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Degradation of Dimethoate and Pirimicarb in Asparagus

Sunny Y. Szeto,* Robert S. Vernon, and Marilyn J. Brown

Dimethoate at 0.25, 0.50, 1.0, and 1.12 kg AI/ha, and pirimicarb at 0.125, 0.25, and 0.50 kg AI/ha were applied as foliar sprays to control the European asparagus aphid, *Brachycolus asparagi*. Partial conversion of dimethoate to dimethoxon, and pirimicarb to (methylamino)pirimicarb and/or formyl(methylamino)pirimicarb occurred in the foliage (fern) as soon as 6–12 h after application. After applications the total residues of both compounds, including their toxic metabolites, decreased by about 90% in 7 days but at a slower rate thereafter. Only traces of pirimicarb (<0.01 ppm) remained 31 days after applications at 0.50 kg AI/ha, and up to 0.03 ppm of dimethoate remained 38 days after applications at 0.50 and 1.0 kg AI/ha. No residue was found above the limit of detection of 0.002 ppm in any asparagus spears following applications of dimethoate and pirimicarb for aphid control.

INTRODUCTION

The asparagus aphid, *Brachycolus asparagi* Mordvilko, is native to Europe and the Mediterranean region (Plant Pest Control Division, USDA, 1970) and was first found in North America in New York in 1969 (Leonard, 1971). Forbes (1981) identified this aphid from asparagus, *A. officinalis altilis*, in the Okanagan Valley of British Columbia in 1979 and suggested that a toxin injected by the aphid in feeding causes severe deformity (bonsai-type or witches' broom-type growth) and even death of the plants. Outbreaks of this pest in the Okanagan Valley of British Columbia and in western Washington state have been observed since 1979 and have caused considerable economic damage. Currently malathion, carbaryl, and mevinphos are the only insecticides registered for use on asparagus in Canada. A drawback to the use of these chemicals, however, is their short residual activity which requires that several sprays be applied during the growing season. This is undesirable since repeated applications in mature asparagus could cause physical damage to the tall foliage or ferns from tractor-mounted boom sprayers. Moreover these are broad-spectrum chemicals and could be detrimental to beneficial insects such as bees and aphid predators.

In 1982 field trials were conducted in Coldstream and Armstrong, British Columbia, to evaluate the effectiveness of dimethoate [*O,O*-dimethyl *S*-[(methylcarbamoyl)-methyl] phosphorodithioate] and pirimicarb (2-(dimethylamino)-5,6-dimethylpyrimidin-4-yl dimethylcarbamate) against the asparagus aphid, and to observe their degradation in asparagus plantings. These two aphicides were evaluated once more in 1983 in Summerland, British Columbia, and the results from both seasons are presented here.

MATERIALS AND METHODS

1982 Field Studies at Coldstream. Postharvest spray trials with dimethoate and pirimicarb were conducted in a 1-year-old stand of asparagus (commercial variety Mary Washington) at Coldstream, British Columbia. This stand

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was considered immature since the first marketable spears were not expected until 1983 or 1984. The experimental plots were 6 m long and 2 rows wide with treatments replicated 4 times in a randomized block design. End-to-end plots within blocks were separated by 1-m buffer strips of asparagus and adjacent rows were 1.5 m apart. A Solo manual backpack sprayer (Solo Leinkleinmotoren, Germany) was used to apply foliar sprays of dimethoate (Cygon 4E, an emulsifiable concentrate, at 1.12 kg AI/ha) and pirimicarb (Pirimor 50 WP, a wettable powder, at 0.50 kg AI/ha) in water at the rate of 2 L per 12 m row on July 24. Dimethoate was reapplied at the same rate on Sept 8 and pirimicarb on Aug 25. At intervals after spraying two plants from each treatment and the control plots were randomly selected and a sprig from the bottom, middle, and top of each plant was removed to form a composite sample for residue analysis. These samples were considered to be representative as the experimental plots were small and the insecticides were applied manually with a backpack sprayer which ensured even distribution of spray mists among plants. In the following spring, composite samples consisting of 10 randomly selected marketable spears were taken to ascertain if any residues had been carried over the winter and into the next crop.

1982 Field Studies at Armstrong. Postharvest spray trials similar to those at Coldstream were conducted in a 17-year-old stand of asparagus (commercial variety Mary Washington) at Armstrong, British Columbia. The treatment plots were 50 m long and 3 rows wide with treatments replicated 4 times in a randomized block design. Adjacent rows were 1.5 m apart. A tractor-mounted boom sprayer operating at 4.2 kg/cm² was used to apply dimethoate at 1.12 kg AI/ha and pirimicarb at 0.50 kg AI/ha at the rate of 675 L/ha on July 29. The application of dimethoate was repeated on Sept 17 and of pirimicarb on Sept 3.

1983 Field Studies at Summerland. Postharvest spray trials were again conducted in a 3-year-old stand of asparagus (commercial variety Mary Washington) at the Agriculture Canada Research Station in Summerland, British Columbia. Treatment plots were 4.5 m long and one row wide with treatments replicated 6 times in a randomized block design. End-to-end plots were separated

by 0.75 m buffer rows of asparagus and adjacent rows were 1 m apart. A Solo manual backpack sprayer was used to apply dimethoate (at 0.25, 0.50, and 1.0 kg AI/ha) and pirimicarb (at 0.125, 0.25, and 0.50 kg AI/ha) in water at the rate of 1100 L/ha on Aug 18 and 19.

Preparation of Plant Tissue Samples. Asparagus ferns were cut up with shears and the spears were chopped in a Braun vegetable shredder. The separate samples were then mixed thoroughly in a plastic bag. The thoroughness of mixing was assessed by taking four 10-g aliquots of the treated asparagus tissues after mixing for the determination of residues. The variability among the four aliquots was within 10%. All samples were stored in plastic bags at −20 °C until analysis within about 90 days.

Determination of Dimethoate and Dimethoxon. Aliquots of 10 g of ferns or 20 g of spears were mixed with 40 g of anhydrous sodium sulfate (Fisher Scientific) and then extracted by blending in a Sorval Omni-Mixer with 100 mL of ethyl acetate (glass distilled, BDH Chemicals Canada Limited) for 5 min while the container was immersed in an ice–water bath for dissipation of heat generated from blending. The extracts were filtered through a Büchner funnel lined with glass fiber filter paper into 500-mL round-bottom flasks. The filter cakes were extracted twice more with 50 mL of ethyl acetate, and the three extracts were combined. The pooled extracts were concentrated in a flash evaporator at 35 °C and the final volumes were adjusted to 10 mL with ethyl acetate.

Glass columns (30 cm × 1.1 cm i.d.) with Teflon stopcocks were packed from the bottom with a glass wool plug, 1.5 cm of anhydrous sodium sulfate, 4 cm of a 2:5 (w/w) mixture of acid-washed Nuchar carbon (Kodak Laboratory Chemicals) and Whatman CF-11 cellulose, 1.5 cm of anhydrous sodium sulfate, and another glass wool plug. The columns were prewashed with 10 mL of ethyl acetate. Crude extracts, equivalent to 2 g of ferns and 4 g of spears, were quantitatively transferred to the cleanup columns and the resulting eluates were collected in 100-mL round-bottom flasks. Dimethoate and dimethoxon were eluted with 20 mL of 20% methanol (glass distilled, BDH Chemicals Canada Limited) in ethyl acetate. The cleaned eluates were concentrated to an appropriate volume for GLC analysis in a flash evaporator at 35 °C.

Dimethoate and dimethoxon were analyzed with a Tracor MT-222 gas chromatograph equipped with a Tracor 702-NP nitrogen/phosphorus detector. The Pyrex glass column (75 cm × 2 mm i.d.) was packed with 2% OV-101 on 80/100 mesh Ultra-Bond 20 M (Ultra Scientific). The operating parameters were as follows: detector temperature 240 °C, inlet and outlet temperatures 210 °C, column temperature 175 °C, column flow rate 50 mL of helium/min, and plasma gas flow rate 3.5 mL of hydrogen/min and 120 mL of air/min. Under the conditions described the absolute retention times of dimethoate and dimethoxon were 2.16 min and 1.44 min, respectively.

Detector response was calibrated daily with authentic standards of dimethoate (99.5+%) and dimethoxon (97.3%) obtained from US Environmental Protection Agency, Research Triangle Park, NC 27711. Quantification was based on average peak heights of these external standards injected before and after the sample. Residue concentrations were all expressed in terms of tissue weight as sampled from the field (fresh wt).

Determination of Pirimicarb and Its Methylamino and Formyl(methylamino) Analogues. Pirimicarb and its toxic methylamino and formyl(methylamino) analogues were extracted with ethyl acetate from asparagus ferns and spears as described for dimethoate and dimethoxon. The

Table I. Recovery of Dimethoate, Dimethoxon, Pirimicarb, and (Methylamino)pirimicarb from Fortified Asparagus Ferns

compound	% recovery ± S.D. (n = 4) fortification level, ppm	
	1.0	0.01
dimethoate	96.5 ± 3.8	92.8 ± 3.4
dimethoxon	98.2 ± 4.1	94.4 ± 4.1
pirimicarb	97.8 ± 2.1	96.3 ± 6.2
(methylamino)- pirimicarb	91.3 ± 3.8	94.7 ± 3.6

pooled extracts were evaporated just to dryness and then made up to 10 mL in acetone. Crude extracts equivalent to 2 g of ferns and 4 g of spears were coagulated with 25 mL of a solution consisting of 15 g of ammonium chloride (Fisher Scientific) and 5 mL of 85% phosphoric acid (Fisher Scientific) in 1 L of water (Szeto and Sundaram, 1980). The acidified samples were allowed to stand at room temperature overnight to convert any formyl(methylamino)pirimicarb to (methylamino)pirimicarb (Bullock, 1973) and then filtered to remove the coagulated plant extractives. After neutralization of the supernatant with 1 N NaOH, pirimicarb and its methylamino analogue were reextracted from the aqueous phase by partitioning 3 times with 25 mL of dichloromethane (glass distilled, BDH Chemicals Canada Limited). The extracts were dried by filtering through anhydrous sodium sulfate, evaporated just to dryness in a flash evaporator at 35 °C, and redissolved in 2 mL of 10% (V/V) hexane (glass distilled, BDH Chemicals Canada Limited) in ethyl acetate. The extracts were further purified on glass chromatography columns (30 cm × 1.1 cm i.d.) packed with a glass wool plug, 1.5 cm of anhydrous sodium sulfate, 5 cm of silica gel (100/200 mesh, Fisher Scientific, used as received), and 1.5 cm of anhydrous sodium sulfate. The columns were prewashed with 10 mL of methanol followed by 10 mL of hexane. After introduction of the crude extracts, pirimicarb was eluted in fraction 1 with 40 mL of 10% hexane in ethyl acetate; (methylamino)pirimicarb was eluted in fraction 2 with 20 mL of 20% methanol in ethyl acetate. Both fractions were concentrated in a flash evaporator at 35 °C to appropriate volumes for GLC analysis.

Pirimicarb and (methylamino)pirimicarb were analyzed as described for dimethoate and dimethoxon except that the column temperature was 165 °C. The absolute retention times were 1.25 min for pirimicarb and 1.99 min for (methylamino)pirimicarb. Authentic analytical standards (99.4%) were supplied by Chipman Inc., Stoney Creek, Ontario L8G 3Z1, Canada.

RESULTS AND DISCUSSION

Samples of asparagus ferns and spears from the control were processed according to the analytical procedures described. There was no GLC response that interfered significantly with dimethoate, pirimicarb or their toxic metabolites. Asparagus ferns and spears were fortified with the chemicals at two concentration levels to determine the accuracy and precision of the analytical methods. The percent recoveries of dimethoate, pirimicarb, and their toxic metabolites ranged from 91.3 to 98.2% for asparagus ferns (Table I). The GLC system used in this study was extremely sensitive in detecting the compounds of interest. Injection of 0.3 ng of (methylamino)pirimicarb, which was the least sensitive compound, produced approximately 20% fullscale response. Since aliquots equivalent to 2 g of ferns and 4 g of spears were cleaned up for GLC analysis, the limit of detection for each compound was at least 0.002 ppm (fresh weight).

Degradation of Dimethoate and Pirimicarb

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Table II. Residues of Dimethoate and Pirimicarb in Asparagus Fern after Their Foliar Application to a 1-Year-Old Asparagus Stand at Coldstream in 1982

posttreatment interval, days	residues, ppm (fresh wt)					
	dimethoate	dimethoxon	total	pirimicarb	(methylamino)pirimicarb[a]	total
			1st Spray[b]			
2	11.0	1.00	12.0	3.08	2.25	5.33
10	1.01	1.02	2.03	0.09	0.18	0.27
17	0.21	0.43	0.64	0.03	0.03	0.06
24				0.01	0.06	0.07
31	tr[c]	0.06	0.06	tr	tr	tr
46	tr	tr	tr			
			2nd Spray[d]			
0				30.8	4.00	34.8
2	4.43	0.45	4.88			
12	0.71	0.65	1.36			
14				0.19	0.23	0.42
21	0.17	0.52	0.69			
26	0.36	0.18	0.54	0.02	0.01	0.03
33	0.12	0.38	0.50	0.02	tr	0.02
46				e	tr	tr
66				e	e	e

[a] The other toxic metabolite, formyl(methylamino)pirimicarb was converted to (methylamino)pirimicarb for analysis. [b] The first spray (dimethoate at 1.12 kg AI/ha and pirimicarb at 0.50 kg AI/ha) was applied on July 24, 1982. [c] tr = less than 0.01 ppm (fresh wt). [d] The 2nd spray (dimethoate at 1.12 kg AI/ha and pirimicarb at 0.50 kg AI/ha) was applied on Sept 8 and Aug 25, 1982, respectively for dimethoate and pirimicarb. [e] Not detected at the limit of detection of 0.002 ppm (fresh wt).

Table III. Residues of Dimethoate and Pirimicarb in Asparagus Fern after Their Foliar Application to a 17-Year-Old Asparagus Stand at Armstrong in 1982

posttreatment interval, days	residues, ppm (fresh wt)					
	dimethoate	dimethoxon	total	pirimicarb	(methylamino)pirimicarb[a]	total
			1st Spray[b]			
5	5.14	1.62	6.76	1.11	0.61	1.72
12	0.43	0.48	0.91	0.08	0.10	0.18
20	0.08	0.29	0.37	c	c	c
26	0.02	0.04	0.06	0.03	0.01	0.04
39	0.10	tr[d]	0.10			
			2nd Spray[e]			
2	22.4	2.12	24.5			
3				0.34	0.91	1.25
9	0.98	0.75	1.73			
16				0.06	c	0.06
23				0.04	0.03	0.07

[a] The other toxic metabolite, formyl(methylamino)pirimicarb, was converted to (methylamino)pirimicarb for analysis. [b] The first spray (dimethoate at 1.12 kg AI/ha and pirimicarb at 0.50 kg AI/ha) was applied on July 29, 1982. [c] Not detected at the limit of detection of 0.002 ppm (fresh wt). [d] tr = less than 0.01 ppm (fresh wt). [e] The 2nd spray (dimethoate at 1.12 kg AI/ha and pirimicarb at 0.50 kg AI/ha) was applied on Sept 17, and Sept 3, 1982, respectively for dimethoate and pirimicarb.

In the 1982 field trial of dimethoate at Coldstream residues of 12 ppm dimethoate plus dimethoxon were detected in the ferns at the first sampling date two days after application (Table II). Conversion of some dimethoate to dimethoxon had occurred in the ferns during this time. The highest concentration of dimethoxon was 1.02 ppm detected after 10 days, which accounted for approximately 50% of the total residues at that time. Thereafter the concentrations of both dimethoate and dimethoxon decreased until only traces (<0.01 ppm, fresh wt) were left at 46 days (Table II).

A second spray was applied on Sept 8, 46 days after the first application. Heavy rain fell the day after the spray. As a consequence, only 4.88 ppm of dimethoate plus dimethoxon were detected in the ferns two days later, compared with 12 ppm two days after the first spray (Table II). The conversion of some dimethoate to dimethoxon and the rapid degradation of both compounds were again observed. Results of the field trials at Armstrong are presented in Table III and are in general agreement with those of the field trials at Coldstream. The partial conversion of dimethoate to dimethoxon and the rapid degradation of both have been observed in wheat plants by Lee and Westcott (1981), in lettuce by Szeto et al. (1984),

and in citrus by Woodham et al. (1974a and 1974b).

In order to further examine the behavior of dimethoate sprays, it was again applied in 1983, at 0.25, 0.50, and 1.0 kg AI/ha, and the results are presented in Table IV. After spraying, 6–12 h were allowed for the spray mists to equilibrate before the first fern samples were taken to determine the initial concentration of residues. The total residues of dimethoate plus dimethoxon were 7.83, 13.8, and 23.8 ppm respectively after applications of dimethoate at 0.25, 0.50, and 1.0 kg AI/ha. The concentrations of initial residues correlated very well with the application rates of dimethoate. Oxidation of dimethoate to dimethoxon was evident shortly after spray application when approximately 0.5 ppm of dimethoxon were found in ferns 6 h after application at the two higher rates. The dimethoxon concentrations peaked two days after application and decreased continually thereafter. After 13 days, dimethoxon levels exceeded those of dimethoate, which declined more rapidly. Ferns collected up to 24 days after application showed the following relationship between dimethoate residues and dimethoxon residues: ferns with higher concentrations of dimethoate contained more dimethoxon also. After 31 days both dimethoate and dimethoxon decreased to a low level ranging from trace

Table IV. Residues of Dimethoate in Asparagus Fern after Its Foliar Application to an Immature Asparagus Stand at Summerland in 1983

posttreatment interval	rate, kg AI/ha	residues, ppm (fresh wt)		
		dimethoate	dimethoxon	total
6 h	0.25			
	0.50	13.3	0.48	13.8
	1.0	23.3	0.52	23.8
12 h	0.25	7.66	0.17	7.83
	0.50			
	1.0			
1 day	0.25	2.37	0.31	2.68
	0.50	8.31	0.63	8.94
	1.0	11.3	0.83	12.1
2 days	0.25	2.25	0.38	2.63
	0.50	5.00	0.90	5.90
	1.0	7.66	1.64	9.30
4 days	0.25	1.86	0.29	2.15
	0.50	2.41	0.74	3.15
	1.0	6.12	1.15	7.27
7 days	0.25	0.57	0.32	0.89
	0.50	1.13	0.51	1.64
	1.0	1.44	0.71	2.15
10 days	0.25	0.26	0.11	0.37
	0.50	0.49	0.26	0.75
	1.0	0.80	0.49	1.29
13 days	0.25	0.06	0.05	0.11
	0.50	0.12	0.12	0.24
	1.0	0.13	0.25	0.38
18 days	0.25	0.01	0.07	0.08
	0.50	0.03	0.19	0.22
	1.0	0.06	0.28	0.34
24 days	0.25	tr[a]	0.01	0.01
	0.50	0.01	0.04	0.05
	1.0	0.01	0.07	0.08
31 days	0.25	tr	0.01	0.01
	0.50	0.01	0.03	0.04
	1.0	0.01	0.02	0.03
38 days	0.25	tr	tr	tr
	0.50	0.01	0.02	0.03
	1.0	0.01	0.01	0.02

[a] tr = less than 0.01 ppm (fresh wt).
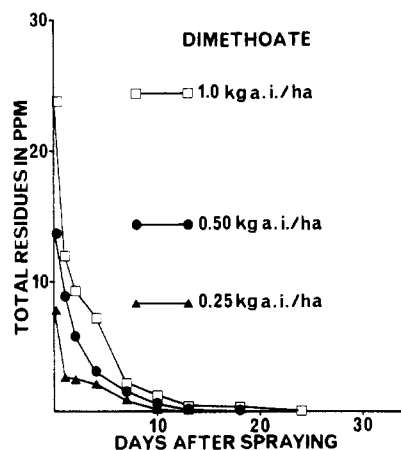
Figure 1. Total residues (dimethoate + dimethoxon) in asparagus ferns after foliar applications of dimethoate at 0.25, 0.50, and 1.0 kg AI/ha.

(<0.01 ppm) to 0.04 ppm and the relationship between the two concentrations was no longer observed. The rates of disappearance of total residues were relatively fast in the first seven days but slowed considerably thereafter (Figure 1). Approximately 90% of the total residues disappeared in seven days and only trace (<0.01 ppm) to 0.03 ppm were present after 38 days.

In all field trials with dimethoate, samples of spears harvested in the following spring contained no detectable residues of either dimethoate or dimethoxon. The lower
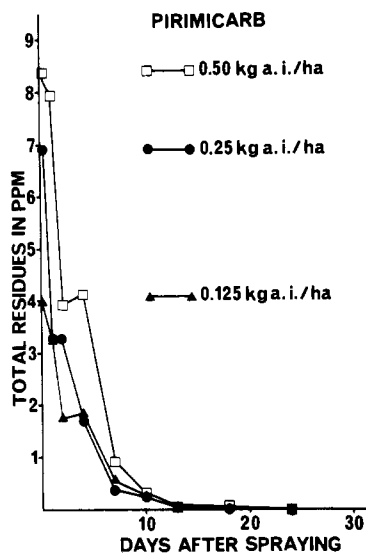
Table V. Residues of Pirimicarb in Asparagus Fern after Its Foliar Application to an Immature Asparagus Stand at Summerland in 1983

posttreatment interval	rate, kg AI/ha	residues, ppm (fresh wt)		
		pirimicarb	(methylamino)-pirimicarb[a]	total
6 h	0.125	1.36	2.69	4.05
	0.25	3.09	3.89	6.98
	0.50	4.81	3.58	8.39
1 day	0.125	1.22	2.01	3.23
	0.25	1.64	1.60	3.24
	0.50	4.54	3.43	7.97
2 days	0.125	0.54	1.20	1.74
	0.25	1.63	1.61	3.24
	0.50	2.47	1.46	3.93
4 days	0.125	0.69	1.17	1.86
	0.25	0.70	1.01	1.71
	0.50	2.03	2.13	4.16
7 days	0.125	0.18	0.35	0.53
	0.25	0.14	0.25	0.39
	0.50	0.39	0.52	0.91
10 days	0.125	0.06	0.23	0.29
	0.25	0.07	0.18	0.25
	0.50	0.12	0.19	0.31
13 days	0.125	0.03	0.06	0.09
	0.25	0.01	0.03	0.04
	0.50	0.03	0.04	0.07
18 days	0.125	b	0.01	0.01
	0.25	0.01	0.02	0.03
	0.50	0.01	0.04	0.05
24 days	0.125			
	0.25	b	tr[c]	tr
	0.50	b	b	b
31 days	0.125			
	0.25	b	b	b
	0.50	b	tr	tr
38 days	0.125			
	0.25	b	b	b
	0.50	b	b	b

[a] The other toxic metabolite, formyl(methylamino)pirimicarb, was converted to (methylamino)pirimicarb for analysis. [b] Not detected at the limit of detection of 0.002 ppm (fresh wt). [c] tr = less than 0.01 ppm (fresh wt).

limit of detection was 0.002 ppm for each compound.

Results of the 1982 field trials with pirimicarb showed that this chemical was partially converted to its toxic methylamino and/or formyl(methylamino) analogues and the total residues persisted in ferns for about 30 days (Tables II and III). These findings were further supported by the 1983 field trials with pirimicarb at three rates (Table V). The total residues including the metabolites initially present in the ferns collected 6 h after application did not correlate well with the application rates. Residues of 4.05, 6.98, and 8.39 ppm respectively were detected after applications of pirimicarb at 0.125, 0.25, and 0.50 kg AI/ha (Table V). This was possibly due to the fact that rapid conversion of pirimicarb to its toxic metabolites and rapid disappearance of total residues occurred within the 6 h prior to the first sampling. The rapid disappearance was also demonstrated by the detection of only 8.39 ppm total residues after 6 h compared with 34.8 ppm found within 1 h after application of pirimicarb at the same rate in the second treatment of the 1982 field trials at Coldstream (Table II). (Methylamino)pirimicarb accounted for approximately 40–60% of the total residues throughout the sampling period (Table V). Based on the 1983 results it was apparent that the rates of disappearance of total residues were fast in the first seven days after application and slowed down greatly thereafter (Figure 2). This disappearance pattern was similar to that of dimethoate discussed previously. Approximately 90% of the total residues disappeared in seven days and only traces (<0.01

Figure 2. Total residues (pirimicarb + (methylamino)pirimicarb and formyl(methylamino)pirimicarb) in asparagus ferns after foliar applications of pirimicarb at 0.125, 0.25, and 0.5 kg AI/ha.

ppm) remained after 24 days. The rapid conversion to toxic metabolites and the disappearance of total residues also occurred in lettuce (Szeto et al., 1984) indicating that pirimicarb is readily degradable in the environment. Spears harvested in the following spring from each field trial were analyzed for residues. None could be detected at the limit of 0.002 ppm.

Based on the results of field trials in 1982 and 1983, it is evident that residues of dimethoate, pirimicarb, and their toxic metabolites degraded readily in asparagus ferns.

After insecticide applications, the total residues including toxic metabolites decreased to negligible levels (<0.1 ppm) in 13 days for pirimicarb and in 24 days for dimethoate. The likelihood of finding toxic residues in marketable asparagus spears resulting from using dimethoate and pirimicarb at rates tested in our studies appears to be remote. The facts that contributed to this conclusion are that all insecticide applications are made after harvesting and treated ferns die down in fall, and the demonstration in our studies that the marketable spears harvested in the following spring showed no sign of measureable residues of these insecticides.

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Structural–Bioactivity Relationship for Tumor Promotion by Cyclopropenes

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Studies with trout measuring the carcinogenic and promotional activity of various cyclopropenoid compounds show that these componds can be divided into two distinct groups: highly active and completely inactive. 1,2-Dioctylcyclopropene and methyl sterculate show equal and significantly higher activity than methyl malvalate. Methyl dihydrosterculate and 1,2-dialkylcyclopropenes with a chain length of 16 and fewer carbons are completely inactive in this system. Sterculic acid is also more active than malvalic toward depressing cytochrome P-450 levels. It is suggested that expression of activity requires incorporation of the intact cyclopropenoid fatty acid into biomembranes.

Two unusual fatty acids, sterculic and malvalic acids, have a highly strained and reactive cyclopropene ring forming the center of their 18 and 17 carbon chains. The

$$CH_3(CH_2)_7-C\overset{\displaystyle CH_2}{=\!\!=\!\!=}C-(CH_2)_nCO_2H$$

sterculic acid, *n* = 7
malvalic acid, *n* = 6
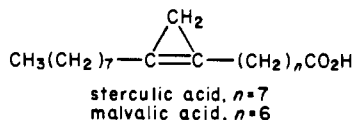
potential intake of these compounds in the human diet may be considerable. Sterculic and malvalic acids are found in the seed lipids from plants of the order Malvales,

which includes cotton, kapok, okra, limes, durian, and china chestnuts (Carter and Frampton, 1964). The nut *Pachira aquatica* contains 58% lipid, 26% of which consists of cyclopropene fatty acids (CPFA) (Bohannon and Kleiman, 1978), and is extensively consumed by humans in Brazil and the West Indies. *Sterculia foetida* beans, over half lipid of which 65% is CPFA, are occasionally consumed in India and tropical countries. In addition there are numerous cultivated and uncultivated plants of the order Malvales which have not been surveyed for CPFA. Many of these plants are in the human diet or are consumed by animals in the human food chain. Although human distribution and metabolism of dietary CPFA are unknown, CPFA in the diet of rats are passed through material milk to infant pups (Nixon et al., 1977a).

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