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Residues of Phenthoate (Cidial) and Its Oxon on Grapefruit, Lemons, Oranges, Their Fractionated Products, and Soil

H. Anson Moye,* Robert F. Brooks,[1] and Susan J. Scherer

An analytical procedure for the analysis of phenthoate insecticide [*O,O*-dimethyl *S*-(α-carboethoxybenzyl) phosphorodithioate, Cidial] and its oxon is described for fresh grapefruit, lemons, and oranges as well as for 15 fractionated products and soil. The phenthoate, in the form of an emulsifiable concentrate (Cidial), was applied to the citrus trees at 4 and 8 oz of active ingredient/100 gal. Fresh fruit and soil exhibited typical first-order decay for phenthoate, with levels after 7 days in peel below 1 ppm; pulp levels never exceeded 0.04 ppm (orange, 7 days). Maximum phenthoate soil levels occurred at the tree drip line near the surface (0.55 ppm) but decayed to 0.12 ppm after 28 days; maximum oxon occurred at 14 days for these samples (0.04 ppm). Lemon peel oil, resulting from the 8 oz/100 gal treatment, incurred the highest phenthoate residues (16 ppm) as well as oxon (2.2 ppm). Wash water (after-water rinse) contained negligible residues of phenthoate and oxon.

Phenthoate [*O,O*-dimethyl *S*-(α-carboethoxybenzyl) phosphorodithioate, Cidial] is a broad spectrum organophosphorous insecticide effective in controlling various mites, thrips, and scale insects. It has an LD_{50} for the rat of 4728 mg/kg and for the common housefly of 5 mg/kg (Pellegrini and Santi, 1972). Phenthoate oxon has been shown to be the major metabolite removable from orange peel surfaces by solvent extraction (Takade et al., 1976) while the major bound residues released by enzymatic and hydrolytic conditions were shown to be ethyl mandelate and mandelic acid (Mallipudi and Fukuto, 1981). The two bound residues are toxicologically innocuous and can be dismissed.

Most Florida citrus production is used for processed products, such as juice concentrate, peel oil, and dried peel and molasses which are combined into cattle feed. The safety of these products in terms of freedom from hazardous pesticide residues is a concern particularly since the potential exists for concentrating the residues by processing. In addition, significant amounts of water are used in a typical citrus processor as the fruit is washed prior to being sized; water contaminated with pesticide could present a problem in its disposal, whether it be returned to a natural body of surface water or to the aquifer or otherwise. Consequently, the ability to ensure safe foods and environment requires analytical procedures for all of the above-named materials.

A method for measuring residues of phenthoate and phenthoate oxon on fresh citrus fruit and leaves, as well as soil, has been reported (Iwata et al., 1977). Acetonitrile was used for extracting citrus fruit, while acetone was used for extracting soil; after partitioning the extracts were concentrated and analyzed by gas chromatography employing either alkali flame ionization detection (AFID) or flame photometric detection (FPD). Gas chromatographic columns used were 3% OV-1, 3% DC-200, or 5% DC-200–7.5% QF-1.

The method described here, while employing gas chromatography with FPD detection, uses modified extraction

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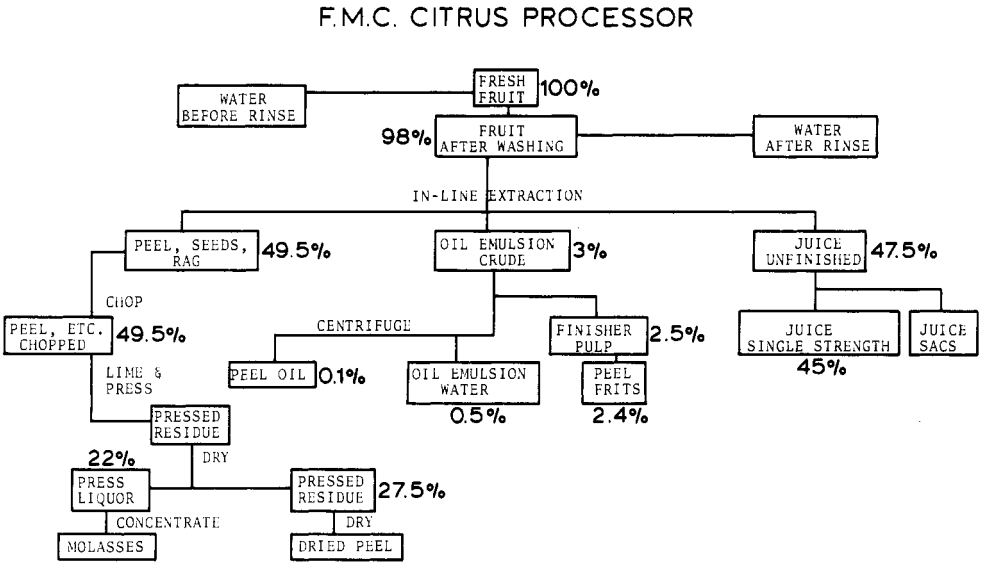

Figure 1. Schematic of the F.M.C. citrus processor used for producing fractions. Approximate weight percentages of each fraction compared to the initial weight of fresh fruit processed are shown.

techniques and a 3% OV-25 column, allowing for the analysis of many fractionated citrus products while preventing interferences from five other organophosphate pesticides most commonly used on Florida citrus. Sample cleanup, other than simple partitioning, was not required, except for peel oil, due to the extreme selectivity of the flame photometric detector.

MATERIALS AND METHODS

Instrumentation. A Hewlett-Packard Model 5840A gas chromatograph equipped with a Model 7671A automatic sampler and a flame photometric detector was used. Except for the GC column selectivity studies a 1.8 m × 2 mm i.d. glass column packed with 3% OV-25 on 100–120 high-performance Chromosorb W (Applied Sciences, State College, PA) was used. The injector, column, and detector temperatures were 225, 200, and 225 °C, respectively. Prepurified N_2 was used as the carrier gas at 50 mL/min. Flame detector gas flows were 30, 40, and 200 mL/min respectively, for O_2, air, and H_2. A Buchi Model R (Brinkmann, Westbury, NY) rotary evaporator was used to reduce sample volumes. Extractions were performed with a Lourdes for all solid sample types other than soil which was extracted on a flat-bed shaker.

Cleanup of oil samples was performed on Model 3400-D-25X60 glass columns, 2.5 cm × 60 cm (Glenco Scientific, Houston, TX), packed with Sephadex LH-20 (Pharmacia, Piscataway, NJ).

All solvents were of reagent-grade quality.

Fractionated citrus fruit products were prepared at the Lake Alfred Research and Education Center, University of Florida, as previously described (Kesterson and Braddock, 1979). A schematic of the processor that was used is shown in Figure 1.

Field Plots. Experiments were conducted on Marsh grapefruit, Bearss lemons, and Valencia oranges as well as soil taken from beneath the orange trees.

Approximately 17-year-old Marsh grapefruit trees were used, 18–20 ft in four-tree plots; one plot was used for each of four field replicates. Two sets of field replicates were studied, one employing Cidial 4E containing 4 oz of active ingredient/100 gal (C1X) and the other employing Cidial 4E containing 8 oz of active ingredient/100 gals (C2X). Cidial 4E was applied on Feb 5, 1979, at 25 gal/tree and on Feb 22 at 26.25 gal/tree. A truck-mounted high-pressure sprayer equipped with a Meyers pump and an FMC handgun was used. Fruit was picked for processing on March 8; on March 12 the fruit was washed and then processed on March 13. Fresh fruit samples were collected 1, 3, 7, 14, 28, 42, and 56 days after the last Cidial application and stored at −20 °C before analysis. Prespray samples were collected for controls as well.

Mature Bearss lemon trees 12 years old and 10–15 ft tall in 10 ft × 10 ft beds were separated into four-tree plots; one plot was used for each of four field replicates. Cidial was applied at the same rate as for the grapefruit but only at the C2X concentration on Oct 5, 1978, and Oct 20, with samples harvested and processed 18 days later on Nov 7. No fresh fruit samplings were made.

Valencia orange trees, 19 years old and 15–18 ft high with dense foliage were selected in 25 × 25 ft plots each containing 24 trees. Field replicates were treated similar to the grapefruit. Twenty gallons per tree was applied on Nov 6, 1978, and Feb 15, 1979, by using a Speed Sprayer 757 with double oscillating volute. Samples for processing were collected April 6, 1979, washed on April 9, and processed April 10. Whole fruit samples were collected at 1, 7, 14, and 42 days after the last Cidial application.

Soil samples were taken from beneath Valencia orange trees that had received a C2X application; the trees were set in 48-tree plots and were sprayed on Nov 6, 1978, in four field replications. A control for each sample type was obtained before spraying, soil being sampled at depths of 0–2.5 and 2.5–5.0 in., both at the drip line of the trees (drip line) and midway between the trunk of the tree and the drip line (midline). Soil samples were taken at 1, 3, 7, 14, 28, 42, and 56 days after the last spraying.

After all samples were collected and processed, they were stored at −20 °C until transportation to the Pesticide Research Laboratory, University of Florida, Gainesville, FL, where they were stored at −20 °C until analyzed.

GC Column Resolution Studies. Five of the most commonly used organophosphate pesticides on citrus in Florida were chosen to ensure that a GC column was selected which prevented their interfering with phenthoate and oxon chromatography. These were malathion, ethion, guthion, trithion, and methidathion (Supracide) (see Table I for the column packings which were examined). The 1.8 m × 2 mm i.d. column was operated at 170 °C with the N_2 carrier gas set at 50 mL/min.

Extraction Studies. A previously reported procedure for the extraction of phenthoate and oxon from soil which

Table I. GC Resolution Study[a]

stationary phase[b]	results
3% OV-1	phenthoate and Supracide unresolvable
5% DC-200	no oxon response
2% OV-101	phenthoate and malathion unresolvable
3% OV-25	full resolution for all organophosphates
3% OV-225	phenthoate and oxon unresolvable
1.5% OV-17-1.95% QF-1	no oxon response
4% SE-30-6% OV-210	phenthoate and malathion unresolvable
5% OV-210	phenthoate and malathion unresolvable
2% SP-2330	no oxon response
2% LAC-2R-446	no phenthoate or oxon response

[a] Organophosphates studied: phenthoate, phenthoate oxon, malathion, Supracide, ethion, guthion, and trithion. [b] Listed in order of increasing McReynold's constants; tested throughout the temperature range.

employed acetone was used (Iwata et al., 1977) and compared with other solvents. Exactly 50 g of soil was shaken with 100 mL of solvent for 1 h. Solvents studied were acetone, methanol, ethyl acetate, ethyl acetate–methanol (1:1), ethyl acetate–2-propanol (1:1), ethyl acetate–benzene (1:1), and acetone–acetonitrile (1:1). These same solvents were also used in overnight Soxhlet extractions. Soil fortifications were made in triplicate only at the 0.1-ppm level.

Fresh orange peel was used to optimize extraction efficiencies from fresh fruit. Once again the blending procedure of Iwata et al. was used (1977); 50 g of peel was blended for 10 min at medium speed with 150 mL of solvent. Solvents studied were acetonitrile, ethyl acetate, methylene chloride, chloroform, and acetone–acetonitrile (1:1).

Residue Procedures. *Replications.* All samples were analyzed as laboratory duplicates; two GC injections were made for each of the two replicates. The lack of field (processed fraction) replicates was necessitated by the large numbers of samples requiring excessive laboratory time and expense.

Fresh Fruit (Peel, Pulp, Finisher Pulp, Chopped Peel, and Peel Frits). Place 50 g of sample into a 1-pt Mason jar along with 150 mL of 1:1 acetone–acetonitrile. Blend on a Lourdes blender at medium speed for 10 min, filter under vacuum through No. 1 filter paper, rinse Mason jar with 30 mL of extracting solvent, and pour through the filter cake. Press the cake and transfer the filtrate to a 500-mL separatory funnel containing 50 mL of saturated NaCl; shake, add 300 mL of benzene, shake again, discard the lower aqueous phase, and drain remaining phase into a 1-L Erlenmeyer flask containing a layer of anhydrous Na_2SO_4. Decant to a 500-mL round-bottom flask with a 30-mL benzene rinse; evaporate to dryness at 40 °C on a Buchi Rotavapor R. Add 50 mL of hexane to the residue and dissolve by sonification; transfer to a separatory funnel with a 50-mL hexane rinse and extract with 2 × 50 mL of acetonitrile. Combine acetonitrile fractions in a 250-mL round-bottom flask and evaporate as before. Dissolve residue and transfer to a 10-mL graduated centrifuge tube with 3 × 3 mL of acetone; concentrate to 1 mL under a stream of dry N_2, transfer to a 2-mL Hewlett-Packard septum vial, fortify with an appropriate quantity of methidathion (internal standard), cap, and store at −20 °C until gas chromatography.

Dried Rind. Use only 25 g of sample and add 50 mL of H_2O to the 150 mL of acetone–acetonitrile for extraction. Otherwise, proceed as in the fresh fruit procedure.

Fruit Juice, Press Liquor, and Emulsion Water. Proceed as for fresh fruit except include 100 mL of saturated NaCl in the extracting solvent. Also, reduce the amount of benzene in the partitioning step to 200 mL.

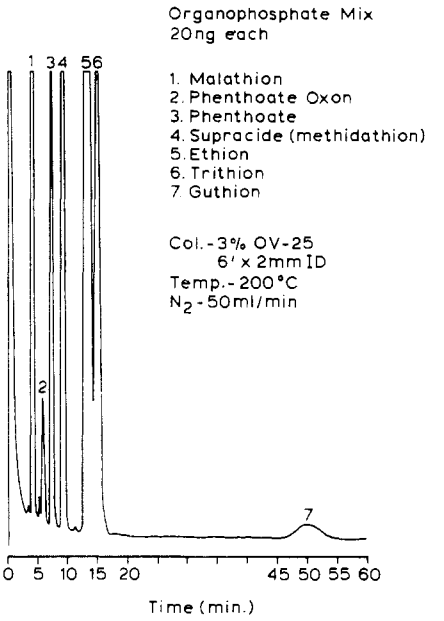

Figure 2. Chromatogram of the organophosphate mixture.

Rinse Water. Place 50 g of sample in a 500-mL separatory funnel, add 100 mL of saturated NaCl solution, shake, add 300 mL of benzene, and shake again. Continue as for fresh fruit.

Molasses. Place 10 g of sample in a 500-mL separatory funnel, add 100 mL of H_2O and 100 mL of saturated NaCl, and shake. Extract with 2 × 100 mL of $CHCl_3$, combine $CHCl_3$ fractions in a 1-L Erlenmeyer flask containing a layer of anhydrous Na_2SO_4 and proceed as in the fresh fruit procedure.

Soil. Place 50 g of sample in a 1-pt Mason jar, add 100 mL of 1:1 acetone–acetonitrile, seal tightly, and place on an oscillating shaker for 1 h at low speed. Filter through No. 1 filter paper under vacuum, rinse jar with 30 mL of solvent, and pour through the filter cake. Transfer the filtrate to a 500-mL round-bottom flask and evaporate to dryness on a rotary evaporator. Proceed as in the fresh fruit procedure.

Peel Oil. Apply 50 g of sample to a 2.5 × 60 cm glass column packed with 25 cm of Sephadex LH-20 which has been slurried with anhydrous ethanol and elute with the same at 1.5 mL/min. Discard the first 145 mL containing pigments and essential oils. Collect the next 60 mL which contains both phenthoate and oxon. Rotary evaporate to dryness and bring volume to 1 mL in a calibrated centrifuge tube. Fortify with methidathion and place in 2-mL capped vials.

RESULTS AND DISCUSSION

GC Column Resolution Studies. Of the eleven columns studied only one was able to provide a strong oxon response as well as full resolution of phenthoate, oxon, and the five most commonly used organophosphates on Florida citrus (malathion, ethion, guthion, trithion, and methidathion; Table I). Consequently, 3% OV-25 on 100–120-mesh Chromosorb W was used for all subsequent studies. A typical chromatogram is shown in Figure 2.

Extraction Studies. Of the seven solvent systems studied for the extraction of phenthoate and oxon from soil the acetone–acetonitrile (1:1) provided best overall recoveries at the 0.1-ppm level, averaging 76% for phenthoate and 75% for oxon. Acetone (Iwata et al., 1977)

Table II. Recoveries from Fresh Lemon Fruit, Processed Fractions, and Soil (Percent)[a]

fraction	phenthoate 0.01 ppm	phenthoate 0.05 ppm	phenthoate 0.1 ppm	phenthoate 1.0 ppm	phenthoate oxon 0.01 ppm	phenthoate oxon 0.05 ppm	phenthoate oxon 0.1 ppm	phenthoate oxon 1.0 ppm
peel, fresh		68	77	71		82	78	78
pulp, fresh		106	108	77		92	97	84
peel frits		76	73	70		80	86	73
finisher pulp	104	92	83	87	106	74	61	60
press liquor	100	82	88	90	100	112	98	86
prewater rinse	89	90	79	71	100	76	78	82
juice	111	87	85	96	104	87	106	91

fraction	phenthoate 0.05 ppm	phenthoate 0.1 ppm	phenthoate 0.5 ppm	phenthoate 1.0 ppm	phenthoate 10 ppm	phenthoate oxon 0.05 ppm	phenthoate oxon 0.1 ppm	phenthoate oxon 0.5 ppm	phenthoate oxon 1.0 ppm	phenthoate oxon 10 ppm
molasses		61					116			
soil	97	81	88	94		116	95	90	96	
oil		90	56	58	100		100	80	65	110

[a] Means of duplicate analyses; relative standard deviation was less than 22%.

was nearly as good, giving phenthoate recoveries averaging 70% and oxon averaging 91% employing 1-h shaking. Overnight Soxhlet extraction showed no improvement in recovery.

In our hands acetonitrile provided poor recoveries of oxon from fresh orange peel at the 0.1-ppm level (0–15%). Of the other four solvents studied (ethyl acetate, methylene chloride, chloroform, and 1:1 acetone–acetonitrile) only the acetone–acetonitrile gave good recoveries for both phenthoate and oxon, averaging 91 and 85%, respectively. The employment of a Polytron ultrasound homogenizer instead of the Lourdes blender provided no improvement in recoveries.

Recoveries. Recoveries for all sample types studied, both fresh fruit, fractionated products and soil ranged, with few exceptions, between 70 and 100%. No differences were observed between lemon, orange, and grapefruit recoveries. Typical recoveries (lemons and soil) are shown in Table II. Because of the large numbers of samples in this experiment recoveries were performed only in duplicate. Somewhat variable and frequently low (<70%) recoveries were obtained for oil, and molasses ranged from 80 to 96%, with an average of 91%; as well as oranges, phenthoate recoveries for oil ranged from 90 to 98%, with an average of 95%. Recoveries were not performed on the "after-water rinse" since it is identical in composition with the "prewater rinse".

Residues. *Replicates.* After an average value was obtained for the duplicate GC injections the residue levels for the two laboratory replicates were averaged to provide the values given in the accompanying figures and tables. Standard deviations for the duplicate analyses ranged from 0.01 to 0.46.

Fresh Fruit. Disappearance curves for phenthoate on grapefruit (Figure 3a) and on oranges (Figure 4a) were quite similar, considering both initial residue levels and rates of disappearance (approximately first-order decay). Even at the C2X concentrations, levels in the peel were well below 1.0 ppm at 7 days after application. Quite different curves were observed for the oxon, however (Figures 3b and 4b), when phenthoate was applied at the C2X concentration. Grapefruit exhibited the typical "oxon" curve, slowly increasing with time and then beginning to decrease slowly at about 40 days; no oxon was observed at levels above the 0.01-ppm detection limit for the phenthoate C1X concentration. Oranges, however, exhibited relatively large amounts of oxon (nearly 0.4 ppm) immediately after spraying at the C2X concentration, which then gave typical first-order decay. The C1X application, however, produced the typical "oxon" curve,

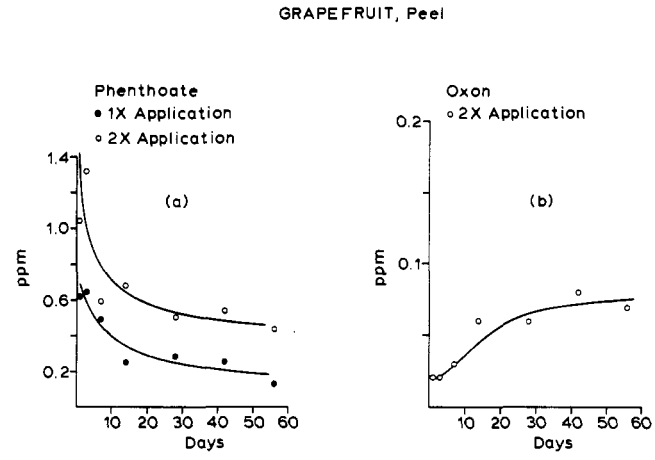

Figure 3. Disappearance curves on grapefruit peel: (a) phenthoate at the C1X level (●) and at the C2X level (○); (b) oxon at the C2X level (○).

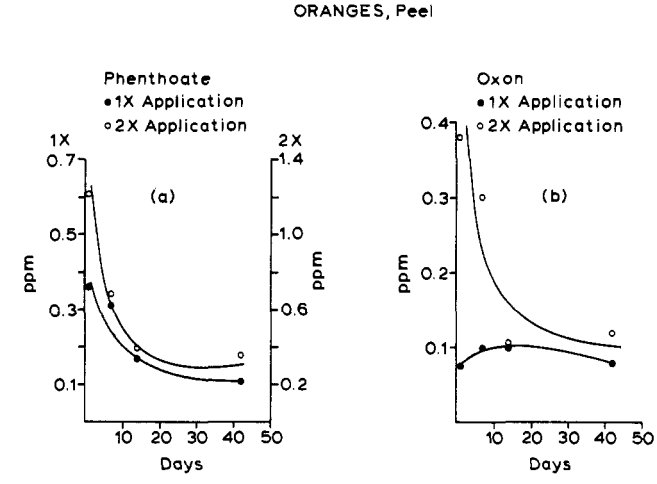

Figure 4. Disappearance curves on orange peel: (a) phenthoate at the C1X level (●) and at the C2X level (○); (b) oxon at the C1X level (●) and the C2X level (○).

maximizing at 7–14 days. Since the same Cidial concentrate was used to prepare both the C1X and C2X sprays only a concentration effect should have been operative for these observations; it would appear that the higher concentration of phenthoate on the orange peel induced some sort of oxidative mechanism in or on the peel. Phenthoate levels in fresh grapefruit and orange pulp were insignificant, reaching a maximum of 0.04 ppm for oranges at 7 days and 0.0007 ppm for grapefruit at 1 day after spraying.

Table III. Residues (Fractionated Products)[a,b]

	grapefruit				lemons				oranges			
	C1X[c]		C2X[d]		C1X		C2X		C1X		C2X	
product	phenth.	oxon	phenth.	oxon	phenth.	oxon	phenth.	oxon	phenth.	oxon	phenth.	oxon
washed peel	0.24	0.08	0.44	<0.01	0.18	<0.01	0.30	<0.01	0.32	0.039	0.68	0.068
washed pulp	0.03	<0.01	0.063	<0.01	0.002	<0.01	0.004	<0.01	0.008	<0.01	0.011	<0.01
unwashed peel	0.17	<0.01	0.68	<0.01	0.09	0.07	0.27	0.10	0.26	0.07	0.88	0.09
unwashed pulp	0.008	<0.01	0.027	<0.01	0.008	<0.01	0.023	<0.01	0.003	<0.01	0.028	<0.01
chopped peel	0.27	0.015	0.40	0.027	0.09	0.027	0.25	0.031	0.34	0.013	0.61	0.025
peel frits	1.1	0.019	2.4	0.031	0.26	0.06	0.64	0.13	0.33	0.06	0.48	0.13
finisher pulp	0.004	<0.01	0.008	<0.01	0.011	<0.01	0.21	<0.01	0.008	<0.01	0.014	<0.01
dried rind	0.73	<0.01	1.4	0.10	2.6	0.01	2.5	0.01	0.15	0.02	0.43	0.027
press liquor	0.14	0.01	0.19	0.01	0.01	0.016	0.023	0.012	0.08	<0.01	0.13	0.01
emulsion water	0.014	<0.01	0.019	<0.01	0.003	0.04	0.009	0.06	0.005	0.043	0.037	0.055
fruit juice	<0.002	<0.01	<0.002	<0.01	0.004	<0.01	0.008	<0.01	0.002	<0.01	0.003	<0.01
after-water rinse	<0.002	<0.01	<0.002	<0.01	<0.002	<0.01	0.005	<0.01	<0.002	<0.01	0.004	<0.01
prewater rinse	<0.002	<0.01	<0.002	<0.01	<0.002	<0.01	<0.002	<0.01	<0.002	<0.01	<0.002	<0.01
molasses	0.038	<0.01	0.066	<0.01	0.01	<0.01	0.01	<0.01	0.049	<0.01	0.059	<0.01
oil	5.5	0.48	7.9	1.1	7.5	2.0	16.0	2.2	3.4	1.3	13.0	1.9

[a] ppm. [b] Average of duplicate analysis. [c] 4 oz of active ingredient/100 gal. [d] 8 oz of active ingredient/100 gal.

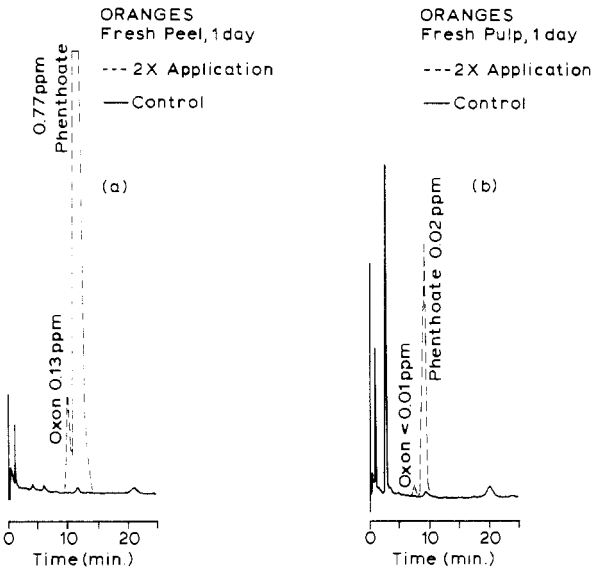

Figure 5. Typical citrus fresh fruit chromatograms: (a) orange peel 1 day after C2X application and control; (b) orange pulp 1 day after C2X application and control.

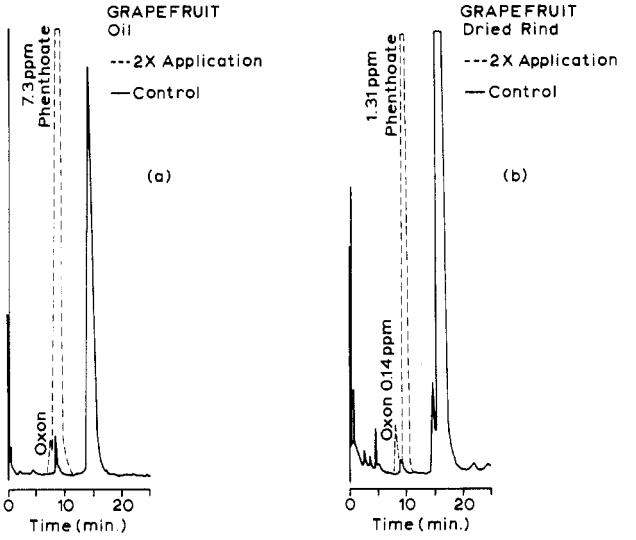

Figure 6. Typical citrus fractionated product chromatograms: (a) grapefruit peel oil, C2X sampling and control; (b) grapefruit dried rind, C2X sampling and control.

The differences in maximum levels and days after spraying were real and could only be explained by conjecture. Typical chromatograms, similar for all three types of citrus studied, are shown in Figure 5.

Fractionated Products. Residues of phenthoate and oxon in fifteen fractionated products from grapefruit, lemons, and oranges are presented in Table III. Highest levels were found in lemon peel oil for the C2X application, 16.0 ppm of phenthoate and 2.2 ppm of oxon; C1X application gave 7.5 ppm of phenthoate and 2.0 ppm of oxon. The only residues found in the after-water rinse was for lemons, only 0.005 ppm of phenthoate and no oxon being found. Almost no residues were found in molasses, and those only phenthoate. Dried rind, the other component of cattle feed, contained significant levels of phenthoate but very little oxon. Lemons appeared to have enhanced capability to retain the pesticide during the extraction and drying processes than did either grapefruit or oranges, about 2.5 ppm appearing in the dried rind (peel) after either C1X or C2X application of pesticide. Oranges and grapefruit retained the chemical significantly less; little oxon was found in any of the dried rind samples. Only almost immeasurable amounts of phenthoate were found

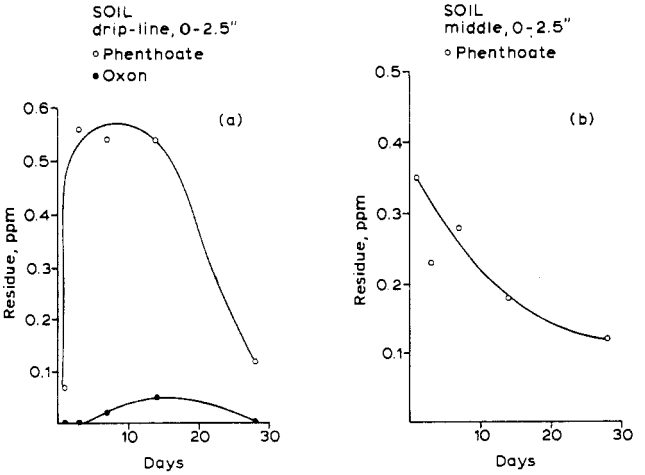

Figure 7. Phenthoate and oxon levels sampled at the 0–2.5-in. depth: (a) drip line; (b) midline.

in lemon and orange juice; none was found in grapefruit juice. No oxon was found in any of the juices. Chromatograms for grapefruit peel oil and dried rind, similar to

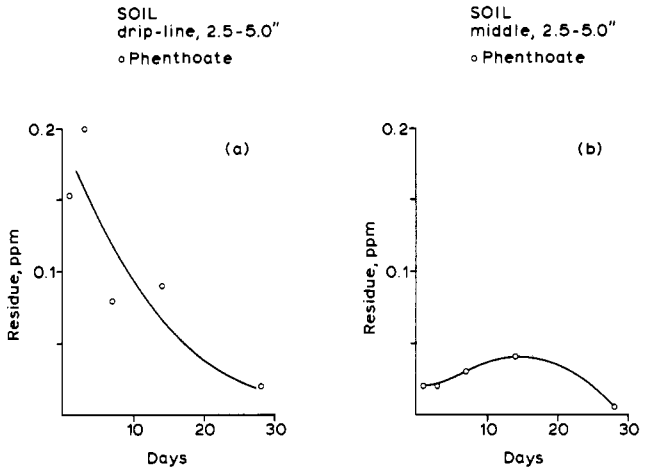

Figure 8. Phenthoate levels sampled at the 2.5–5.0-in. depth: (a) drip line; (b) midline.

the same fractions of oil and lemon, are shown in Figure 6.

Soil. As would be expected, highest levels of phenthoate were found at the tree drip lines and at the shallower sampling depth (0–2.5 in.). In addition, oxon levels were found for these samples only. Figure 7 shows residues for the 0–2.5-in. sampling depth as a function of time after spraying. Immediately after, and the same day, that the chemical was applied the grove received 0.23 in. of rain, accounting for the sharp increase in soil phenthoate levels which decayed slowly. Maximum oxon was measured in the 14-day sample (0.04 ppm). Figure 8 shows the phenthoate residues found at the 2.5–5.0-in. sampling depth. Expectedly, less phenthoate was found and no oxon; maximum phenthoate levels occurred at the drip line 3 days after application (0.2 ppm) and decayed slowly to 28 days. Less phenthoate was found in the soil beneath the tree midline.

Conclusions. Phenthoate disappears by first-order decay from the peel of citrus fruit and never reaches levels above 1 ppm, even immediately after application of the C1X concentration; fruit sprayed at the C2X level gave residues slightly higher. Residues in the interior of the fruit were negligible, with no oxon detectable. Fruit sprayed at the C1X level produced peel oil with 5.5, 7.5, and 3.4 ppm of phenthoate for grapefruit, lemons, and oranges, respectively; for these fruit oxon was found at the 0.48-, 2.0-, and 1.3-ppm levels, respectively. Since the oxon is approximately 70 times more toxic to the rat than is phenthoate it is clearly of more significance in the oil. While dried lemon rind contained 2.6 ppm of phenthoate for fruit sprayed at the C1X rate only 0.01 ppm of oxon was found. Molasses contained insignificant amounts of phenthoate and no oxon. No environmental contamination should be expected from after-water rinse upon disposal. Residues of phenthoate in soil never reached significant levels and decayed away; oxon was generally not measurable.

Registry No. Phenthoate, 2597-03-7; phenthoate oxon, 3690-28-6.

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N-(2,6-Dihalobenzylidene)arenesulfinamide Herbicides and Analogous Compounds. 1. Synthesis and Biological Activity

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A series of benzylidenearenesulfinamides was prepared and evaluated for preemergent herbicidal activity. While *N*-(2,6-dichlorobenzylidene) analogues were shown to decompose in situ to the corresponding benzonitrile (dichlobenil) over extended periods of time, many of these compounds demonstrated both increased activity and crop selectivity with respect to a dichlobenil standard. Structural modification through preparation of analogous thiosulfinates or vinyl sulfoxides resulted in a complete loss of herbicidal properties. Replacement of a benzylidene hydrogen with a methyl group gave increased activity against broadleaf species but resulted in the absence of activity against grasses. This sterically hindered compound type could not be prepared by standard procedures and a new method was developed for its synthesis.

The herbicidal activity of 2,6-dichlorobenzonitrile (dichlobenil) and other nitriles has been known for some time. Dichlobenil, while demonstrating good preemergent activity against a wide variety of grasses and broadleaves, is highly phytotoxic to crops and is therefore not useful for crop application. It was felt that structural modification of nitrile herbicides might result in a more selective and efficacious class of compounds. To this end, a series of *N*-(2,6-dichlorobenzylidene)arenesulfinamides was prepared. Benzylidenearenesulfinamides have been shown to undergo a thermal elimination of an arenesulfenic acid, affording the corresponding nitrile (Davis et al., 1974).

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