

ACARICIDE RESIDUES

Persistence of Residues of 2,3-*p*-Dioxanedithiol *S,S*-bis(*O,O*-diethyl Phosphorodithioate) as an Acaricide on and in Mature Lemons and Oranges

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Residues of the acaricidal material 2,3-*p*-dioxanedithiol *S,S*-bis(*O,O*-diethyl phosphorodithioate) (Hercules AC-528) on navel oranges and lemons have been evaluated, using a semispecific colorimetric procedure. Half-life values for persisting residues of the acaricide on field-sprayed navel oranges and lemons were determined to be about 95 and 85 days, respectively. Less than 0.03 p.p.m. of this material was found in the edible portion of the fruit.

THE COMPOUND 2,3-*p*-dioxanedithiol *S,S*-bis(*O,O*-diethyl phosphorodithioate) (Hercules AC-528, recently known as Delnav), a general acaricide against several species of mites, has been shown to be effective in controlling citrus red mite, *Metatetranychus citri* (McG.), and other Tetranychid mites injurious to citrus (4). A study of the magnitudes of persisting residues of Hercules AC-528 on and in mature lemons and navel oranges treated in the field in a commercial manner is presented herein.

A semispecific analytical method for determining residues of Hercules AC-528 on and in citrus fruits has been described (7). This method determines

glyoxal quantitatively released from the acaricide by a cleavage-hydrolysis procedure of heating the residue with alcoholic mercuric chloride and aqueous 2,4-dinitrophenylhydrazine perchlorate. The glyoxal is determined colorimetrically (λ_{max} , 614 m μ) as its 2,4-dinitrophenylosazone in alkaline solution. Several chromatographic separations are used so as to determine only the glyoxal 2,4-dinitrophenylosazone derived from unchanged Hercules AC-528 residue.

Data from this study indicate that residues on and in lemons and navel oranges are in agreement with previously established (2, 3) degradation and persistence behavior of other acaricides on and in citrus fruits.

Materials and Methods

Mature navel orange trees were sprayed February 20, 1956, with an emulsifiable-concentrate formulation of Hercules AC-528 (4 pounds per gallon) at the rate of 6, 12, and 24 fluid ounces per 100 gallons of water, and with 24 ounces of a 25% wettable-powder formulation of Hercules AC-528 per 100 gallons of water. Mature Eureka lemon trees were sprayed March 19, 1956, with the same emulsifiable-concentrate formulation but at the rate of 12, 24, and 48 fluid ounces per 100 gallons of water, and with the same 25% wettable-powder formulation described above. Applications were made as

Table I. Persistence of Hercules AC-528 Residues on and in Peel of Field-Sprayed Navel Oranges^a and Lemons^b

Elapsed Days	Emulsifiable Concentrate per 100 Gallons								25% Wettable Powder (24 Ounces/100 Gal.)		Control	
	6 Ounces		12 Ounces		24 Ounces		48 Ounces		Sample 1	Sample 2	Sample 1	Sample 2
	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2	Sample 1	Sample 2				
Navel Oranges, P.P.M. ^c												
Pretreated	0.1	0.1	0.2	0.0	0.0	0.0	0.0	0.1	0.0
0 ^d	1.3	3.4	5.0	4.5	7.8	8.8	3.6	3.5	0.3	...
2	3.1	3.5	4.6	4.7	8.3	9.7	2.8	2.4	0.0	0.0
7	2.2	2.9	4.3	5.3	7.1	6.8	2.1	2.1	0.8	0.1
14	2.3	2.7	4.8	4.9	7.9	7.3	1.0	1.6	0.0	0.6
21	2.6	2.9	4.5	5.1	8.8	7.8	1.0	1.7	0.4	0.2
35	2.0	2.0	3.9	3.0	6.6	5.1	1.6	1.1	0.1	0.1
51	1.8	1.9	3.5	3.3	6.1	6.3	1.0	0.7	0.3	0.2
64	1.9	1.7	3.5	2.4	6.3	5.6	1.2	0.7	0.1	0.0
86	1.5	1.8	2.7	2.4	4.3	5.0	1.0	0.8	0.1	0.1
Lemons, P.P.M. ^c												
Pretreated	0.1	0.2	0.1	0.1	0.2	0.1	0.3	0.1	0.1	0.0
0 ^d	6.0	10.4	9.8	16.1	24.8	19.5	8.6	8.4	0.6	2.1
2	8.4	7.0	15.2	14.0	15.3	22.6	7.5	10.0	1.2	1.9
7	7.5	8.7	10.4	9.9	19.2	14.2	5.4	5.6	1.3	0.7
14	6.3	7.5	11.3	9.6	15.8	16.2	4.8	4.9	0.6	0.4
21	5.8	7.5	9.7	10.8	18.8	16.6	5.6	6.4	0.7	0.6
36	6.3	7.0	17.0	21.9	6.3	7.5	0.7	0.6
49	4.9	5.2	9.1	6.5	14.0	14.8	2.7	3.5	0.5	0.4
71	4.0	4.5	8.3	7.2	12.8	13.9	1.9	2.1	0.1	...
98	3.2	3.8	3.8	4.9	7.3	9.5	1.6	1.4	0.1	0.1

^a Based on weight of peel only, mature navel oranges have 22.1 ± 7.3 wt. % peel from 567 measurements.

^b Based on weight of peel only, mature lemons have 30.0 ± 8.5 wt. % peel from 632 measurements.

^c All values corrected for recovery (106.5%).

^d Samples collected within 4 hours after application.

^e All values corrected for recovery (86.0%).

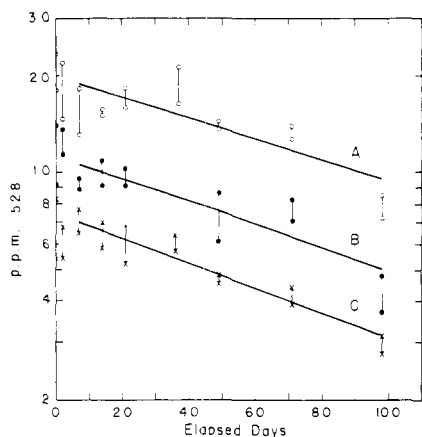


Figure 1. Persistence of Hercules AC-528 residues on and in the peel of navel oranges sprayed with an emulsifiable-concentrate formulation

A, 24 ounces; B, 12 ounces; and C, 6 ounces per 100 gallons of water

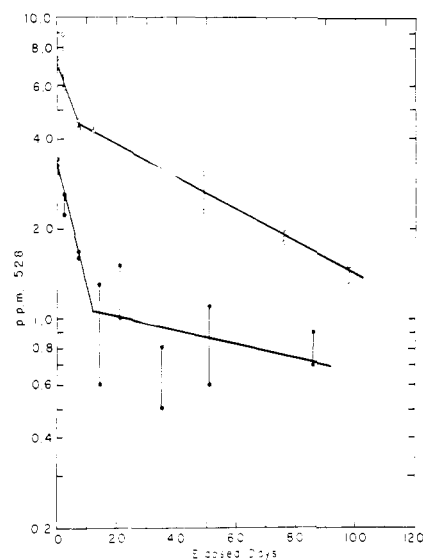
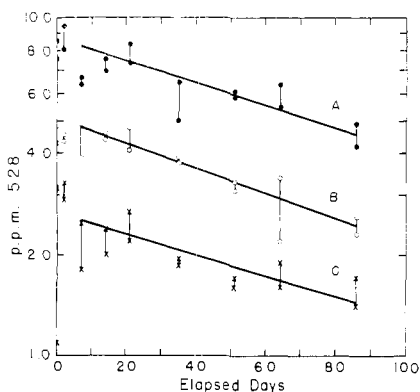


Figure 2. Degradation and persistence residues of Hercules AC-528 on and in peel of navel oranges (lower curve) and lemons (upper curve) sprayed with a wettable-powder formulation

Figure 3. Persistence of residues of Hercules AC-528 on and in peel of lemons sprayed with an emulsifiable-concentrate formulation

A, 48 ounces; B, 24 ounces; and C, 12 ounces per 100 gallons of water

conventional sprays, using a high-pressure reciprocating pump and manually operated spray guns. Sprays were applied at the rate of approximately 1500 and 2500 gallons per acre to the lemon and orange trees, respectively.

Mature orange and lemon fruit samples for assay of residues were collected before treatment and at specified intervals after treatment (Table I). Four fruits (one from each quadrant) were picked from each of eight trees in each plot, and the resulting 32-fruit sample was processed as a unit. The two replicates for each treatment were processed separately.

The unwashed fruits were peeled and processed with petroleum ether as previously described (2), to afford final stripping solutions.

Lemon fruits harvested 71 days after the 24-ounce treatment were peeled for the preparation of a sample of dried citrus cattle feed. This peel was ground with a food grinder, sprinkled with hydrated lime at the rate of 4 grams per kg. of peel, mixed thoroughly, and allowed to stand for 1 hour. The mixture was then pressed in a Carver press at 500 p.s.i. to remove liquids. The resulting solids were spread to a depth of about $\frac{3}{4}$ inch and dried in a forced-draft oven at 50° C. for 16 hours.

From 1875 grams of fresh peel, 207 grams of dried citrus cattle feed were obtained. The dried product was equilibrated with petroleum ether in the usual manner (2) to afford final stripping solutions.

Duplicate aliquots of the stripping solutions were analyzed for Hercules AC-528 by the glyoxal colorimetric method (7).

Results

Navel Oranges and Lemons. Residue values for Hercules AC-528 on and in navel orange and lemon peel as determined by the glyoxal method are collated in Table I and presented graphically in Figures 1, 2, and 3. Values for pulp (edible portion) analyses never exceeded an apparent 0.03 p.p.m. of Hercules AC-528 throughout this study.

An aliquot of a control stripping solution from each set of samples of navel orange peel was fortified at 0.1 p.p.m. with purified (7) Hercules AC-528 at the time of storage at 10° C., awaiting analysis. Subsequent analyses of these fortified controls demonstrated no losses of the acaricide in these solutions up to 3 months at 10° C.

Dried Citrus Cattle Feed. Freshly ground field-treated lemon peel origi-

Table II. Half-life Values, in Days, for Persistence and Degradation Residues of Hercules AC-528 on and in Peel of Field-Sprayed Lemons and Navel Oranges

Formulation, Ounces/100 Gal. Water	Persistence Residue	
	Lemons	Oranges
Emulsifiable concentrate ^a	6	101
	12	80
	24	82
	48	94
25% Wettable powder	24	10 ^b , 55
		6 ^b , 137

^a Hercules AC-528, 4 pounds per gallon of formulated material.

^b Degradation residue.

nally containing a residue of 7.6 p.p.m. of Hercules AC-528 contained a residue of 41.6 p.p.m. of the acaricide after being processed into dried citrus cattle feed. This is equivalent to 4.6 p.p.m. in fresh peel or a 61% retention of the original residue during the processing treatment.

Discussion

The intermediate longevity of residues of Hercules AC-528 on and in navel oranges and lemons is shown by the half-life (2) values listed in Table II. These values are similar to the residues found for many insecticides and acaricides (2, 3).

The rapidly penetrating emulsifiable formulations of Hercules AC-528 (Figures 1 and 3) show only a persistence type of residue, whereas the wettable-powder formulations (Figure 2) show both degradation and persistence residue behavior. Processing of residue-containing fresh citrus peel into dried citrus cattle feed resulted in a 40% reduction in acaricide content.

Literature Cited

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Received for review May 14, 1957. Accepted August 22, 1957. Paper No. 983, University of California Citrus Experiment Station, Riverside, Calif. Division of Agricultural and Food Chemistry, 131st Meeting, ACS, Miami, Fla., April 1957. Irrespective of the information contained in this report, the pesticide chemical discussed may not be used unless a tolerance has been established or an exemption from the requirement of a tolerance has been granted for each specific use.