10	0.36-0.38	0.025	0	0.22	0.1	0.32	
					7	0.06	<0.05	0.1	
					14	<0.05	<0.05	0.05	
UK Gloucester-shire	EC	10	0.46-0.5	0.098	0	0.2	0.1	0.3	Lees, 1998h
1997 T 3					7	<0.05	<0.05	0.05	
					14	<0.05	n.d	<0.05	
	WP	10	0.49-0.5	0.098	0	0.18	0.07	0.25	
					7	<0.05	<0.05	0.05	
					14	<0.05	<0.05	<0.05	
UK Kent	EC	10	0.49-0.51	0.098	14			0.08	Lees, 1998h
1997 T 4	WP	10	0.47-0.5	0.098	14			0.07	

[1] Calculated from the sum of 6 peaks unless otherwise stated
[2] Average of 4 replicates
[3] Sum of 4 peaks

Grapes. Several field trials were conducted on grapes in France, Germany, Greece, Italy and Portugal representing northern and southern European regions.

Three field trials were carried out in France and six in Portugal in 1991. Only summary data were submitted. Samples were first analysed by a method that quantified only the parent compound and then re-analysed (Conraux, 1993d) by the method of Brackett (1991).

In a field trial in France in 1992 residues were determined in Merlot grapes, must and wine after 6 applications at 0.21 kg ai/ha (Conraux, 1993m). The reported LOD was 0.04 mg/kg and the recovery 78.5 ± 12.4 %. Grape samples were stored at -18ºC for 90 days before analysis. Residues in the must and wine were below the LOD.

In two field trials in Southern France in 1996 the EC formulation was applied 6 times almost to run-off to Ugni Blanc and Syrah grapes by knapsack sprayer at intervals of 10-14 days. The interval

before the last application was 7 days. The first applications were made 12 weeks before mid-normal commercial harvest. Samples harvested 0, 14 and 21 days after the last application were stored frozen for 240-270 days before analysis (Lees, 1998b).

In 1997 in Northern France and Germany different wine grape varieties were treated eight times with the EC or WP formulations at 10-14 day intervals at 0.021 kg/hl, the first treatment at a growth stage 6-7 leaves unfolded and the last at the beginning of ripening. The SAI ranged from 57 to 127 days (Fielden 1998a). Recoveries ranged from 70 to 107%. It was reported that processing studies with grapes from these trials were in progress.

Residues of dinocap were determined in grapes, grape juice, and young and mature wine at two locations in Germany in 1996. The EC formulation was applied eight times by motorised knapsack sprayer at intervals of 10 to 16 days. Residues of 2,4-dinocap were higher than those of 2,6-dinocap at all time (Lees, 1998a)

In two trials in 1997 in Greece plots of grapes (1 row of 14.4m /plot) were sprayed six times with the EC or WP formulations in volumes of 1500 l/ha at intervals of 10 days (14 days before the last treatment). Harvested samples were stored frozen for 36-57 days before analysis (Sutcliffe, 1998b).

Five field trials were carried out at different locations in Italy in 1993 and grapes were vinified in two of them. The reported LOD was 0.05 mg/kg and recoveries >90%. Details were not reported (Pessina, 1993e).

In two trials at two locations in Italy in 1992 on two grape varieties and their processed products there were 6 applications to plots of 90 plants starting at the pre-flowering stage at intervals of 17-22 days. Samples were stored at -20ºC for approximately 3 months. The reported LOD was 0.04 mg/kg (Pessina, 1993g).

In 1993 four trials were conducted in Italy with dinocap WP and EC. Six sprays were applied from flowering to pre-ripeness at intervals of 10 to 22 days. Dinocap was applied at high volume (1000-1500 l/ha) with a knapsack sprayer to two wine varieties in plots of 46-52 plants. Samples harvested at maturity were analysed with a reported LOD of 0.04 mg/kg and recoveries of 103-114%. The SAI was 140-150 days (Pessina, 1994e).

In two trials in Italy in 1996 the EC formulation was applied almost to run-off 6 times to Chardonnay and Riesling vines by a knapsack sprayer at intervals of 10-14 days (7 days before the last application). The first applications were 12 weeks before mid-normal commercial harvest (pea-size berries). Samples taken 0, 14 and 21 days after the last application were stored frozen for 240-270 days before analysis (Lees, 1998b).

In other trials in Italy in 1997 on different varieties of wine grapes the EC and WP formulations were applied to plots of 8-14 plants six times at intervals of 10-14 days. Samples were stored at -18ºC for 60-178 days before analysis (Sutcliffe, 1998b).

In two trials in Portugal in 1992 the EC formulation was applied at 0.18 kg ai/ha to triplicate plots of 10 plants. Samples were stored at -18ºC before analysis for 83 days. The reported LOD was 0.04 mg/kg and the mean recovery 79.3 ± 12% (Conraux, 1993g).

A residue decline trial was carried out in Portugal in 1992, with 1 or 2 applications at 0.18 kg ai/ha, the first at the beginning of the colour change of the grapes. Samples were stored at -18ºC for 84

days before analysis. The reported LOD was 0.04 mg/kg and the mean recovery 76.8%. Residues decreased from 1.65 mg/kg at 0 day to <0.04 mg/kg after 28 days (Conraux, 1993h). The results were corrected for recovery.

Five trials were conducted in Spain in 1991. The EC formulation (350 g/l), dinocap (325 g/l) + myclobutanil (75 g/l), and dinocap (160 g/l) + fenbuconazole (75g/l) formulations were applied to table grapes. Samples were stored at -18ºC for 40 days before analysis. The analytical method quantified only the total diphenyl crotonates. The reported LOD was 0.02 mg/kg and the recovery 90%.

The results are shown in Table 38.

Table 38. Residues of dinocap in grapes. Underlined residues are from treatments according GAP.

Country, Year	Application				PHI, days	Dinocap, mg/kg			Ref.
	Form	No.	kg ai/ha	kg ai/hl		2,4-	2,6-	Total	
France 1991	EC	8	0.096	0.019	45			<0.02	Conraux, 1993d
	EC	7	0.096	0.48	46			<0.02	Conraux, 1993d
	EC	10	0.21	0.11	21			<0.04	
France South 1992	EC	6	0.21		14			0.1 (0.07-0.13)	Conraux, 1993m
France South 1992	EC	6	0.21		14			0.1	Conraux, 1994b
France South 1996	EC	6	0.17-0.21	0.021	0	0.14	0.08	0.22	Lees, 1998b
					14	<0.05	<0.05	<0.05	
					21	<0.05	<0.05	<u><0.05</u>	
France South 1996	EC	6	0.15-0.16	0.021	0	0.05	<0.05	0.08	Lees, 1998b
					14	n.d.	<0.05	<0.05	
					21	<0.05	n.d.	<u><0.05</u>	
France North 1997	EC	8	0.06-0.22	0.021	0	0.64	0.3	0.94	Fielden, 1998a
T 1					7	0.21	0.12	0.33	
					14	0.20	0.12	0.32	
					21	0.09	0.05	<u>0.14</u>	
					28	0.14	0.08	0.22	
France North 1997	EC	8	0.08-0.34	0.021	0	1.31	0.75	2.06	Fielden, 1998a
T 2					7	0.58	0.34	0.92	
					14	0.43	0.25	0.68	
					21	0.26	0.16	<u>0.42</u>	
					28	0.20	0.13	0.33	
France North 1997	EC	8	0.06-0.22	0.021	0	0.82	0.4	1.22	Fielden, 1998a
T 3					7	0.37	0.22	0.59	
					14	0.23	0.12	0.35	
					21	0.22	0.13	<u>0.35</u>	
					28	0.14	0.08	0.22	
France North 1997	EC	8	0.09-0.34	0.021	0	1.02	0.48	1.50	Fielden, 1998a
T 4					7	0.51	0.29	0.80	
					14	0.31	0.16	0.47	
					21	0.37	0.22	<u>0.59</u>	

Country, Year	Application				PHI, days	Dinocap, mg/kg			Ref.
	Form	No.	kg ai/ha	kg ai/hl		2,4-	2,6-	Total	
					28	0.27	0.17	0.44	
France North 1997	WP	8	0.07-0.22	0.021	0	0.62	0.31	0.94	Fielden, 1998a
T 1					7	0.31	0.17	0.48	
					14	0.15	0.08	0.23	
					21	0.14	0.08	0.22	
					28	0.18	0.09	0.27	
France North 1997	WP	8	0.08-0.34	0.021	0	1.38	0.64	2.02	Fielden, 1998a
T 2					7	0.78	0.4	1.18	
					14	0.49	0.29	0.78	
					21	0.32	0.18	0.50	
					28	0.28	0.16	0.44	
France North 1997	WP	8	0.06-0.21	0.021	0	0.74	0.37	1.11	Fielden, 1998a
T 3					7	0.46	0.26	0.72	
					14	0.25	0.14	0.39	
					21	0.17	0.11	0.28	
					28	0.18	0.10	0.28	
France North 1997	WP	8	0.08-0.34	0.021	0	0.70	0.27	0.97	Fielden, 1998a
T 4					7	0.46	0.19	0.65	
					14	0.38	0.20	0.58	
					21	0.14	0.08	0.22	
					28	0.28	0.15	0.43	
Germany 1996	EC	8	0.08-0.42	0.021	0	1.30	0.67	1.97	Lees, 1998a
T 1					7	0.96	0.56	1.52	
					14	0.40	0.25	0.65	
					21	0.41	0.25	0.66	
					28	0.26	0.16	0.42	
Germany 1996	EC	8	0.20-0.35	0.063	0	1.16	0.60	1.76	Lees, 1998a
T 2					7	0.63	0.40	1.03	
					14	0.46	0.28	0.74	
					21	0.40	0.27	0.67	
					28	0.28	0.18	0.46	
Germany 1996	EC	8	0.09-0.33	0.021	0	0.82	0.48	1.30	Lees, 1998a
T 3					7	0.5	0.32	0.82	
					14	0.33	0.22	0.55	
					21	0.20	0.13	0.33	
					28	0.27	0.19	0.46	
Germany 1997	EC	8	0.08-0.34	0.021	0	0.45	0.23	0.68	Fielden, 1998a
T 1					7	0.45	0.25	0.70	
					14	0.20	0.12	0.32	
					21	n.d..	n.d.	n.d.	
					28	0.11	0.07	0.18	
Germany 1997	EC	8	0.08-0.34	0.021	0	1.07	0.67	1.74	Fielden, 1998a
T 2					7	0.29	0.21	0.50	
					14	0.26	0.15	0.41	

Country, Year	Application				PHI, days	Dinocap, mg/kg			Ref.
	Form	No.	kg ai/ha	kg ai/hl		2,4-	2,6-	Total	
					21	0.13	0.09	0.22	
					28	0.09	0.05	0.14	
Germany 1997	WP	8	0.09-0.34	0.021	0	0.86	0.43	1.29	Fielden, 1998a
T 1					7	0.51	0.28	0.79	
					14	0.23	0.13	0.36	
					21	0.16	0.1	0.26	
					28	0.12	0.07	0.19	
Germany 1997	WP	8	0.08-0.34	0.021	0	1.03	0.69	1.72	Fielden, 1998a
T 2					7	0.40	0.22	0.62	
					14	0.32	0.17	0.49	
					21	0.24	0.12	0.36	
					28	0.15	0.07	0.22	
Greece 1997	EC	6	0.31	0.021	0	0.74	0.44	1.18	Sutcliffe, 1998b
					14	0.07	0.06	0.13	
					21	0.10	0.10	0.20	
Greece 1997	WP	6	0.32	0.021	0	0.80	0.41	1.21	Sutcliffe, 1998b
					14	0.14	0.10	0.24	
					21	0.06	0.05	0.11	
Italy 1991	EC	7	0.175	0.06	0			0.20	Pessina, 1993e
					32			<0.05	
Italy 1991	EC	5	0.16	0.018	0	0.36	0.74	1.10	Pessina, 1993e
					20	0.13	0.17	0.30	
Italy 1991	EC	3	0.18	0.06	54	<0.05	<0.05	<0.05	Pessina, 1993e
Italy 1991	EC	5	018	0.018	0	0.09	0.21	0.30	Pessina, 1993e
					20	<0.05	<0.05	<0.05	
					40	<0.05	<0.05	<0.05	
					60	<0.05	<0.05	<0.05	
Italy 1991	WP	7		0.11	32			<0.05	Pessina, 1993e
Italy 1992	EC	6	0.27-0.31	0.018	0			0.26	Pessina, 1993g
					20			<0.04	
Italy 1992	EC	6	0.17-0.21	0.018	0			0.27	Pessina, 1993g
					20			<0.04	
Italy 1993	WP	6	0.17-0.26	0.022	0			0.30	Pessina, 1994e
					20			<0.04	
Italy 1993	EC	6	0.24-0.32	0.021	0			0.65	Pessina, 1994e
					20			<0.04	
Italy 1993	WP	6	0.25-0.33	0.022	0			0.54	Pessina, 1994e
					20			<0.04	
Italy 1993	EC	6	0.16-0.24	0.021	0			0.34	Pessina, 1994e
					20			<0.04	
Italy 1996	EC	6	0.21-0.32	0.021	0	0.31	0.16	0.47	Lees, 1998b
					14	0.05	<0.05	0.09	
					21	0.05	<0.05	0.08	
Italy 1996	EC	6	0.21-0.32	0.021	0	0.38	0.23	0.61	Lees, 1998b
					14	0.06	<0.05	0.09	
					21	0.06	<0.05	0.09	
Italy 1997	EC	6	0.21-0.32	0.021	0	0.17	0.10	0.27	Sutcliffe, 1998b
T 1					14	n.d.	n.d.	<0.05	
					21	n.d.	n.d.	<0.05	
Italy 1997	WP	6	0.22-0.32	0.021	0	0.31	0.13	0.44	Sutcliffe, 1998b

Country, Year	Application				PHI, days	Dinocap, mg/kg			Ref.
	Form	No.	kg ai/ha	kg ai/hl		2,4-	2,6-	Total	
T 1					14	n.d.	n.d.	<0.05	
					21	n.d.	n.d.	<0.05	
Italy 1997	EC	6	0.22-0.32	0.021	0	0.39	0.2	0.59	Sutcliffe, 1998b
T 2					14	0.1	0.05	0.15	
					21	0.06	0.05	0.11	
Italy 1997	WP	6	0.2-0.32	0.021	0	0.54	0.21	0.75	Sutcliffe, 1998b
T 2					14	<0.05	<0.05	<0.05	
					21	n.d.	n.d.	n.d.	
Italy 1997	EC	6	0.21-0.32	0.021	0	0.3	0.19	0.49	Sutcliffe, 1998b
T 3					14	0.18	0.11	0.29	
					21	n.d.	n.d.	<0.05	
Italy 1997	WP	6	0.21-0.32	0.021	0	0.19	0.09	0.28	Sutcliffe, 1998b
T 3					14	<0.05	<0.05	<0.05	
					21	<0.05	<0.05	<0.05	
Portugal 1991	EC	1	0.18	0.073	0			<0.04 [1]	Conraux, 1993d
					7			0.15	
					14			<0.04	
Portugal 1991	EC	2	0.18	0.073	0			2.1 [2]	Conraux, 1993d
					7			0.28	
					14			0.05	
					22			<0.02	
Portugal 1991	EC	1	0.18	0.073	0			0.62	Conraux, 1993d
					7			0.07	
					14			0.06	
					22			<0.04	
Portugal 1991	EC	8	0.18	0.073	14			<0.04 [1]	Conraux, 1993d
Portugal 1991	EC	7	0.18	0.073	15			<0.04 [1]	Conraux, 1993d
Portugal 1992	EC	1	0.18	0.073	0			0.79	Conraux, 1993g
					7			0.06	
					14			0.06	
					21			0.06	
					28			<0.04	
		2	0.18	0.073	0			0.22	
					7			0.06	
					14			<0.04	
					21			<0.04	
					28			<0.04	
Portugal 1992	EC	1	0.18	0.073	0			0.93	Conraux, 1993h
					7			0.33	
					14			0.2	
					21			0.2	
					28			<0.04	
		2	0.18	0.073	0			1.65	
					7			0.36	
					14			0.08	
					21			0.3	
					28			<0.04	
Spain 1991	EC	7	0.065-0.21	0.028	36			<0.02	Jousseaume, 1993a
Spain 1991	EC	7	0.065-0.73	0.028	35			<0.02	
Spain 1991	EC	6	0.1-0.66		36			<0.02	

Country, Year	Application				PHI, days	Dinocap, mg/kg			Ref.
	Form	No.	kg ai/ha	kg ai/hl		2,4-	2,6-	Total	
Spain 1991	EC	6	0.1-0.66		35			<0.02	
Spain 1991	EC	1	0.26	0.021	0			<0.02	
					14			<0.02	
					22			<0.02	
					28			<0.02	

[1] Re-analysed
[2] Not re-analysed

Strawberries. Several trials were conducted in France, Italy, Spain and the UK.

Summary data were submitted from two field trials in France in 1991, where the EC formulation was applied to two 5 m plots of strawberries (two varieties) with spray volumes of 400-500 l/ha at intervals of 7 days, starting at flowering. Samples were stored frozen for 13 months before analysis. The reported LOD was 0.04 mg/kg and the mean recovery 74.9% (Conraux, 1993b).

A trial was carried out in France in 1992 where dinocap was applied 6 times to a plot of 80 plants, with spray volumes of 500 l/ha and application intervals of 7 days. Samples were stored at -18ºC for 57 days before analysis. The reported LOD was 0.05 mg/kg and the mean recovery 69.7% (Conraux, 1993n)

In field trials in Southern France in 1996 at different locations and on different varieties the EC formulation was applied with the first application at flowering and the last application when most fruit were ripe. Strawberry plots (52 to 72 m^2) were sprayed with 400 to 900 l/ha at intervals of 10-14 days. Samples harvested 0, 3 and 7 days after the last treatment were stored at -20ºC up to 398 days before analysis (Lees, 1998d).

In indoor trials in Italy in 1997 the EC and WP formulations were applied 4 times at rates of 0.16 to 0.33 kg ai/ha. Samples were harvested 0, 3 and 7 days after the last treatment. Residues decreased from 1.57 mg/kg at day 0 to 0.08 mg/kg at day 7. Since detailed reports of the trials were not submitted the results were not evaluated.

Two field trials were conducted in Spain (Gerona) in 1992, where a 4 m^2 strawberry plot was treated with one and two applications of the EC formulation at 0.26 kg ai/ha, starting at the mature growth stage with a 7-day application interval and spray volumes of 800 l/ha. Samples were stored at -18ºC for 112 days before analysis (Conraux, 1993i).

Two small-plot trials and two growers trials with 5-7 applications were carried out in the UK in 1990, the first (T.1) with application intervals of 12-38 days and a spray volume of 250 l/ha, the second with application intervals of 11 to 25 days, and the third and fourth with intervals of 4 to 18 days. The spray volume in the last three trials was 2000 l/ha. Samples were stored for about 16 months at -18ºC before analysis with an LOD of 0.05 mg/kg and mean recovery of 80% (Murray, 1992b).

Four small field trials on 30 m^2 plots in the UK in 1993 were with EC and WP treatments at rates of 0.49 kg ai/ha and 0.98 kg ai/ha, at intervals of 10-14 days and spray volumes of 500 l/ha. Samples were stored at -18ºC for 3-4 months before analysis by GLC with an ECD (Murray, 1994).

In another two field trials at two locations in the UK in 1996 the EC formulation was applied to strawberry plots (each 4 rows of 150 m) starting at flowering at intervals of 10 days with spray volumes of 1200-1600 l/ha. Samples were taken 0 and 3 days after the last treatment and stored at -18ºC for a maximum of 362 days before analysis. Samples from day 3 were processed to jam and preserves (Lees, 1998f).

The results are shown in Table 39.

Table 39. Residues of dinocap in strawberries. Underlined residues are from trials according to GAP.

Country Year	F/G	Application				PHI, days	Dinocap, mg/kg			Reference, Comments
		Form.	No.	kg ai/ha	kg ai/hl		2,4-	2,6-	Total	
France 1991	F	EC	7	0.18	0.044	0			0.18	Conraux, 1993b
						3			<0.04	re-analysed samples
						7			<0.04	
France 1991	F	EC	6	0.18	0.035	0			0.18	
						3			0.06	
						7			<0.04	
France 1992	F	EC	6	0.18	0.035	0			0.36	Conraux, 1993n
						3			0.16	
						7			0.06	
France 1996	F	EC	6	0.09-0.12	0.021	0	0.19	0.1	0.28	Lees, 1998d
T 1						3	<0.05	<0.05	0.05	
South						7	<0.05	<0.05	<0.05	
France 1996	F	EC	6	0.09-0.12	0.021	0	0.18	0.09	0.27	Lees, 1998d
T 2						3	<0.05	<0.05	0.05	
South						7	<0.05	<0.05	<0.05	
France 1996	F	EC	6	0.08-0.2	0.021	0	0.14	0.06	0.21	Lees, 1998d
T 3						3	0.05	<0.05	0.06	
						7	<0.05	<0.05	<0.05	
France 1996	F	EC	6	0.16-0.2	0.021	0	0.3	0.29	0.59	Lees, 1998d
T 4						3	0.22	0.1	0.33	
						7	0.08	<0.05	0.11	
Italy 1997	G	EC	4	0.31-0.32	0.021	0	0.9	0.39	1.29	No report submitted
						3	0.99	0.39	1.38	
						7	0.72	0.35	1.06	
Italy 1997	G	EC	4	0.16-0.23	0.021	0	0.28	0.11	0.4	
						3	0.12	0.06	0.19	
						7	0.07	<0.05	0.1	
Italy 1997	G	WP	4	0.24-0.33	0.021	0	1.13	0.44	1.57	
						3	0.94	0.42	1.36	No report submitted
						7	0.6	0.26	0.86	
Italy 1997	F	WP	4	0.16-0.23	0.021	0	0.34	0.14	0.47	No report submitted
						3	0.12	0.06	0.18	
						7	0.05	<0.05	0.08	
Spain 1992	F	EC	1	0.26	0.033	0			0.42	Conraux, 1993i

Country Year	F/G	Application				PHI, days	Dinocap, mg/kg			Reference, Comments
		Form.	No.	kg ai/ha	kg ai/hl		2,4-	2,6-	Total	
						7			<0.04	
						13			<0.04	
			2	0.26	0.033	0			0.32	
						7			<0.04	
						13			<0.04	
UK 1990 T 1	F	EC	5	0.21	0.084	5			<0.05	Murray, 1992b
						8			<0.05	Grower trial
						12			<0.05	
						15			<0.05	
UK 1990 T 2	F	EC	7	<0.49	0.024	3			0.58	Murray, 1992b
						6			0.31	Grower trial
						13			0.11	
						16			0.05	
UK 1990 T 3	F	EC	6	<0.49	0.024	0			1.66	Murray, 1992b
						5			0.24	
						8			0.08*	*average of 4 analyses
						15			0.05	
						18			<0.05	
UK 1990 T 4	F	EC	6	<0.49	0.024	0			1.05	Murray, 1992b
						4			0.25	
						7			0.09	
						14			<0.05	
						17			<0.05	
UK 1993 T 1	F	EC	5	0.49	0.1	0			0.79	Murray, 1994
						3			0.32	
						7			0.14	
						14			<0.05	
	F	EC	5	0.98	0.2	0			2.31	
						7			0.37	
UK 1993	F	WP	5	0.49	0.1	0			0.76	Murray, 1994
T 1						7			0.33	
		WP	5	0.98	0.2	0			2.56	
						7			0.44	
UK 1993	F	EC	5	0.49	0.1	0			0.26	Murray, 1994
T 2						3			0.19	
						7			0.06	
						14			<0.05	
UK 1993	F	WP	5	0.49	0.1	0			0.1	
T 2						7			<0.05	
UK 1993	F	EC	5	0.49	0.1	0			0.85	Murray, 1994
T 3						3			0.58	
						7			0.21	
						14			0.06	
UK 1993	F	WP	5	0.49	0.1	0			0.67	
T 3						7			0.06	
UK 1993										
T 4	F	EC	5	0.49	0.1	0			1.53	Murray, 1994

Country Year	F/G	Application				PHI, days	Dinocap, mg/kg			Reference, Comments
		Form.	No.	kg ai/ha	kg ai/hl		2,4-	2,6-	Total	
						3			0.9	
						7			0.32	
						14			0.13	
UK 1993	F	EC	5	0.49	0.1	0			0.67	
T 4						7			0.06	
UK 1996	F	EC	6	0.32-0.41	0.027	0	0.34	0.17	0.5	Lees, 1998f
						3	0.15	0.08	0.23	
UK 1996	F	EC	6	0.37-0.44	0.027	0	0.5	0.24	0.74	
						3	0.2	0.11	0.31	

Apricots. A single field trial was conducted in Italy in 1995, where a plot of 6 trees was sprayed 4 times with the EC formulation at a rate of 0.021 kg ai/hl at 14-day intervals with spray volumes of 1000-1500 l/ha. Samples were stored for approximately 11 months before analysis. The results are shown in Table 40 (Pessina, 1995).

Peaches. In a field trial in Greece in 1997 the EC formulation was applied four times on plots of 6 trees at intervals of 10-14 days. Samples were stored at -20ºC for 126-153 days before analysis (Sutcliffe, 1998d).

Trials were conducted at two locations in Italy in 1991 on plots of 28 trees. Only a summary of these trials was reported (Pessina, 1993d).

Trials in Italy in 1992 on 10-tree plots of two varieties of peaches were with 3 applications of the EC formulation by knapsack sprayer with 15-day application intervals and spray volumes of 1500 l/ha. The first application was to fruit of 6 cm diameter and the last at pre-ripening. Samples were stored at -20ºC for 6 months before analysis (Pessina 1993j).

In another field trial in Italy in 1993 4 applications of the EC or WP formulation were made to plots of 9 plants, variety Maria Bianca, with spray volumes of 1000-1200 l/ha and application intervals of 7 days. The first application was made to nut-sized fruit and the last to fully grown peaches. Samples were taken 0, 7 and 14 days after the last treatment and were stored at -20ºC for 6 months before analysis. The fruit without stones were analysed but the results were expressed on a whole-fruit basis (Pessina, 1994d).

In trials on three peach varieties at three different locations in Italy in 1997 dinocap was applied to plots of 8 trees four times during the growing season by backpack lance sprayer at a rate of 0.021 kg ai/hl (1200-1500 l/ha) at intervals of 10-14 days. Samples were stored at -20ºC for 66 to 163 days before analysis. Residues were expressed on the whole fruit including stone. Samples from day 14 were processed to juice and preserve. The reported LOD was 0.05 mg/kg and recoveries were 81-95% (Sutcliffe, 1998d).

Trials in Spain in 1992 were with 1 or 2 applications of the EC formulation at a rate of 0.026 kg ai/hl to plots of 3 trees with spray volumes of 1000 l/ha. Samples were stored at -18ºC for 114 days before analysis. The reported LOD was 0.04 mg/kg and the mean recovery 83.5 ± 13.7%.

The results are shown in Table 40.

Table 40. Residues of dinocap in stone fruits. Underlined residues are from trials according to GAP.

CROP Country Year	Application				PHI, days	Dinocap, mg/kg			Reference Comments
	Form	No	kg ai/ha	kg ai/hl		2.4-	2.6-	Total	
APRICOTS									
Italy 1995	EC	4	0.31	0.021	0			0.21	Pessina, 1995a
					3			<0.04	
					7			0.05	
					14			<0.04	
					21			<u>0.04</u>	
PEACHES									
Greece 1997	EC	4	0.27-0.31	0.021	0	0.45	0.2	0.66	Sutcliffe, 1998d
					3	0.26	0.15	0.41	
					7	0.19	0.11	0.3	
					14	0.05	<0.05	0.09	
					21	<0.05	<0.05	<u>0.05</u>	
Italy 1991	EC	4	<0.35	0.018	7	<0.04	<0.04	<u>0.04</u>	Pessina, 1993d
					14	<0.04	<0.04	<0.04	
					27	<0.04	<0.04	<0.04	
					38	<0.04	<0.04	<0.04	
Italy 1991	EC	4	<0.26	0.018	0	0.12	0.06	0.18	Pessina, 1993d
					7	<0.04	<0.04	<0.04	
					20	<0.04	<0.04	<u>0.04</u>	
					30	<0.04	<0.04	<0.04	
Italy 1992	EC	3	<0.26	0.018	0			0.12	Pessina, 1993j
					15			<0.04	
Italy 1992	EC	3	<0.26	0.018	0			0.08	Pessina, 1993j
					15			<0.04	
Italy 1993	WP	4	0.2	0.018	0			0.21	Pessina, 1994d
					7			<u>0.04</u>	
					14			<0.04	
Italy 1993	EC	4	0.22	0.018	0			0.18	Pessina, 1994d
					7			<u>0.04</u>	
					14			<0.04	
Italy 1997	EC	4	0.25-0.32	0.021	0	0.18	0.09	0.27	Sutcliffe, 1998d
					3	0.09	0.05	0.14	
					7	0.05	<0.05	<u>0.09</u>	
					14	n.d.	n.d.	n.d.	
					21	n.d.	n.d.	n.d.	
Italy 1997	EC	4	0.25-0.32	0.021	0	0.29	0.15	0.44	Sutcliffe, 1998d
					3	<0.05	<0.05	0.05	
					7	<0.05	<0.05	<u>0.05</u>	
					14	n.d.	n.d.	<0.05	
					21	n.d.	n.d.	n.d.	
Italy 1997	EC	4	0.26-0.32	0.021	0	0.23	0.1	0.33	Sutcliffe, 1998d
					3	0.06	<0.05	0.09	
					7	<0.05	<0.05	<u>0.05</u>	
					14	<0.05	<0.05	<0.05	
					21	n.d.	n.d.	n.d.	
Spain 1992	EC	1	0.26	0.026	0			0.27	Conraux, 1993j
					15			<0.04	

CROP Country Year	Application				PHI, days	Dinocap, mg/kg			Reference Comments
	Form	No	kg ai/ha	kg ai/hl		2.4-	2.6-	Total	
					22			<0.04	
					29			<0.04	
		2	0.26	0.026	0			0.71	
					15			0.24	
					22			0.05	
					29			<0.04	

Cucumbers. Two protected field trials were carried out in Southern France in 1996, where the EC formulation was sprayed 6 times on cucumber plots (8-9.5 x 10 m) almost to run-off at intervals of 10-11 days. The first applications were made when the first flowers opened or first fruits developed, and the last near ripening. The SAIs were 327-341 days (Lees, 1998e).

Protected field trials were conducted with dinocap EC in Spain in 1993 and 1996. In 1993 plants were treated with 3 sprays at a rate of 0.39 kg ai/ha, with spray volumes of 1200-2030 l/ha and application intervals of 7 days. Samples were taken 0, 3, 7 and 14 days after the last treatment. No residues above the LOD (0.04 mg/kg) were detected in any of the samples. Samples were stored at -18ºC for 42 days before analysis (Jousseaume, 1994a). In 1996 3-3.8 x 10 m plots were sprayed 5 or 6 times almost to run-off at intervals of 10-14 days, from flowers developing to fruits developing. Samples were stored for 305-348 days before analysis. The reported LOD was 0.05 mg/kg and the mean recovery 84-88% (Lees 1998e).

The results are shown in Table 41.

Table 41. Residues of dinocap in cucumbers from protected trials. Underlined residues are from trials according to GAP.

Country Year	Application				PHI, days	Dinocap, mg/kg			Ref.
	Form	No.	kg ai/ha	kg ai/hl		2,4-	2,6-	Total	
France 1996	EC	6	0.14-0.21	0.021	0	<0.05	<0.05	0.05	Lees, 1998e
					3	<0.05	n.d	<u><0.05</u>	
					7	n.d.	n.d.	n.d.	
France 1996	EC	6	0.16-0.18	0.021	0	<0.05	<0.05	<0.05	Lees, 1998e
					3	<0.05	n.d.	<u><0.05</u>	
					7	n.d.	n.d.	n.d.	
Spain 1993	EC	3	0.39	0.019	0			<0.04	Jousseaume 1994b
					3			<0.04	
					7			<u><0.04</u>	
					14			<0.04	
		2	0.39	0.019	7			<0.04	
Spain 1996	EC	6	0.28-0.63	0.021	0	0.07	<0.05	0.09	Lees, 1998e
					3	<0.05	<0.05	0.05	
					7	<0.05	<0.05	<u><0.05</u>	
Spain 1996	EC	5	0.47-0.74	0.021	0	0.05	<0.05	0.08	Lees, 1998e
					3	0.05	<0.05	0.08	
					7	n.d	n.d.	n.d.	

<u>Melons</u>. In two trials in France in 1993 the EC or WP formulation was applied four times to triplicate plots (10 m^2) with spray volumes of 400 l/ha. The last applications were made at maturity. Samples were stored at -18ºC for 174 days before analysis. (Conraux, 1994a).

In one field trial in Greece in 1997 there were six applications at intervals of 10 days, the first at 3-4 leaves unfolded and the last when the fruits reached final size. The SAI was 134 days (Sutcliffe, 1998c).

Field trials were conducted in Italy from 1991 to 1995. In 1991 critical information was not submitted (Pessina, 1993b).

In two other trials in 1992 the EC formulation was applied three times to plots of 100 or 200 m^2 at 7-day intervals with a knapsack sprayer. Spray volumes were 600 l/ha. Samples were harvested 0, 7 and 14 days after the last treatment and stored frozen for 96-150 days before analysis (Pessina, 1993h). In two field trials in 1993 the EC or WP formulation was sprayed 3 times at 7-day intervals on 50 m^2 plots at fruit ripening with spray volumes of 920 to 990 l/ha. Samples were stored at -20ºC for 6-7 months before analysis. The reported LOD was 0.04 mg/kg and recoveries ranged from 86 to 114% (Pessina, 1994a). In two trials in 1995 on different varieties the EC formulation was applied six times at a higher rate than GAP, the first application in an open glasshouse and the last in the field at 10% ripeness, at intervals of 10-14 days. Samples were frozen for 6 months before analysis (Pessina, 1996).

Field trials were carried out in Spain in 1991 (2), 1992 (2) and 1997 (1). In 1991 melons were sprayed with the EC formulation at 0.175 kg ai/ha and a spray volume of 825 l/ha. Samples were stored at -18ºC for 20-22 months before analysis. Jousseaume (1993) used a method that measured only phenyl

crotonates. The samples were re-analysed by Conraux (1993a). The residues were all below the LOD (0.04 mg/kg).

In 1992 dinocap was applied once or twice to melon plots (20 m^2) with spray volumes of 1000 l/ha. Samples were stored for 272 days at -18ºC before analysis. The reported LOD was 0.04 mg/kg and the mean recovery 85%. No residues above the LOD were found in any of the samples taken from 7 to 21 days after the last treatment (Conraux, 1993l). In 1997 (glasshouse) five sprays were applied, the first when flowers were visible and the last when fruits reached maturity. The SAI was 137 days (Sutcliffe, 1998c).

The results are shown in Table 42.

Table 42. Residues of dinocap in melons. Underlined residues are from trials according to GAP.

Country Year	F/G	Application				PHI, days	Dinocap, mg/kg	Reference
		Form	No	kg ai/ha	kg ai/hl			
France 1993	F	EC	4	0.175	0.044	0	<0.04	Conraux, 1994a
						4	<u><0.04</u>	
	F	WP	4	0.175	0.044	0	<0.04	
						4	<u><0.04</u>	
Greece 1997	F	EC	6	0.1-0.25	0.021	0	0.05	Sutcliffe, 1998c
						3	n.d.	
						7	n.d.	
Italy 1991	F	EC	3	<0.11	0.018	0	<0.04	Pessina, 1993b 3 replicates
						3	<0.04	
						7	<u><0.04</u>	
						14	<0.04	
Italy 1991	F	EC	3	<0.11	0.018	0	<0.04	Pessina, 1993b
						3	<0.04	
						7	<u><0.04</u>	
						14	<0.04	
Italy 1992	F	EC	3	<0.11	0.018	0	0.08	Pessina, 1993h
						7	<u><0.04</u>	
						14	<0.04	
Italy 1992	F	EC	3	<0.11	0.018	0	<0.04	Pessina, 1993h
						7	<u><0.04</u>	
						14	<0.04	
Italy 1993	F	WP	3	0.17-0.18	0.018	0	0.04 (<0.04-0.06)	Pessina, 1994a
						3	<0.04	
						7	<u><0.04</u>	
Italy 1993	F	EC	3	0.16-0.17	0.018	0	0.04	Pessina, 1994a
						3	<0.04	
						7	<u><0.04</u>	
Italy 1995	F	EC	6	0.29-0.32	0.032-0.063	0	<0.04	Pessina, 1996
Mirabella						3	<0.04	
						7	<0.04	
Italy 1995	F	EC	6	0.29-0.32	0.032-0.063	0	<0.04	Pessina, 1996a
Ferrara						3	<0.04	
						7	<0.04	
Spain 1991	F	EC	1	0.18	0.021	0	<0.04	Conraux, 1993a (re-analysed)
						1	<0.04	
						3	<0.04	

Country Year	F/ G	Application				PHI, days	Dinocap, mg/kg	Reference
		Form	No	kg ai/ha	kg ai/hl			
Spain 1991	F	EC	1	0.18	0.021	0	<0.04	Conraux, 1993a (re-analysed)
						13	<0.04	
Spain 1992	F	EC	2	<0.26	0.026	0	0.5	Conraux, 1993l
						7	<0.04	
						14	<0.04	
						21	<0.04	
			1	0.26	0.026	0	0.36	
						7	<0.04	
						14	<0.04	
						21	<0.04	
Spain 1997	G	EC	5	0.27-0.48	0.021	0	0.06	Sutcliffe, 1998c
						3	0.06	
						7	<0.05	

F: field
G: glasshouse

Summer squash. Summary information on two field trials in Southern France in 1991 was submitted. The EC formulation was sprayed once or twice on small plots (3-4 m^2) of different varieties. Samples were analysed three months after harvest (only total diphenyl crotonates were determined) and re-analysed 19 months later after storage at -18ºC for 22 months (Conraux, 1993c).

Two other field trials were carried out in France in 1992 with dinocap EC. In one 3 replicate plots of 5 plants were sprayed 5 times with volumes of 500 l/ha (Conraux, 1993k). In the other there were 4 sprays of 750 l/ha at a rate 0.35 kg ai/ha. Samples were stored below -18ºC for 226 days before analysis. No residues above the LOD (0.04 mg/kg) were detected in samples taken 3 and 7 days after the last treatment (Conraux, 1993f).

Two field trials were conducted in Italy in 1991. The EC formulation was sprayed 3 times with a volume of 600 l/ha. Only a summary was reported (Pessina, 1993c).

Two other trials were carried out at different locations in Italy in 1992 where the EC formulation was applied 3 times to plots of 100 m^2 and 200m^2, the first at flowering and the last at maturity with application intervals of 6 days and spray volumes of 600 l/ha. Samples were stored frozen for 5 to 7 months before analysis. The reported LOD was 0.04 mg/kg and recoveries 78 to 130% (Pessina, F., 1993i).

In two field trials in Italy in 1993 (Pessina, 1994b) the EC and WP formulations were sprayed 3 times to plots of 47 plants starting at the flowering stage at intervals of 7 days and spray volumes of 946-1013 l/ha. Samples were stored at about -20ºC for 3-4 months before analysis.

In Spain in 1993 the EC formulation was sprayed two or three times at intervals of 7 days by atomiser at spray volumes of 1388 l/ha on plots of 36 m^2 (Jousseaume, 1994d). The SAI was 210 days at -18ºC.

The results are shown in Table 43.

Table 43. Residues of dinocap in summer squash (zucchini). Underlined residues are from trials according to GAP.

Country Year	Application				Sample	PHI, days	Dinocap, mg/kg	Reference
	Form	No	kg ai/ha	kg ai/hl				
France 1991	EC	1	0.175	0.035	whole fruit	0	0.29	Conraux, 1993c
T 1						3	<u><0.04</u>	
						7	<0.04	
						14	<0.04	
France 1991	EC	2	0.175	0.035	whole fruit	0	0.08	Conraux, 1993c
T 2						3	<u><0.04</u>	
						7	<0.04	
						14	<0.04	
France 1992	EC	5	0.18	0.044	whole fruit	0	<0/04	Conraux, 1993k
						3	<u><0.04</u>	
						7	<0.04	
France 1992	EC	4	0.35	0.046	whole fruit	0	0.11	Conraux, 1993f
						3	<0.04	
						7	<0.04	
Italy 1991	EC	3	0.11	0.018	fruit	0	0.06	Pessina, 1993c
T 1						3	<0.04	
						7	<0.04	
						14	<0.04	
Italy 1991	EC	3	0.11	0.018	fruit	0	<0.04	Pessina, 1993c
T 2						3	<0.04	
						7	<0.04	
						14	<0.04	
Italy FD'Albero 1992	EC	3	0.11	0.018	fruit	0	0.26	Pessina, 1993i
						3	<0.04	
						7	<u><0.04</u>	
Italy Boara	EC	3	<0.11	0.018	fruit	0	0.04	Pessina, 1993i
1992						3	<0.04	
						7	<u><0.04</u>	
Italy 1993	EC	3	0.18	0.018	fruit	0	0.07	Pessina, 1994b
						3	<0.04	
						7	<u><0.04</u>	
	WP	3	0.19	0.018	fruit	0	0.08	Pessina, 1994b
						3	<0.04	
						7	<u><0.04</u>	
Spain 1993	EC	3	0.39	0.028	fruit	0	0.32	Jousseaume, 1994d
						3	<0.04	
						7	<u><0.04</u>	
						14	<0.04	
		2	0.39	0.028	fruit	7	<u><0.04</u>	

<u>Peppers</u>. Trials were carried out with the EC formulation in Greece (one in 1997), Italy (3 in 1997) and Spain (1 in 1993 and 4 in 1996). In Greece 6 applications were made to a plot of 6 rows x 7 m in a glasshouse with spray volumes of 1500 l/ha and application intervals of 10 days. The reported LOD was 0.05 mg/kg and the recovery 80% (Fielden, 1998b).

In Italy two trials were under a tunnel and the third in a glasshouse. The EC formulation was sprayed 6 times almost to run-off on plots of 4-5 rows x 9-10 m every 14 days, starting when the plant organs began to develop and ending at maturity. The spray volume increased from 800 l/ha at the first application to 1500-3000 l/ha at the last. Samples were stored at -20ºC for 91-150 days before analysis (Fielden, 1998b).

In the field trial in Spain in 1993 the EC formulation was sprayed three times, first at flowering, with a volume of 980 l/ha at intervals of 14 days on a plot of 202 m^2. Samples were taken 7 days after the second treatment and 0, 3, and 7 days after the third, and stored at -18ºC for 192 days before analysis (Jousseaume, 1994e).

In 1996 protected plots (4 rows of 10 m) at different locations were sprayed 6 times at a higher rate than GAP, with application intervals of 10-14 days and spray volumes of 980-2500 l/ha. In three trials the first application was when the flowers opened and in the fourth 24 days earlier. At harvest, the fruits in trials 1, 2 and 4 had reached a typical size and in trial 3 they were ripening. Samples were stored at -20ºC for 228 to 409 days before analysis (Lees, 1998g). The results are shown in Table 44.

Table 44. Residues of dinocap in peppers. Underlined residues are from trials according to GAP.

Country Year	F/G/P	Application				PHI, days	Dinocap, mg/kg			Ref.
		Form	No	kg ai/ha	kg ai/hl		2,4-	2,6-	Total	
Greece 1997	G	EC	6	0.17-0.32	0.021	0	0.09	<0.05	0.13	Fielden, 1998b
						3	0.08	<0.05	0.06	
						7	0.07	<0.05	<u>0.06</u>	
Italy 1997	G	EC	6	0.17-0.72	0.021	0	0.09	<0.05	0.13	Fielden, 1998b
						3	<0.05	<0.05	<u>0.12</u>	
						7	<0.05	<0.05	0.12	
Italy 1997	P	EC	6	0.17-0.48	0.021	0	0.23	0.1	0.33	Fielden, 1998b
						3	0.15	0.09	0.23	
						7	<0.05	<0.05	<u>0.06</u>	
Italy 1997	P	EC	6	0.17-0.32	0.021	0	0.13	0.06	0.2	Fielden, 1998b
						3	0.05	<0.05	0.09	
						7	<0.05	<0.05	<u><0.05</u>	
Spain 1993	F	EC	2	0.39	0.04	7[1]			0.04	Jousseaume, 1994e
			3	0.39	0.04	0			0.43	
						3			0.21	
						7			0.16	
Spain 1996	P	EC	6	0.27-0.54	0.021	0	0.23	0.11	0.34	Lees, 1998g
T1						3	0.1	0.06	0.16	
						7	<0.05	<0.05	<u>0.05</u>	
Spain 1996	P	EC	6	0.3-0.48	0.021	0	0.35	0.18	0.53	Lees, 1998g
T2						3	0.08	0.05	0.13	
						7	0.06	<0.05	<u>0.11</u>	
Spain 1996	P	EC	6	0.3-0.41	0.021	0	0.16	0.07	0.24	Lees, 1998g
T 3						3	0.06	<0.05	0.1	
						7	<0.05	<0.05	<u>0.06</u>	
Spain 1996	P	EC	6	0.19-0.34	0.021	0	0.07	<0.05	0.11	Lees, 1998g
T 4						3	0.1	<0.05	0.15	
						7	0.05	<0.05	<u>0.07</u>	

[1] After second of three treatments.

F: field; G: glasshouse; P: protected

Tomatoes. A field trial was conducted in Southern France in 1997. The EC formulation was sprayed 4 times almost to run-off on a 108 m^2 plot, starting at flowering, at intervals of 10 days and spray volumes of 1300-1700 l/ha. Samples were stored at -20ºC for a maximum of 133 days before analysis. Samples from day 7 were processed to juice, purée, preserves and ketchup (Howie, 1998).

In a field trial in Italy in 1992 the EC formulation was applied three times to a commercial variety, starting at fruit enlargement, with 7-day application intervals and spray volumes of 600 l/ha. The reported LOD was 0.04 mg/kg and recoveries ranged from 73 to 120% (Pessina, 1993k).

Two other field trials were carried out in Italy in 1993 on commercial tomato plots (37 m^2 and 20 m^2). Three applications of the EC or WP formulation with spray volumes of 900-100 l/ha were made, starting at the change of fruit colour at intervals of 7 days. Samples were stored at -20ºC less than 5 months before analysis (Pessina 1994c).

Two other field trials were conducted in Spain in 1991 with 1 application of the EC formulation to Cristina and Bornia varieties with spray volumes near 1000 l/ha. The plot sizes were 30 m^2. Samples were first analysed by a method that measures only phenyl crotonate esters (Jousseaume, 1993e), but re-analysed by the Brackett method where the reported LOD was 0.05 mg/kg and the recovery 74.9%. Samples were stored at -18ºC for 12 months before analysis (Conraux, 1993e).

In two other fields trials in Spain in 1991 the EC formulation was applied once or twice to plots of 30 m^2 at 0.26 kg ai/ha and spray volumes of 1000 l/ha with an application interval of 7 days. Samples were stored at -18ºC for a maximum of 343 days before analysis (Conraux, 1993o).

Two indoor trials with 3 applications of the EC formulation at intervals of 7 days were conducted in Spain in 1993. In one dinocap was applied to a plot of 20 x 1.6 m with spray volumes of 1000-1500 l/ha. Summary details were submitted. The samples were stored below -18ºC for 42 days before analysis (Jousseaume, 1994b).

In the other indoor trial the plots were 26 m^2 and spray volumes 1100 l/ha. Samples were stored at -18ºC for 79 days before analysis. The reported LOD was 0.04 mg/kg and the mean recovery 72.7% (Jousseaume, 1994c).

None of the trials complied with GAP. The results are shown in Table 45.

Table 45. Residues of dinocap in tomatoes.

Country Year	F/G	Application				PHI, days	Dinocap, mg/kg	Reference, Comments
		Form	No	kg ai/ha	kg ai/hl			
France 1997	F	EC	4	0.29-0.36	0.021	0	0.08	Howie, 1998
South						3	0.06	
						7	<0.05	
Italy 1992	F	EC	3	0.11	0.018	0	0.08	Pessina, 1993k
						7	<0.04	
						14	<0.04	
Italy 1993	F	WP	3	0.18	0.018	0	0.24	Pessina, 1994c
						3	0.07	
						7	<0.04	
Italy 1993	F	EC	3	0.17	0.018	0	0.09	Pessina, 1994c
						7	<0.04	

Country Year	F/G	Application				PHI, days	Dinocap, mg/kg	Reference, Comments
		Form	No	kg ai/ha	kg ai/hl			
						14	<0.04	
Spain 1991	F	EC	1	0.26	0.026	0	0.29	Jousseaume, 1993b
						3	<0.04	Re-analysed Conraux, 1993e
Spain 1991	F	EC	1	0.26	0.026	0	0.11	Jousseaume, 1993b
						3	<0.05	Re-analysed Conraux, 1993e
Spain 1991	F	EC	1	0.26	0.026	0	0.11	Conraux, 1993o
						3	0.05	
						8	0.04	
						15	<0.04	
		EC	2	0.26	0.026	0	0.26	
						3	0.1	
						8	<0.04	
						15	<0.04	
Spain 1993	G	EC	2	0.39	0.025	8	0.18	Jousseaume, 1994b
			3	0.39	0.025	0	<0.04	
						3	0.21	
						7	0.08	
						14	<0.04	
Spain 1993	G	EC	1	0.39	0.036	0	0.06	Jousseaume, 1994c
			2	0.39	0.036	7	<0.04	
			3	0.39	0.036	0	0.09	
						3	0.06	
						7	<0.04	
						14	<0.04	

Animal feeding studies

No information.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No information.

In processing

Processing studies were conducted on apples, grapes, peaches, strawberries and tomatoes.

Apples. In two trials in France in 1997 (one at a twofold rate), unwashed apples harvested 14 days after the last treatment were processed into juice and purée. Filtered and decanted apple juice was heated to 88-90ºC and sterilized in glass jars in boiling water for 5 minutes. For apple purée 5 kg of apples were blanched, crushed and sieved, sugar was added and dissolved by heating, and the purée was heated in glass jars at 80-85ºC. Samples were analysed by GLC with an ECD. The reported LOD for juice and purée was 0.05 mg/kg and the mean recoveries were 77% for juice and 88% for purée. Wet and dry pomace were not analysed. The SAI was 246 days (Lees, 1998c).

Two other studies were carried out with apples from two sites in the UK where apple trees were treated according to GAP. The procedures were reported as typical of processes that would be used for commercial manufacture. For the preparation of juice, washed apples were milled and pressed, the weight of extracted juice was recorded and the juice canned and pasteurized for 10 minutes at 100ºC. The cans were cooled and frozen at -18ºC. The SAI was 100 days for purée and 58 days for juice. Pomace was collected and frozen at -18ºC.

Processing to purée and juice reduced the residues since none were detected in any analysed samples. There was no concentration in pomace. The results are shown in Table 46.

Table 46. Residues of dinocap in apples and processed products.

Country Location Year	kg ai/hl/kg ai/ha	No. of applicn.	PHI, days	Sample	Dinocap, mg/kg	Reference
France St.Porchaire 1997	0.021 kg ai/l	6	14	whole fruit	<0.05	Lees, 1998c
				juice	n.d.	
				purée	n.d.	
France Villemade 1997	0.021 kg ai/hl	6	14	whole fruit	0.09	Lees, 1998c
				juice	n.d.	
				fruit	n.d.	
U.K. Nottinghamshire 1997	0.36-0.38 kg ai/ha	10	14	whole fruit unwashed	0.06	Lees, 1998h
				pomace	0.06	
				juice	n.d.	
				purée	n.d.	
UK Gloucestershire 1997	0.46-0.5 kg ai/ha	10	14	whole fruit unwashed	<0.05	Lees, 1998h
				pomace	<0.05	
				juice	n.d.	
				purée	n.d.	

Grapes. Residues of dinocap in must and wine from a Merlot grape trial in France in 1992 were reported, but no information about the vinification process was submitted. Must and wine samples were stored for 351 days at -18ºC before analysis, The LOD for all samples was 0.04 mg/kg and the mean recoveries 94.8 and 85.9% for must and wine respectively (Conraux, 1994b).

Two vinification trials in 1991, one in 1992 and three in 1993 were conducted in Italy with 6-7 applications at rates ranging from 0.11 to 0.28 kg ai/ha. No information on the vinification process was reported for the 1992 trial.

In 1991 white grapes were cooled at 2ºC and pressed, and the must was clarified. After remixing the must was kept 12 hours at 8ºC, then fermented with native yeast under controlled temperature. At the end of the fermentation the alcohol concentration was adjusted. Red grapes were stored at room temperature and then pressed. The must was separated and fermented with native yeast under controlled temperature, no higher than 25ºC. The fermented wine was filtered (Pessina, 1993e)

In 1993 a simple vinification procedure was adopted to define the effects of processing on residue levels. About 200 kg of grapes were divided into three containers and processed separately. The grapes were pressed and SO_2 was added. During fermentation the mixture was aerated twice a day. The fermented wine was kept 10 days in a refrigerator at -2ºC to precipitate tartrates. The wine was bottled after a month. Samples of must, wine and lees were analysed by GLC with an NPD, with an LOD of 0.04 mg/kg for all samples and mean recoveries of 108%, 97% and 98% for grapes, must and wine respectively (Pessina, 1994e).

Samples taken at a 21-day PHI from trials in Germany in 1996 were processed into must and young and mature wine according to standard commercial procedures in a pilot plant (Lees, 1998a). Samples were analysed by GLC with an ECD. The LOD was 0.05 mg/kg and recoveries were 76%, 74% and 91% for grapes, must and wine respectively. The SAI for must and wine was 358 days.

The results are shown in Table 47.

Table 47. Residues of dinocap in grapes and vinification products.

Country Year Variety	Application		PHI, days	Total dinocap, mg/kg					Ref.
	No	kg ai/hl		Grapes	Must	Young wine	Mature wine	Lees	
France 1992	6	0.14	14	0.1 whole bunch	<0.04		<0.04		Conraux, 1994b
Italy 1991	6	0.018	20	<0.05	<0.05		<0.05		Pessina, 1993e
Italy 1991	7	0.011	48	<0.05	<0.05		<0.05		Pessina, 1993e
Italy 1992		0.018	20	<0.04	<0.04		<0.04	<0.04	Pessina, 1993g
Italy 1993 Barbera	6 WP	0.022	20	<0.04	<0.04		<0.04	<0.04	Pessina, 1994e
Italy 1993 Pinot nero	6 WP	00.22	20	<0.04	<0.04		<0.04	<0.04	
Italy 1993 Pinot nero	6 EC	0.022	20	<0.04	<0.04		<0.04	<0.04	
Italy 1993	6 EC	0.21	20	<0.04	<0.04		<0.04	<0.04	
Germany 1996	8	0.063	21	0.67	<0.05	n.d.	n.d.		Lees, 1998a
Germany 1996	8	0.021	21	0.33	<0.05	n.d.	n.d.		Lees, 1998a

No residues were found above the LOD in the must or wine in any of trials where grapes were treated at or above the recommended rate. Residues in pomace, which can be used as animal feed, were not determined.

Peaches. Peaches from two trials at the recommended rate (0.021 kg/hl) were processed into juice and preserved fruit in Italy in 1997.

Control and treated peaches (3 and 6 kg) were blanched for 2 minutes at 85-90ºC, then peeled and sliced. A mixture of water and sugar was added and the mixture was sterilized in glass jars at 115ºC, then cooled and refrigerated or frozen.

To prepare juice 14.6 kg of peaches were cut, destoned and sieved to extract the juice (3.5 kg). In another trial 12.9 kg of peaches were cut, ground and sieved to obtain 3.7 kg of juice. The juice was sterilized.

The residues in the raw peaches and the processed products were all below the LOD. The results are shown in Table 48.

Table 48. Residues of dinocap in peaches and their processed products (Sutcliffe, 1998d).

Country Year	Application		PHI, days	Sample	Residues, mg/kg
	No	kg ai/hl			
Italy 1997	4	0.021	14	whole fruit	<0.05
				juice	<0.05
				Preserved fruit	n.d
Italy 1997	4	0.021	14	whole fruit	<0.05
				juice	n.d.
				Preserved fruit	n.d.

Strawberries. In two trials in the UK in 1996 strawberries picked 3 days after treatment according to GAP were processed to jam and preserved fruit. For the preparation of jam 2-3 kg of strawberries were washed for at least 2 minutes under a spray of potable water, then boiled with sugar (3 kg), water and pectin (16-17 g) in a steam pan until the soluble solids reached a concentration of approximately 63º Brix. Citric acid was added.

To prepare preserved fruit about 5 kg of strawberries were sorted, freed from foreign material and rotten fruit and washed. The strawberries were filled into glass jars, and water at 92ºC was added before pasteurisation at an initial temperature of 55-60ºC increasing to 90ºC.

After processing all samples were transferred to frozen storage at -18ºC for 319 days before analysis by GLC with an ECD. The LOD was 0.05 mg/kg and the mean recovery from jam and preserved fruit 74% (Lees, 1998f). The results are shown in Table 49.

Table 49. Residues of dinocap in strawberries and their processed products (Lees, 1998f).

Country Year	Application			PHI, days	Sample	Dinocap, mg/kg	Processing factor
	Form	No.	kg ai/hl				
UK 1996	EC	6	0.027	3	whole fruit	0.23	
					jam	0.08	0.35
					preserved fruit	<0.05	0.22
UK 1996	EC	6	0.027	3	whole fruit	0.31	
					jam	0.07	0.23
					preserved fruit	0.11	0.35

The average processing factor for jam and preserved strawberries was 0.29.

Tomatoes. In a trial in France in 1997 tomatoes treated with the EC formulation were processed into juice, purée, preserved tomatoes and ketchup. To prepare juice, crushed tomatoes were sieved and cooking salt was added. The juice was sterilized at 115ºC for 2 minutes in glass bottles and frozen at -20ºC for 126 days until analysis. To prepare purée, the cut tomatoes were reduced in a double saucepan

to 11º Brix, sieved, and sterilized in glass bottles. The bottles were stored at -20ºC for 112 days before analysis.

Some of the purée was reduced again to prepare ketchup. Preserved tomatoes, peeled tomatoes and juice were sterilized for 2 minutes at 115ºC in glass bottles. Samples were frozen at -20ºC for 97 days until analysis by GLC with an ECD. The LOD was 0.05 mg/kg and mean recoveries were 86% for juice, 77% for purée, 80% for ketchup and 92% for preserved tomatoes (Howie, 1998a).

The residues were below the LOD in the raw tomatoes and undetectable in the products. The results are shown in Table 50.

Table 50. Residues of dinocap in tomatoes and their processed products (Howie, 1998a).

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Country Year	Application			PHI, days	Sample	Dinocap, mg/kg
	Form	No.	kg ai/hl			
France 1997	EC	4	0.021	7	raw tomatoes	<0.05
					juice	n.d.
					purée	n.d.
					preserved tomatoes	n.d.
					ketchup	n.d.

Residues in the edible portions of food commodities

No data were provided except those included in the processing trials. The residues in most of the fractions were at or below the LOD.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

The results of monitoring carried out in the UK in 1989-1991 were reported to the Meeting. Dinocap was not found above the reporting limit. The results are shown in Table 51.

Table 51. UK monitoring data for dinocap, 1989-91.

Commodity	Reporting limit, mg/kg	Samples	
		1989-90	1991
Dessert apples	0.1-1	40 UK produced	25 UK produced
		63 imported	36 imported
French beans	0.05	4 UK produced	
		20 imported	
Runner beans	0.2		7 UK produced
			1 imported
			3 unknown
Brussels sprouts	0.05	30 UK produced	
		4 imported	
		1 unknown	
Green cabbage	0.02		17 UK produced
			5 imported
Calabrese	0.02		26 UK produced

Commodity	Reporting limit, mg/kg	Samples	
		1989-90	1991
			23 imported
Cauliflower	0.02		17 UK produced
			4 imported
Cucumber	0.05	36 UK produced	
		37 imported	
Gooseberries	0.01	7 UK produced	
		1 imported	
Grapes	1	65 imported	
Greengages	1	3 UK produced	
Melons	0.01	25 imported	
Nectarines	1	24 imported	
Peaches	1	23 imported	
Pears	0.5	21 UK produced	
		24 imported	
Tomatoes	1	22 UK produced	
		23 imported	

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs were reported.

Country	Commodity	MRL, mg/kg
Austria	Apple	1
	Cucurbits	1
	Grapes	1
	Pepper	1
	Tomatoes	1
	Stone fruits	1
	Strawberry	1
Australia	Apple	0.1
	Cucurbits	0.1
	Grapes	0.1
	Stone fruits	0.1
	Strawberry	0.1
Belgium	Apple	1
	Cucurbits	1
	Grape	1
	Pepper	1
	Tomatoes	1
	Stone fruits	1
	Strawberry	1
Canada	Apple	0.1
	Cucurbits	0.1
	Grapes	0.1
Denmark	Berries and small fruits	0.1
	Leafy vegetables	0.1
	Pome fruits	0.1
	Other fruits	0.1
	Stone fruit	0.1
	Potatoes	0.1
Finland	Apples	0.5

Country	Commodity	MRL, mg/kg
	Cucurbits	0.5
	Grape	0.5
	Pepper	0.5
	Stone fruit	0.5
	Strawberry	0.5
France	Fruit and Vegetables	0.1
Germany	Cucumber	1
	Grape	1
	Melon	1
	Pome fruit	1
	Stone fruit	0.1
	Strawberry	0.1
Hungary	Apple	0.2
	Cucurbits	0.2
	Grape	0.2
	Pepper	0.2
	Stone fruit	0.2
	Strawberry	0.2
Italy	Artichoke	1
	Cardoon	1
	Carrot	1
	Celery	1
	Chard	1
	Fennel	1
	Fruits	1
	Lettuce	1
	Maize	1
	Vegetables	1
	Wheat	0.05
Luxembourg	Fruit and Vegetables	1
	Other foods of vegetable origin	0.05
Netherlands	Apples	0.5
	Fruiting Vegetables	0.1
	Other food	0.05
New Zealand	Apple	1
	Cucurbits	1
	Grape	1
	Pepper	1
	Stone fruits	1
	Strawberry	1
South Africa	Apple	1
	Cucurbits	1
	Grape	1
	Peach	1
	Pepper	1
Spain	All plant products	0.1
Switzerland	Apple	0.05
	Cucurbits	0.05
	Grape	0.05
	Pepper	0.05
	Stone fruits	0.05
	Strawberry	0.05
Yugoslavia	Apple	0.1
	Cucurbits	0.1
	Grape	0.1

Country	Commodity	MRL, mg/kg
	Pepper	0.1
	Stone fruits	0.1
	Strawberry	0.1
U K	Apple	0.1
	Strawberry	0.5
USA	Apple	0.1
	Grape	0.1

APPRAISAL

Dinocap is a contact fungicide used to control powdery mildew on many crops and is also used as a non-systemic acaricide. It has been evaluated several times by the JMPR. In 1992 the JMPR recommended withdrawal of the temporary MRLs and in 1993 the CAC agreed to delete dinocap from the Codex list. In the present evaluation dinocap is therefore considered as a new compound.

Dinocap is marketed as WP and EC formulations, and is also formulated with other fungicide such as myclobutanil and fenbuconazole.

Dinocap is composed of a mixture of six isomeric dinitrooctylphenyl crotonates, three isomers of 2,4-dinitro-6-octylphenyl crotonate (2,4-DNOPC) and three of 2,6-dinitro-4-octylphenyl crotonate (2,6-DNOPC), where "octyl" is a mixture of 1-methylheptyl, 1-ethylhexyl and 1-propylpentyl groups. The ratio of the 2,4-DNOPC to the 2,6-DNOPC isomers in technical dinocap is approximately 2:1, and that of the octyl isomers 1:1:1.

The metabolic degradation of dinocap has been studied in rats and mice with 2,4-DNOPC uniformly labelled with ^{14}C in the aromatic ring.

In an early feeding study with rats, radioactivity was rapidly excreted in the faeces and urine. Another study with male mice and rats showed different metabolite profiles in the two species and it was also observed that in mice but not in rats the proportion of the administered radioactivity excreted in the urine decreased with increasing dose. Metabolites in the faeces and urine samples were characterized by HPLC with UV detection.

In a study to characterize the urinary metabolites in rats and mice after the oral administration of labelled 2,4-DNOPC, the DNOPC was rapidly metabolized with the rats excreting approximately 30.9% and mice approximately 58.3% of the administered ^{14}C in the urine over a 4-day period: in both species, more than 90% of the total was excreted within 24 hours. Twelve metabolites in rats and 13 in mice were identified. In both species the pattern of metabolites was consistent with a metabolic pathway involving hydrolysis of the crotonate ester, β- or α-oxidation of the methylheptyl group and β-oxidation, followed in rats only by reduction of the nitro groups and *N*-acetylation. Although there were qualitative and quantitative differences in the metabolic profile in rats and mice, the main metabolites in the urine of both species were the same, namely 6-(4-carboxy-1-methylbutyl)-2,4-dinitrophenol and 6-(3-carboxy-1-methypropyl)-2,4-dinitrophenol.

In cows dosed with radiolabelled 2,4-DNOPC at levels equivalent to 0.1, 0.3 and 1 ppm in the diet the main route of elimination was in the faeces with small amounts in the urine. No radioactive residues were detectable in the milk or tissues at any dosing level.

Bluegill sunfish were exposed to concentrations of 1 or 0.2 µg/l of [^{14}C]2,4-DNOPC in water tanks for 28 days, followed by a depuration period of 14 days. Bioconcentration was observed with accumulation increasing during the first 3 days, after which a steady level was reached and maintained until the end of the exposure period. Loss of residue during depuration was rapid. At the end of the depuration period more than 90% of the radioactivity in whole fish had been eliminated. The half-lives calculated for the ^{14}C in whole fish were 0.6 and 0.9 days for the low and high dose respectively.

The fate of residues in plants was studied in apples, cucumbers and squash with radiolabelled 2,4-DNOPC. Studies on apples showed that more than 92% of the radioactivity in the fruit was associated with the peel. Two groups of compounds, the parent 2,4-DNOPC isomers and the corresponding phenols 2,4-DNOP, were identified in the fruit. The phenol metabolites represented 2-4% of the total radioactivity at all sampling intervals. The calculated half-life of 2,4-DNOPC was 5.2 days. The relatively constant concentration of the phenols throughout the sampling period showed that they did not accumulate. They appeared to be metabolized to more polar compounds.

In another study on apples, peel samples were extracted with methanol, partitioned with hexane and analysed by TLC, HPLC and GC-MS. Five minor unknown compounds were isolated from the peel, each of which accounted for less than 0.5% of the total residue. The results suggest that photolysis is a potential degradation pathway for 2,4-DNOPC.

In cucumbers, the metabolism of 2,4-DNOPC produced 28 metabolites, but only the parent mixture and 2,4-DNOP were identified. 2,4-DNOPC dissipated rapidly from cucumber leaves and stems.

In squash the residues in mature fruit were mainly associated with the peel. Six unidentified metabolites were found in the fruit and 10 in the leaves at low concentrations.

The half-lives of the total radioactive residues on cucumber and squash leaves were 11.8 and 8 days respectively.

Dinocap metabolites from squash and cucumber were very similar in their TLC behaviour and more similar to rat faecal metabolites than to urinary metabolites.

In summary, plant metabolism studies indicated that the metabolic pathways of dinocap in crops are complex, resulting in a large number of metabolites present at low concentrations. The isolation of sufficient quantities of most of the metabolites to allow identification was not possible. The only significant metabolite found was 2,4-DNOP. Residues are associated with the peel and it was found that dinocap is rapidly degraded on fruit and leaf surfaces, suggesting that photolysis is a significant pathway of degradation.

Four studies were carried out to determine the rate of dissipation of dinocap in different soils. A study with two standard soils and one agricultural soil showed that dinocap was slowly degraded in the standard soils but readily degraded to CO_2 in a typical agricultural soil. It can be concluded that moisture and microbial activity play an important role in the degradation of dinocap in soil.

The route and rate of degradation of 2,4-DNOPC was also investigated in sandy loam, silty loamy sand, loamy sand and clay loam at two temperatures. 2,4-DNOPC was degraded rapidly in all the soils at rates which appear to be dependent on the soil pH rather than other characteristics, indicating that chemical hydrolysis to 2,4-DNOP is a major route of degradation. The half-life ranged from 4.1 days at pH 7.1 to 24 days at pH 4.8 at 20ºC.

The degradation of 2,4-DNOPC and 2,6-DNOPC was studied in a sandy loam soil (pH 5.8) in aerobic conditions. Both were degraded rapidly, the 2,6- isomers more rapidly than the 2,4-. Calculated half-lives were 10 and 4.5 days for 2,4- and 2,6-DNOPC respectively. The main degradation products were 2,4- and 2,6-DNOP. After 120 days of incubation significant mineralization was observed (22.4% of the applied 2,4-DNOPC and 36.7% of the 2,6-DNOPC).

A study of the adsorption and desorption of [^{14}C]2,4-DNOPC in four different agricultural soils showed that it was strongly adsorbed in the soils studied and could be classified as having very low mobility in soil.

The leaching behaviour of [^{14}C]dinocap was studied in five different fresh soils, in sandy loam soil after ageing for 30 days and in silt loam after ageing for 102 days before leaching. Radioactivity was detectable in the leachate from only two of the fresh soils (silt loam and clay loam). Between 74% and 99% of the applied radioactivity was recovered in the top layers of all the soils. It can be concluded that it is very unlikely that dinocap or its degradation products could be leached even under exaggerated laboratory conditions.

The octanol/water partition coefficient was determined for 2,4- and 2,6-DNOPC and their phenol metabolites. The coefficients showed that DNOPC isomers are fat-soluble (log P_{ow} 2,4-DNOPC 6.55, log P_{ow} 2,6-DNOPC 6.45).

The rates of hydrolysis of the isomeric forms of DNOPC and the corresponding phenols were determined in buffer solutions at pH 4, 7 and 9 at 20º and 30ºC. It was concluded that hydrolysis of the crotonates was highly dependent on pH and temperature, being more rapid at basic pH. Degradation of the phenols was found to be negligible at all pH values and temperatures.

The photolysis of 2,4-DNOPC was investigated in a pH 5 aqueous buffer solution irradiated with a xenon arc for 367 hours. Degradation was biphasic with initial and terminal half-lives equivalent to 4.9 and 57.2 hours of summer sunlight. The major degradation product was $^{14}CO_2$. The free phenol 2,4-DNOP was an important initial product. In another study the aqueous photolysis of the isomeric forms of DNOPC and DNOP was measured in sterile, aqueous buffer (50 µg/l, pH 4) irradiated with a xenon arc for up to 10 hours for DNOPC and 96.1 hours for DNOP. The half-life was 0.63 and 0.73 days for 2,4- and 2,6-DNOPC respectively and 8.7 and 20.8 days for 2,4- and 2,6-DNOP. The only photodegradation product of DNOP identified was CO_2. Other photodegradation products were not resolved by HPLC.

The aerobic aquatic degradation of [^{14}C]2,4-DNOPC was studied in two water/sediment systems from natural environment sites at 20ºC in the dark. There was rapid transfer of radioactivity from water to sediment and an apparent rapid degradation of DNOPC to DNOP, which was further degraded to CO_2. At the end of the 100-day study 40.7% to 78.4% of the applied radioactivity was associated with sediments and 6.4 to 11.8% with the water phases.

Analytical methods for the determination of residues of dinocap have been developed for several crops and their processed products, and for soil and water. All the methods are similar. They include extraction with methanol, either by Soxhlet or maceration with the solvent. Juices and wine are simply diluted with methanol. The dinocap isomers are converted to the corresponding phenols by basic hydrolysis, and the extracts partially purified by partition into hexane. After solvent evaporation the residue is taken up in diethyl ether, methylated with diazomethane, and purified by silica gel column chromatography. The methylated phenols are determined by GLC with an ECD or NPD, the sum of the peak areas or heights being measured. The method was validated for many crops. The mean recoveries of dinocap from fruit

were above 70% with reported LODs of 0.05 mg/kg. Crop samples were fortified with 2,4-DNOPC and 2,6-DNOPC and the analytical standards were the methyl esters of 2,4-DNOP and 2,6-DNOP.

In studies of the storage stability of residues in frozen analytical samples of apples and grapes stored for 24 months, the residues in grapes showed good stability, but there was a marked decrease of the dinocap residue during the storage of apples. In another study, the storage stability of dinocap at levels of 1 mg/kg was determined in cucumbers, tomatoes, peaches, apples and strawberries over a period of 9 months in the dark at approximately –20ºC. Dinocap residues were found to be stable in all the crops for at least 9 months. The analytical method for apples was modified slightly by increasing the volume of the extraction solvent. This modification improved the extraction efficiency. It was reported that studies on cucumbers, peaches, apples and strawberries would be continued for a total of 24 months.

The results of metabolism studies showed that the dinocap isomers are readily hydrolysed to the corresponding phenols. The analytical methods used in residue trials quantify residues of dinocap and their phenol metabolites as the methylated phenols and express the results as dinocap. The Meeting concluded that the residues should be defined as the sum of dinocap isomers and the dinocap phenols, expressed as dinocap.

Dinocap is fat-soluble but metabolism, feeding and bioaccumulation studies showed that residues do not accumulate in tissues. This is probably because dinocap is rapidly degraded and the metabolites that constitute the main residues are not fat-soluble.

Residues resulting from supervised trials

Data from trials on apples, grapes, strawberries, stone fruits and cucurbits in European countries were evaluated.

Residues of 2,4- and 2,6-DNOPC in the trials were calculated from the sum of 6 peak areas or heights. The residues of the two groups of isomers were generally recorded separately and their sum expressed as dinocap. If the calculated concentration of each isomeric group was <0.05 mg/kg the total dinocap residue was recorded as <0.05 mg/kg.

Apples. Trials in France, Greece, Italy and the UK were reported. In two trials in France and two in Greece according to GAP the residues were <0.05 mg/kg. Six trials according to Italian GAP yielded total residues between <0.04 and 0.09 mg/kg. In the UK, 18 trials complied with GAP, with residues from <0.05 to 0.08 mg/kg.

The dinocap residues in rank order (median underlined) were <0.04 (2), <u>≤0.05</u> (18), 0.05, 0.05, 0.06, 0.07, 0.08 (3) and 0.09 mg/kg. The Meeting estimated a maximum residue level of 0.2 mg/kg and an STMR of 0.05 mg/kg for apples.

Grapes. Numerous field trials on vines in France, Germany, Greece, Italy and Portugal were reported to the Meeting. Ten of thirteen trials in France were according to GAP: the residues ranged from <0.05 to 0.59 mg/kg. Six field trials in Germany complied with French GAP, with residues from 0.22 to 0.67 mg/kg. In two field trials in Greece according to Italian GAP the residues were 0.1 and 0.2 mg/kg. In sixteen trials in Italy and three in Portugal complying with the national GAP the residues ranged from <0.04 to 0.3 mg/kg.

The residues of dinocap in rank order (median underlined) were <0.04 (7), <0.05 (7), 0.06, 0.08, 0.09, 0.1, 0.11, 0.14, 0.18, 0.2 (2), 0.22 (2), 0.26, 0.28, 0.3 (2), 0.35, 0.36, 0.42, 0.43, 0.46, 0.5, 0.59 and 0.66 mg/kg.

The Meeting estimated a maximum residue level of 1 mg/kg and an STMR of 0.105 mg/kg.

Strawberries. Trials were conducted in France, Italy, Spain and the UK. In four French trials complying with French GAP the residues were 0.05-0.33 mg/kg. Two Spanish trials complying with GAP gave residues below the LOD of 0.04 mg/kg. In ten trials in the UK according to GAP (5 applications, 0.49 kg ai/ha, 7 days PHI) the residues ranged from <0.05 to 0.33 mg/kg.

The dinocap residues in rank order (median underlined) were <0.04 (2), <0.05, 0.05, 0.05, 0.06 (4), 0.08, 0.09, 0.14, 0.21, 0.32 and 0.33(2) mg/kg.

The Meeting estimated a maximum residue level of 0.5 mg/kg and an STMR of 0.06 mg/kg.

Stone fruits. A single trial in Italy on apricots according to GAP, with residues at 21 days PHI below the LOD (0.04 mg/kg) was insufficient to estimate a maximum residue level.

Residues in a trial on peaches in Greece complying with GAP were below the LOD (0.05 mg/kg). Six of nine trials in Italy complied with French GAP (0.018 kg ai/hl, 7 days PHI), giving residues from <0.04 to 0.09 mg/kg. In two trials in Spain according to GAP the residues were <0.04 and 0.05 mg/kg. The dinocap residues in peaches in rank order (median underlined) were <0.04 (5), <0.05 (3), 0.05 and 0.09 mg/kg.

The Meeting estimated a maximum residue level of 0.1 mg/kg and an STMR of 0.05 mg/kg.

Cucumbers. Two protected trials in France and three in Spain according to GAP gave residues below the LOD (0.05 and 0.04 mg/kg). The residues were <0.04 (3) and <0.05 (2).

Melons. Several field trials were carried out in France, Greece, Italy and Spain, and one indoor trial in Spain. In two trials in France at a higher spray concentration than the recommended GAP (0.18 kg ai/hl, 3 day PHI) the residues were below the LOD (0.04 mg/kg). In one trial in Greece, 6 trials in Italy and two in Spain according to GAP the residues were all <0.04 or <0.05 mg/kg. In summary, dinocap residues in melons from 9 trials according to GAP and 2 at a higher rate were all below the LOD.

Summer squash. Residues in three trials in France, 4 in Italy and 2 in Spain according to national GAP were all below the LOD.

The use patterns on cucumbers, melons and summer squash are similar. The residues in all these crops were below the LOD, which is consistent with the results of metabolism studies. The Meeting therefore estimated a maximum residue level of 0.05* mg/kg and an STMR of 0.05 mg/kg for cucurbits.
Peppers. Eight protected trials carried out on peppers in Greece, Italy and Spain complied with Greek GAP (0.018 kg ai/hl, 7 days PHI). The residues in rank order (median underlined) were <0.05, 0.05, 0.06, 0.06, 0.06, 0.07, 0.11 and 0.12 mg/kg.

The Meeting estimated a maximum residue level of 0.2 mg/kg and an STMR of 0.06 mg/kg for peppers.

Tomatoes. Field and protected trials were conducted in Southern France, Italy and Spain. There is no GAP for tomatoes in France or Italy and all the trials were at much higher application rates than allowed by GAP in Spain (0.011 kg ai/hl, 7 days PHI) and shorter PHIs than GAP in Greece.

As no trials according to GAP were reported, the Meeting could not estimate a maximum residue level.

Processing studies

Apples. Unwashed apples from 2 trials in France with sprays of 6 x 0.021 kg ai/hl and 14 days PHI were processed to juice and purée. Residues were not detected in the processed commodities. In two studies in the UK apples treated according to GAP were processed according to commercial practice to juice, purée and pomace. Dinocap residues were not detected in the juice or purée and residues in the pomace were similar to those in the raw commodity.

The data indicated that there is no concentration of residues in apple juice. On the basis of the STMR of 0.05 mg/kg for apples, the Meeting estimated an STMR of 0.05 mg/kg for apple juice.

Grapes. Data from processing studies in France and Germany indicated that residues of dinocap decreased in wine and must and were below the LOD or not detected. Studies with higher residue levels in the raw grapes in Germany showed a processing factor of 0.07 for both must and wine. The Meeting therefore estimated STMRs for must and wine of 0.007 mg/kg, derived from the STMR for grapes of 0.105 mg/kg.

Peaches. Peaches treated according to GAP in two trials in Italy were processed into juice and preserves. Residues in the raw peaches were below the LOD and no concentration was detected in the processed commodities.

Tomatoes. Tomatoes from one supervised trial were processed into juice, purée, preserve and ketchup. Residues of total dinocap in the tomatoes were below the LOD (0.05 mg/kg) and residues were not detected in the processed commodities.

The Meeting could not calculate processing factors for peaches and tomatoes since the residues in the raw commodities were below the LOD.

Strawberries. Two processing trials in the UK showed that residues do not concentrate in strawberry jam or preserved strawberries. The average processing factor was 0.29 for both commodities. On the basis of an STMR of 0.06 mg/kg for strawberries, the Meeting estimated an STMR of 0.017 mg/kg for strawberry jam and preserved strawberries.

RECOMMENDATIONS

On the basis of data from supervised trials the Meeting estimated the maximum residue levels and STMRs listed below. The maximum residue levels are recommended for use as MRLs.

Definition of the residue for compliance with MRLs and for the estimation dietary intake: sum of dinocap isomers and dinocap phenols, expressed as dinocap.

Commodity		Recommended MRL, mg/kg		STMR
CCN	Name	New	Previous	
FP 0226	Apple	0.2	-	0.05
JF 0026	Apple juice			0.05
VC 0045	Fruiting vegetables, Cucurbits	0.05*	-	0.05
FB 0269	Grapes	1	-	0.105
	Grape must			0.007
FB 0275	Strawberry	0.5	-	0.06
	Strawberry jam and preserved			0.017
FS 0247	Peach	0.1	-	0.05
VO 0051	Peppers	0.2	-	0.06
	Wine			0.007

*At or about the limit of determination.

FURTHER WORK OR INFORMATION

Desirable

1. Processing studies with raw commodities containing dinocap residues at higher concentrations.

2. Animal feeding studies

3. Final report of the completed study of the storage stability of residues in analytical samples that was reported to be in progress.

DIETARY RISK ASSESSMENT

STMRs have been estimated for apples, grapes, strawberries, peaches, peppers and cucurbits. The International Estimated Daily Intakes of dinocap for the five GEMS/Food regional diets were in the range of 0 to 1% of the ADI. The Meeting concluded that the intake of residues of dinocap resulting from its uses that had been considered by the JMPR is unlikely to present a public health concern.

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