to enhance red color formation without stimulating ripening.

Another concern is how to predict the onset of the climacteric if our aim is to harvest the fruits just several days before that physiological event. A great variation in maturity among fruits on the same tree was noticed. Our judgment probably should be based on a small but significant fraction of early maturing fruits. In this study the onset of the climacteric meant the time when at least 1 fruit in each of the duplicate 5-fruit samples had an elevated CO_2 and ethylene production rates. An initial several-fold increase in internal ethylene prior to the start of the climacteric might be a useful signal. Unfortunately the signal comes too late to be of great practical value. Furthermore, measuring the length of preclimacteric periods of harvested fruits is too time consuming to be practical. The correlation between the minimum treatment time required for 10 ppm ethylene to trigger the climacteric (MTT) and the length of the preclimacteric period may be more useful. The time required to determine the MTT was about 2 days for very immature fruits, but was less than 24 hr for fruits harvested 1 week prior to the natural onset of the climacteric.

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J. Amer. Soc. Hort. Sci. 103(3):392–394. 1978.

Residues of Acephate and Methamidophos in Greenhouse Tomatoes[1]

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Additional index words. pesticide, *Lycopersicon esculentum*

Abstract. **Acephate was applied to greenhouse tomatoes (*Lycopersicon esculentum* Mill.) as single and multiple applications, and residues on the fruits were determined several times after treatment. Immediately after application, residues of acephate averaged 0.46, 0.83, and 1.81 ppm for plots receiving 0.56, 1.12, and 2.24 kg/930 liter solutions, respectively. By day 7 residues of acephate, averaged over all rates, were 5.4% of day 0 values. Residues of methamidophos, a metabolite of acephate, were detected in all samples except those for day 0, but differences between rates and days after application were not significant. A statistical comparison of residue data showed that total residues (acephate plus methamidophos) were significantly greater after spraying once a week for 4 weeks than after a single application.**

Acephate (*O,S*-dimethyl acetylphosphoramidothioate) and its primary metabolite methamidophos (*O,S*-dimethyl phosphoramidothioate) are effective for controlling a wide variety of insect pests (2, 4). Because of its low mammalian toxicity and effectiveness, there is considerable interest in obtaining registration of acephate on greenhouse tomatoes. Therefore studies were designed to determine the disappearance rate of acephate and methamidophos from tomato fruit after application at several rates to greenhouse tomatoes and to compare residue levels from single and multiple spray applications.

Materials and Methods

First expt. Acephate was applied once to 6 plots of greenhouse tomatoes in the fall of 1974. Each plot contained 5 'Michigan-Ohio Hybrid' plants. Spray solutions containing 0.56, 1.12, and 2.24 kg ai of acephate (75% SP formulation) per 930 liters were applied with a constant-pressure CO_2 sprayer. Spraying pressure was 1.2 kg/cm^2, and the plants were sprayed to runoff (equivalent to 930 liters/ha). An untreated control was maintained in each replication. A 1-kg sample of red fruit was taken from each plot in 2 replicates 1, 2, and 4 days after application. Samples were packed in insulated boxes containing dry ice for transport to the laboratory where they were stored at −18°C until analyzed 6 weeks later.

Second expt. Applications were made to 9 plots of greenhouse tomatoes in the spring of 1975. Each plot contained 8 'Manapal' plants. Untreated controls were included. Formulation of acephate and rates and method of application were identical to those employed in expt. 1. Samples weighing 1 kg were taken at 0, 1, 2, 3, 4, and 7 days after application in each of 3 replicates.

Immediately after the day 7 sampling, 3 additional weekly sprays were applied at the same rates and to the same plots. Samples were taken at 2, 3, and 4 days after the final (4th) application. Sample wt and processing before analysis were

[1]Received for publication January 16, 1978. Paper No. 5092 of the Journal Series of the North Carolina Agricultural Experiment Station, Raleigh, NC 27650.

the same as those employed in the expt. 1, except that the samples were analyzed the day after harvest. Fruit diam in most samples varied from 4 to 12 cm, but at all 3 harvests after the 4 weekly sprays, fruit were smaller, ranging from 4 to 7 cm in diam.

Residue determinations. Subsamples, consisting of 8 to 10 tomatoes, were removed from each sample and macerated in a blender, and 50 g were transferred to an 850-ml glass jar, and 150 ml of ethyl acetate added. Anhydrous sodium sulfate, 250 g, was added slowly with stirring to prevent the sodium sulfate-tomato mixture from caking. This mixture was blended 5 min at 2000 rpm. The homogenate was filtered through sodium sulfate into a Kuderna-Danish evaporator, and the tomato-sodium sulfate mixture was extracted twice more with 100-ml portions of ethyl acetate. The combined filtrate was evaporated to 5 to 8 ml on a 100°C water bath.

Interfering substances were removed with the cleanup method developed by Leary (1). Residue levels were determined by GLC after column cleanup and concn to 5 to 8 ml on an 80°C water bath.

The gas chromatograph was a Tracor Model MT 220 with a flame photometric detector operated in the phosphorous mode. Columns were U-shaped glass (183 by 0.64 cm) packed with 4% SE-30 + 6% QF-1 on Gas Chrom Q (80/100 mesh). Nitrogen was the carrier gas with a flow rate of 80 ml/min. Gases to the detector were hydrogen, air, and oxygen at flow rates of 95, 28, and 33 ml/min, respectively. Temp conditions were as follows: oven 190°C; detector 200°; and inlet 210°. Columns were preconditioned at 250° for 48 hr before use. Standards containing 0.25μg/ml of acephate or methamidophos were used for quantitation, and residue levels were determined by the peak height method. The sensitivity of detection was 5 ppb for each compound.

The efficiency of the analytical method was determined by adding known amounts of acephate and methamidophos at concn varying from 0.01 to 0.5 ppm to untreated tomato homogenates and analyzing the fortified samples by the same procedure. Two fortified samples were analyzed with each set of 12 experimental samples.

Concn of acephate and methamidophos were transformed for statistical analysis to the logaritham of X + 1 (3), X being the concn of acephate or methamidophos in ppm.

Results

The average recovery of acephate, added to 27 samples of 50 g of untreated tomatoes and 22 samples of 5 ml of water, which were carried through column cleanup, was 90%; for methamidophos average recoveries were 101% from tomatoes and 98% from water. Residue levels in the samples were not corrected.

One day after application in expt. 1 residue levels of acephate averaged 0.54, 0.78, and 3.15 ppm for the 0.56, 1.12, and 2.24 kg/ha rates, respectively (Table 1). By day 4, acephate residues averaged 61, 65, and 32% of day 1 levels, respectively, at the 0.56, 1.12, and 2.24 kg/ha rates. Residue levels of methamidophos were 0.06 to 0.08 ppm for both 0.56 and 1.12 kg/ha rates and 0.32 and 0.17 ppm for the 2.24 kg/ha rate on days 2 and 4, respectively. The interaction of days after application X rates of application was significant for both acephate and methamidophos residues.

In samples from expt. 2, residues of acephate averaged 0.46, 0.83, and 1.81 ppm immediately after application of the 0.56, 1.12, and 2.24 kg/ha, respectively (Table 1). There was a gradual decline of residue at all rates between days 1 and 4; and by day 7, residues of acephate averaged over all rates was 5.4% of day 0 values. The statistical analysis showed significant differences among logarithm means of acephate residues for time after application, rate of application, and the interaction or rate of application × time after application. Residues of methamidophos were detected in all samples except those for day 0, but differences between rates, days after application, and the interactions of rate × time were not significant.

Table 1. Acephate and methamidophos residues in greenhouse tomatoes resulting from a single-spray application.

Rate of applic. (kg/ha)	Time from applic. to harvest (days)	Expt. 1 Acephate (ppm)	Expt. 1 Methamidophos (ppm)	Expt. 2 Acephate (ppm)	Expt. 2 Methamidophos (ppm)
0.0	0	–[z]	–[z]	0.11	<0.005
	1	<0.005	<0.005	0.10	<0.005
	2	<0.005	<0.005	<0.005	<0.005
	3	–	–	<0.005	<0.005
	4	<0.005	<0.005	<0.005	<0.005
	7	–	–	<0.005	<0.005
0.56	0	–	–	0.46	<0.005
	1	0.54	<0.005	0.38	<0.005
	2	0.55	0.06	0.17	0.05
	3	–	–	0.13	0.03
	4	0.53	0.06	0.05	0.03
	7	–	–	0.01	0.03
1.12	0	–	–	0.83	<0.005
	1	0.78	<0.005	0.62	<0.005
	2	0.52	0.06	0.97	0.17
	3	–	–	0.21	0.09
	4	0.51	0.08	0.21	0.06
	7	–	–	0.08	0.12
2.24	0	–	–	1.81	<0.005
	1	3.15	<0.005	0.89	<0.005
	2	2.70	0.32	0.62	0.13
	3	–	–	0.24	0.10
	4	1.02	0.17	0.05	0.04
	7	–	–	0.08	0.07

[z]Samples not taken on days 0, 3, and 7 from Expt. 1.

Table 2 records acephate and methamidophos residues in tomatoes sampled 2, 3, and 4 days after the last of 4 successive weekly applications of acephate. Residue levels of acephate declined about 30% in the 1.12 and 2.24 kg/ha rates from day 2 to 3. From day 3 to day 4, a decrease in residue concn was observed only with the 2.24 kg/ha rate. There was no change between day 2 and 4 in the 0.56 kg/ha samples.

The total residues (acephate + methamidophos) on sampling days 2, 3, and 4, expressed as ppm on the fruit, were significantly

Table 2. Acephate and methamidophos residues in greenhouse tomatoes 2, 3, and 4 days after the last of 4 successive weekly applications of acephate (expt. 2).

Rate of application (kg/ha)	Time from application to harvest (days)	Acephate concn (ppm)	Methamidophos concn (ppm)
0	2	0.03	0.1
	3	0.01	0.005
	4	0.01	0.005
0.56	2	0.31	0.12
	3	0.32	0.05
	4	0.21	0.04
1.12	2	1.42	0.44
	3	0.73	0.05
	4	0.43	0.04
2.24	2	2.33	0.70
	3	1.33	0.63
	4	0.65	0.20

Table 3. Comparison of total residues (acephate plus methamidophos) on greenhouse tomatoes from either a single or multiple application.

Rate of application (kg/ha)	Type of application	Total residues (ppm) Day 2	Day 3	Day 4
0.56	Single	0.22	0.16	0.08
	Multiple[z]	0.43	0.37	2.25
1.12	Single	1.14	0.30	0.27
	Multiple[z]	1.86	0.78	0.47
2.24	Single	0.75	0.34	0.09
	Multiple[z]	3.03	1.96	0.85

[z]Plots sprayed once a week for 4 weeks and harvested 2, 3, and 4 days after the last application.

greater after a multiple-spray application than after a single application (Table 3). Total residues in ppm from multiple applications were from 2 to 9 times greater than those from a single application

Discussion

The observed variation of residue levels of acephate and methamidophos could be due to several factors, but tomato size was probably of major importance. The concn of residue in a large fruit with a lower surface area to weight ratio would be smaller than that for a small fruit with a larger surface area to weight ratio with the same deposit of spray per unit area on the fruit surface. The generally lower acephate residues in expt. 2 (after single application) might be due, also, to the spring vs. fall planting and differences in the environmental conditions in the greenhouse.

Fruit varied from 4 to 12 cm in diam in most samples; and differences in fruit size probably contributed to variations of the residue values. Fruit for all 3 harvests following the 4 weekly sprays were smaller (ranging from 4 to 7 cm in diam with some immature fruit) than those from the harvests after the single application. Therefore, differences between residues on samples harvested after 4 weekly sprays and those on samples after the single spray can be attributed, at least in part, to the effect of the surface area to weight ration on residues. Some of the difference might also have been due to accumulation of residues on samples that received multiple sprays.

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J. Amer. Soc. Hort. Sci. 103(3):394–397. 1978.

Inhibition of Ripening Processes in Pears by Inhibitors of Cyanide-resistant Respiration and by Silver[1]

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Additional index words. cyanide-insensitive respiration, *Pyrus communis*

Abstract. **Various concentrations of salicylhydroxamic acid and alpha, alpha-dipyridyl (reported inhibitors of cyanide-insensitive respiration) applied to fruit of 'Bosc' pear (*Pyrus communis* L.) reduced fruit softening. The application of silver ions, reported to inhibit ethylene action, delayed ripening.**

The initiation of the ripening process in climacteric fruit is attributed to the action of ethylene as it increases in tissues approaching senescence (5). The action of ethylene in promoting fruit ripening can be minimized by rapidly removing this volatile from fruit tissues. This is done by increasing the diffusion of ethylene to the environment by storing fruit under hypobaric conditions (6). The action of ethylene can also be antagonized by high CO_2 and low oxygen tensions (7). Recently Beyer (3) showed that silver will antagonize such ethylene-dependent responses in plants as leaf, flower, and fruit abscission in cotton, floral senescence in orchids, and the "triple response" in etiolated peas. Other methods to antagonize the action of ethylene may be based on inhibiting the metabolic action of the compound. Solomos and Laties (16) suggested that ethylene stimulates the cyanide-resistant respiration (the "alternate respiratory pathway"). In this view, stimulating fruit ripening by ethylene may reflect the initiation of the cyanide-resistant respiration (15). Consequently, inhibiting this respiratory path may result in a corresponding inhibition of ethylene-stimulated ripening processes in fruit.

In the present study, we examined this concept and we show that inhibitors of the cyanide-resistant respiration inhibit ripening processes in pear. Likewise, silver, the ethylene antagonist, is a potent inhibitor of fruit ripening.

Materials and Methods

'Bosc' pear, obtained from Pine Grove, Pa, were harvested in the mature-green preclimacteric state and stored under hypobaric conditions at 0°C until used (up to 2 months). Average fruit wt was 125 g. Hypobaric conditions were 1/10th atmospheric pressure with the continuous flow of water saturated air through the chamber to prevent disication.

A vacuum infiltration technique (10) was employed to apply test compounds to intact fruit. The test solutions were applied in a 0.3 M mannitol solution as a carrier. The fruits were infiltrated at an average rate of 5 ml of test solution/100 g of

[1]Received for publication Nobember 18, 1977.

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