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Table VI. A Comparison of Rates of Application to Alfalfa, Residues at Harvest, Residues in Milk, and Acute Oral Toxicity to Rats of Endrin, Toxaphene, and DDT

Insecticide	Rate of Appl., Lb./Acre	Residue at Harvest, P.P.M.	Residue Expected in Milk, P.P.M.	Acute Oral Toxicity to Rats, Mg./Kg. (9)	Relative Safety Margin[a]	Reference
Endrin	$^1/_8$–$^1/_4$	0.15	0.02	18	9	This paper
Toxaphene	2	120	2.5	90	0.36	(3)
DDT	2	12.1	3.3	225	0.7	(4)

[a] Relative safety margin = LD_{50} per p.p.m. in milk × 100.

INSECTICIDE RESIDUES

Field Persistence Comparisons of Residues of the Insecticide, Diazinon, in Lemons and Valencia Oranges and Effects on Juice Flavor

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Residues of the insecticide, Diazinon, were determined by an ultraviolet spectrophotometric procedure on and in lemons and oranges. The persistence of these residues is illustrated by the half-life values of 12 to 13 days for lemons and 16 to 17 days for Valencia oranges; Diazinon residues are short-lived compared to most other insecticides and acaricides as residues on citrus fruits. Triangular-type tests of juice from Diazinon-treated fruits showed no detectable flavor changes; citrus peel appears to be an efficient barrier against penetration into citrus juices by odors or flavors from outside sources.

The compound *O,O*-diethyl *O*-(2-isopropyl - 4 - methyl - 6 - pyrimidinyl) phosphorothioate, or Diazinon, is a useful insecticide against certain insects (*4, 12*) and shows promise in the control of some California citrus pests—notably soft scale, *Coccus hesperidum* L. (*3*). In the present paper, magnitudes and half lives of residues of Diazinon on and in lemons and Valencia oranges treated in the field with commercial formulations are compared with residues from a number of other insecticides and acaricides.

Residue Studies

An analytical method suitable for determining magnitudes of residues of Diazinon on and in citrus tissues was proposed by Harris (*13*) and modified by Blinn and Gunther (*1*) for use in this study. This procedure is based on the ultraviolet determination of 2-isopropyl-4-methyl-6-pyrimidinol, a hydrolytic product of Diazinon. The method is semispecific, as only compounds that hydrolyze to a pyrimidinol will respond.

Materials and Methods. Average-sized Valencia orange trees were sprayed on June 4, 1956, either with 2.0 pounds of a 25% wettable-powder formulation of Diazinon per 100 gallons of water or with 2.0 pounds of a 25% emulsifiable-concentrate formulation of Diazinon per 100 gallons of water. Identical sprays were applied to average-sized lemon trees on November 12, 1956. Applications were made as conventional sprays, using a high-pressure reciprocating pump and manually operated spray guns. Final sprays were applied at the rate of approximately 1700 gallons per acre for the oranges and 1125 gallons per acre for the lemons.

Mature orange fruit samples for assay of residues were collected immediately before treatment, within 4 hours after the spray deposit had dried, and then 1, 4, 7, 14, 21, and 28 days after treatment. Mature lemon fruit samples for assay of residues were collected before treatment and 1, 4, 14, 21, and 28 days after treatment. One fruit was picked from each quadrant of each of eight trees in each plot, and the resulting 32 fruits were processed as a unit. The three replicates for each treatment were processed separately.

The fruits were peeled, and 1-pound subsamples of the minced peel and of the minced pulp were processed separately with petroleum ether in a manner previously described (*5*), to afford final stripping solutions. Aliquots of stripping solutions were assayed by the ultraviolet spectrophotometric procedure (*1*).

Results. Field-replicated residue values for Diazinon and field-treated lemons and Valencia oranges are collated in Table I and presented graphically in Figures 1 and 2. No Diazonon was found in the pulp (edible portion) of either fruit from any of the samples by this method in which control fruit pulp samples had a background of 0.1 p.p.m. of apparent Diazinon.

Discussion. There has been both field (*3*) and laboratory (*7*) evidence to support the prediction that Diazinon would be short-lived as an exposed residue. The half-life values, both as degrading residues—residues subject to the physical and chemical attrition of weathering—and as persisting residues—penetrated residues subject principally to chemical and metabolic action—(*5*), for Diazinon on and in lemon peel and Valencia orange peel (Table II) validate this prediction. Both the degradation residue and the persistence residue are short-lived in comparison with residues of many pesticidal materials on citrus fruits (*5, 6*), which range from 2 to 30 days for degrading residues and from 17 to over 300 days for persisting residues.

The detailed, replicated residue values in Table I show much greater 1-day residues on lemons than on oranges from both formulations. This disparity may be extended to include the magnitudes of the initial deposits on both fruits by extrapolation to zero days in Figure 1. From the close agreement among the half-life data in Table II for Diazinon on lemons *vs.* oranges, this disparity is clearly a function only of initial deposit and is not assignable to differences in the degradation or persistence behavior in the peel of the two fruits. Differences in initial depositing properties of this sort are probably related to nature and maturity of substrate—for example, these lemons were treated at the green stage of the lemon maturity cycle, whereas the oranges were fully orange-colored at time of treatment.

Initial deposits, heavier on lemons than on oranges, with the same formulation and the same dosage for a given material, have also been found by chemical assay for other insecticides and acaricides, including 2-(*p-tert*-butylphenoxy)-1-methylethyl 2-chloroethyl sulfite (Aramite), *p*-chlorophenyl *p*-chlorobenzenesulfonate (ovex), 1,1-bis(*p*-chlorophenyl)-2,2,2-trichloroethanol [FW-293 or Kelthane], *O,O*-diethyl *O-p*-nitrophenylphosphorothioate (parathion), 2,3-*p*-dioxanedithiol *S,S*-bis(*O,O*-diethyl phosphorodithioate) (compound 528 or Delnav), *S*-(*p*-chlorophenylthio)methyl *O,O*-diethyl phosphorodithioate (trithion), and 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane (DDT), as reproduced in Table III for comparison.

Half-life values in days are also incorporated into Table III for comparative purposes. Although the initial deposits are consistently higher on lemons than on oranges, the half-life values for a given material on lemons are also consistently less than the corresponding values for residues on and in the oranges. These limited data show that, although initial deposits are higher, harvest-time residues of a given material in mature lemons may actually be lower than the residues of the same material in mature oranges treated with the same amount of the same formulation.

The systemic insecticides octamethyl pyrophosphoramide (schradan) and the hydrogen oxalate salt of *O,O*-diethyl *S*-(2-diethylamino)ethyl phosphorothioate (Tetram) do not show this preferential heavier deposition upon lemons, as reported by Metcalf *et al.* (*14, 15*).

Table I. Apparent Diazinon Residues in Peel[a] of Field-Treated Lemons and Valencia Oranges

	Apparent Residues, P.P.M.					
	2 Lb. of 25% Wettable Powder[b]		2 Lb. of 25% Emulsifiable Concentrate[b]		Untreated Controls	
Elapsed Days	Lemons	Oranges	Lemons	Oranges	Lemons	Oranges
0[c]	—	2.8, 3.5, 4.2	—	3.3, 4.4, 4.3	0.2, 0.2	0.2, 0.2, 0.2
1	11.1, 12.1	2.4, 2.0, 1.3	8.1, 8.1	1.0, 0.9, 1.5	0.2, 0.1	0.2, 0.1, 0.2
4	3.7, 4.6, 4.8	0.4, 0.4, 0.8	8.1, 7.0	1.1, 0.9, 0.6	0.1, 0.1	0.3, 0.2, 0.3
7	2.6, 3.0, 2.2	0.5, 0.5, 0.7	3.9, 4.8	0.7, 0.9, 1.0	0.2, 0.1	0.1, 0.1, 0.1
14	2.6, 2.5, 2.8	0.5, 0.3, 0.3	3.8, 2.2	0.4, 0.7, —	0.2, 0.2	0.1, 0.1, 0.1
21	1.0, 1.1, —	0.4, 0.1, 0.3	1.6, 2.3	0.2, 0.3, 0.2	0.1, 0.1	0.1, 0.1, 0.1
28	0.8, 0.8, 0.8	0.1, 0.6, 0.3	2.0, 1.3	0.3, 0.3, 0.4	0.1, 0.1	0.1, 0.1, —

[a] Based upon weight of peel only. Mature lemons have 30.0 ± 8.5 wt. % peel from 632 measurements; mature Valencia oranges have 18.7 ± 6.3 wt. % peel from 297 measurements.
[b] All values corrected for recovery (100, 98, and 103% for lemons at 1.0 p.p.m.; 107, 103, and 120% for oranges at 1.0 p.p.m.) and for background of untreated control samples. Wettable powder = 27.1% Diazinon, emulsifiable concentrate = 25.6% Diazinon, by ultraviolet analytical method.
[c] Zero-day samples collected within 4 hours after applications were made.

Table II. Half-Life Values for Residues of Apparent Diazinon in Peel of Field-Treated Lemons and Valencia Oranges

	Half Life, Days[a]			
	Lemons		Oranges	
Treatment	Degrading	Persisting	Degrading	Persisting
2.0 pounds 25% wettable powder/100 gallons water	2.5	12	0.5	17
2.0 pounds 25% emulsifiable concentrate/100 gallons water	6.5	13	2	16

[a] From Figures 1 and 2.

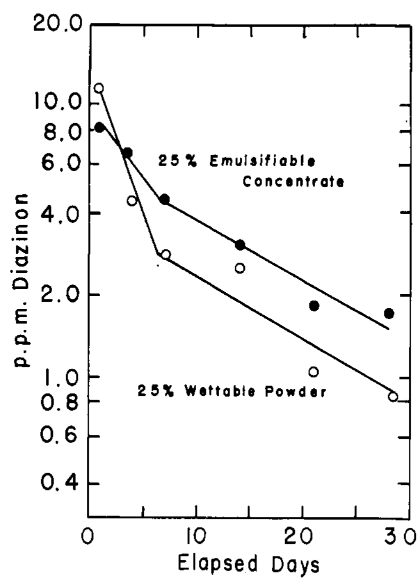

Figure 1. Persistence of apparent Diazinon residues in lemon peel

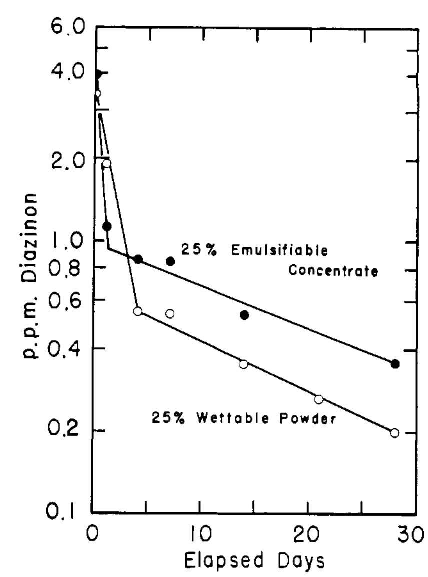

Figure 2. Persistence of apparent Diazinon residues in Valencia orange peel

Flavor Evaluation Studies

Routine triangular-type tests were used to determine whether field treatments of Diazinon resulted in flavor changes in Valencia orange juice or in lemon juice.

Materials and Methods. In each test 32 mature fruits (four from each of eight trees, as above) were harvested from each of the three replicated plots for each treatment and for the untreated control plot. The three 32-fruit samples were then pooled, and 50 fruits were selected at random for the final sample. Juice was extracted by hand-reaming fruit held in storage at 40° F. Undiluted orange juice and lemonade (see recipe in footnote *a*, Table IV) were served immediately after preparation, without further chilling, to the members of the flavor-evaluation panel.

This panel of 18 members included both men and women; all were experienced in flavor-evaluation tests, but none had been trained to taste Diazinon specifically. Each panelist tasted two series of three samples in the forenoon between 9 o'clock and 12 noon and again in the afternoon between 2 and 5 o'clock. A sample consisted of 20 ml. of orange juice or lemonade served in a small paper cup. More material was available if the panelist wished, but more was seldom called for, as flavor changes in citrus juice are usually detected immediately upon tasting or not at all. Sensitivity is rapidly lost by repeated tastings over a short period of time.

Results and Discussion. Results summarized in Table IV show that none of the treatments with Diazinon caused detectable flavor changes in the juice of Valencia oranges or lemons. This corroborates results obtained in flavor studies conducted during the past 5 years by this Department of Entomology on citrus fruit harvested from trees treated with a wide variety of insecticides (*3*). These flavor evaluations indicate that, in general, the citrus peel is an efficient barrier against deep penetration by odors or flavors from outside sources. Even heavy applications of certain organic thiophosphates—some formulations of which have extremely strong unpleasant odors—have not resulted in detectable flavor effects in citrus juice (*3*).

Table III. Initial Deposits and Persisting Half-Life Values for Several Insecticides and Acaricides in Peel of Field-Treated Lemons and Valencia Oranges

		Lemons		Oranges		
Material[a]	Formulation[b]	Initial deposit, p.p.m.	Half life, days	Initial deposit, p.p.m.	Half life, days	Literature Citation
Aramite	W.P.	0.9	13	0.6[c]	—	(*8*)
Compd. 528	E.C.	12.9	88	8.3[d]	92[d]	(*11*)
	W.P.	8.5	55	3.5[d]	137[d]	(*11*)
DDT	Soln.	13.1	33	6.3	38	(*2*)
FW-293	E.C.	14.5	130	4.4	205	(*7*)
	W.P.	7.6	123	3.2	333	(*7*)
Ovex	W.P.	4.3	30	2.5	—	(*9*)
Parathion	W.P.	15.9	61	12.4	78	(*2*)
Trithion	E.C.	17.0	21	10.0[d]	37[d]	(*10*)
	W.P.	17.0	21	12.0[d]	38[d]	(*10*)

[a] Common or trade name. See text for chemical designation of active major component. Dosage uniform for formulations of a given material, but different among materials.
[b] W.P., wettable powder; E.C., emulsifiable concentrate; Soln., solution.
[c] Corrected to 20 pounds of Aramite 15% wettable powder per acre (the amount used on the lemons). [d] Washington navel oranges.

Table IV. Summary of Triangular Flavor Tests on Diazinon-Treated Lemons and Valencia Oranges

APPLICATION DATA

Date of Application and Product Tasted	Pounds Actual Compd. Per Acre	Days between Application and Harvest
Diazinon 25% W.P., 6–4–56 Valencia orange juice	10	45
11–12–56 Lemonade[a]	12.5	28
Diazinon 25% E.C., 11–12–56 Lemonade[a]	12.5	28

FLAVOR DATA

		Correct Triangular Separations				
			No. Times Flavor Was Objectionable		Times Preferred or Flavor Rating[b]	
Treatment and Product Tasted	No. of Judgments	Total No.	Treated	Control	Treated	Control
Diazinon 25% W.P., Valencia orange juice	36	12	1	0	3[c]	7[c]
Lemonade[a]	36	13	0	0	6.2	5.5
Diazinon 25% E.C., Lemonade[a]	36	17	1	2	5.8	5.3

[a] Lemonade recipe: 250 ml. of fresh lemon juice, 950 ml. of water, and 100 grams sugar.
[b] Numerical scale: 0.0 to 2.0, very poor; 2.1 to 4.0, poor; 4.1 to 6.0, fair; 6.1 to 8.0, good; 8.1 to 10.0, excellent.
[c] The panelists were asked simply to indicate their preference for the odd or for the duplicate samples. Among the 12 persons correctly separating the treated and untreated samples, 7 preferred the control samples.

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