Persistence of Residues of Dimethoate on and in Mature Valencia Oranges and in Laboratory-Processed Citrus Pulp Cattle Feed

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The insecticide dimethoate (Cygon, Rogor) has been evaluated as a persisting residue on and in mature Valencia oranges. The RL_{50} (half-life) value for this citrus insecticide under field conditions is approximately 19 days for these oranges. Persisting residues are subsurface and are not removed by detergent washing, but they can be essentially eliminated from cattle feed made from treated orange peel and pulp by extending the heating period in the final drying procedure. Dimethoate oxygen analog did not survive the total analytical method used.

THE COMPOUND *O,O*-dimethyl *S*-(*N*-methylcarbamoylmethyl) phosphorodithioate (Cygon, Rogor) is promising for the control of citrus thrips, *Scirtothrips citri* (Moult.), citrus aphid, *Aphis spiraecela* Patch, and California red scale, *Aonidiella aurantii* (Mask.). The results of a 59-day study of the magnitudes and persistence of unchanged dimethoate on and in mature Valencia oranges which were treated in the field to simulate probable commercial practice are presented. No indication of even partial removal of any of these persisting subsurface residues by washing with dilute detergent solution is demonstrated. The amount of dimethoate retained by laboratory-processed citrus pulp cattle feed is dependent upon the length of time heat is applied in the final drying procedure.

Dimethoate residues *in situ* normally contain up to about 15% of the metabolically induced oxygen analog (*S* → *O*) (*1*, *8*). Dimethoate oxygen analog does not survive the total analytical procedure utilized, and, therefore, present data are for the parent compound only. Using P^{32}-labeled dimethoate, de Pietri-Tonelli (*1*) and coworkers have established that this compound translocates in minimal quantities from sprayed lemon leaves or twigs or trunk into nearby fruits, penetrating even into the seeds. From many experiments, these workers concluded that in "citrus the substance reaches higher concentrations in unripe fruits than in ripe ones, and in the peel to a greater extent than in the pulp" (edible portion). Their conclusion that dimethoate reaches higher concentrations in the peel is verified by the experimental results reported herein. Further results show that dimethoate residues can be reduced when peel is processed into so-called citrus pulp cattle feed.

Materials and Methods

Mature Valencia orange trees, spaced 90 per acre, were sprayed with a 4-pounds per gallon E.C. (emulsible concentrate) formulation of dimethoate at the rates of 1 pint and 2 pints per 100 gallons of water. All sprays were applied at the rate of approximately 25 gallons per tree to 8-tree plots on March 8, 1963. Four of the 8 trees in each plot received a second treatment identical to the first on March 26, 1963. Triplicate samples of 32 fruits were taken from each plot on the dates indicated in Table I. Rainfall and irrigation data recorded for the period of investigation are also shown in Table I.

The usual procedures for processing citrus peel and pulp and for pre-

Table I. Dimethoate Residues Found in Valencia Oranges[a] Following a Single Field Application on March 8, 1963

Sample Date	Elapsed Days	Rainfall Since Previous Sampling, Inches	Dimethoate Residue in Fruit, P.P.M.					
			1 Pint of 4 Lb./Gal. E.C./100 gal.		2 Pints of 4 Lb./Gal. E.C./100 Gal.		Control	
			Peel[b]	Pulp[c]	Peel[b]	Pulp[c]	Peel[b]	Pulp[c]
3/1	Pretreat.	...	0.0, 0.0, 0.0	0.0, 0.0, 0.0	0.0, 0.0, 0.0	0.0, 0.0, 0.0	0.0, 0.0, 0.0	0.0, 0.0, 0.0
3/11	3	0.09	10.8, 5.5, 9.8	0.0, 0.0, 0.0	13.2, 15.8, 14.0	0.0, 0.0, 0.1	0.8, 1.3, 2.1	0.2, 0.2, 0.1
3/14	6	0.13	10.1, 5.2, 4.2	0.0, 0.0, 0.0	10.8, 14.0, 14.1	0.0, 0.0, 0.0	2.1, 1.0, 1.1	0.1, 0.1, 0.1
3/18	10	0.96	5.4, 4.2, 3.6	0.0, 0.0, 0.0	6.0, 5.7, 9.3	0.0, 0.0, 0.1	1.4, 1.6, 1.6	0.0, 0.1, 0.1
3/25	17	0.05	6.5, 4.2, 2.8	0.0, 0.0, 0.0	5.2, 8.0, 7.4	0.0, 0.0, 0.0	1.9, 2.0, 2.0	0.1, 0.1, 0.1
4/1	24	0.31	4.5, 2.1, 1.3	0.0, 0.1, 0.0	6.7, 3.5, 6.1	0.1, 0.0, 0.0	2.0, 1.5, 1.2	0.1, 0.1, 0.2
4/8	31	0.00[d]	4.6, 1.4, 2.6	0.0, 0.0, 0.0	3.5, 5.2, 3.4	0.0, 0.0, 0.0	1.0, 0.5, 0.4	0.0, 0.1, 0.1
4/22	45	1.12	3.7, 1.2, 0.9	0.0, 0.0, 0.0	6.4, 7.4, 3.8	0.0, 0.1, 0.0	0.8, 0.8, 1.3	0.1, 0.1, 0.1
5/6	59	0.58	1.4, 0.6, 1.0	0.0, 0.0, 0.0	3.7, 3.6 2.8	0.0, 0.0, 0.0	0.9, 0.9, 1.0	0.1, 0.1, 0.0
4/8	31	Washed[e]	7.5, 3.5, 4.0	0.0, 0.0, 0.0	3.8, 7.4, 4.8	0.0, 0.0, 0.0	0.7, 1.7, 0.4	0.1, 0.1, 0.1

[a] The peel and pulp portions of triplicate field samples were separated, and the results are based on the weight of the peel or pulp analyzed.
[b] All values corrected for recovery (average 85 ± 9%) from 30 fortified controls (2.0 to 8.0 p.p.m.). Lower limit of detection was 8 μg. per 50 grams of peel.
[c] All values corrected for recovery (average 90 ± 9%) from 20 fortified controls (1.0 p.p.m.). Lower limit of detection was 8 μg. per 100 grams of pulp.
[d] Plots were irrigated on April 8, 9, and 10, 1963.
[e] Hand-washed with dilute Triton X-100 solution before processing.

Table II. Dimethoate Residues Found in Valencia Oranges[a] Following Two Field Applications,[b] March 8 and 26, 1963

Sample[c] Date	Days Since Second Treatment	Dimethoate Residue in Fruit, P.P.M.[d] 1 Pint of 4 Lb./Gal. E.C./100 Gal. Peel	1 Pint of 4 Lb./Gal. E.C./100 Gal. Pulp	2 Pints of 4 Lb./Gal. E.C./100 Gal. Peel	2 Pints of 4 Lb./Gal. E.C./100 Gal. Pulp
4/1	6	11.4, 5.1, 5.6	0.0, 0.0, 0.0	10.8, 11.4, 13.5	0.1, 0.0, 0.0
4/8	13	9.8, 6.2, 3.0	0.0, 0.0, 0.0	8.5, 8.8, 12.0	0.0, 0.0, 0.0
4/22	27	7.3, 4.1, 8.8	0.1, 0.1, 0.0	11.6, 15.1, 5.2	0.0, 0.0, 0.1
5/6	41	4.5, 1.0, 3.6	0.0, 0.0, 0.0	3.1, 5.3, 2.8	0.0, 0.0, 0.0
4/8[e]	13	10.8, 6.9, 5.8	0.0, 0.1, 0.0	7.4, 9.8, 8.5	0.0, 0.0, 0.0

[a] The peel and pulp portions of triplicate field samples were separated and the results based on the weight of peel or pulp analyzed.
[b] Rainfall and irrigation data are the same as in Table I.
[c] Control values for these dates are listed in Table I.
[d] All values corrected for recovery as described in Table I.
[e] Hand-washed with dilute Triton X-100 solution before processing.

Table III. Residues of Dimethoate in P.P.M.[a] Found in the Processing of Laboratory Valencia Pulp Cattle Feed

Sample A Moisture, %	Sample A P.p.m.[a]	Sample B Moisture, %	Sample B P.p.m.[a]
FRESH GROUND PEEL			
77.5	2.5	80	2.6
77.5	2.6	80	3.2
77.5	2.2	80	2.0
77.5	3.1	80	2.3
DRIED CATTLE FEED			
14	2.2	1	Nil[b]
14	3.5	1	Nil
14	2.7	1	Nil
14	2.8	1	Nil
14	2.2	1	Nil
14	2.2	1	Nil

[a] All p.p.m. values were corrected for background and recovery of dimethoate added at the time of equilibration. Recovery from four samples of fortified ground peel (2.0 to 4.0 p.p.m.) was 76 ± 4% and from four samples of final fortified cattle feed (4.0 to 8.0 p.p.m.) was 81 ± 10%.
[b] Nil means less than 7.0 micrograms per sample aliquot or less than 0.3 p.p.m.

paring and processing citrus pulp cattle feed have been previously described (*6*) in detail. These procedures were rigorously followed with the single exception that methylene chloride rather than hexane was used to strip the insecticide from the chopped samples. Control samples were fortified as previously described (*3*, *4*, *5*) and routinely analyzed in parallel with the corresponding field-treated samples.

A modification of the cleanup procedure described by Waldron (*7*) was used. Briefly, this procedure involved drying the methylene chloride stripping solution with sodium sulfate, swirling with Nuchar, filtration and evaporation of the methylene chloride solvent through a water layer, hexane washing of the water phase, chromatography of the water phase through a polyethylene-coated alumina column, partitioning into methylene chloride, drying with sodium sulfate, and evaporation. The present modification was the addition of the washing of the water layer with hexane; this additional step was necessary because of the large amounts of citrus oils which floated on the surface of the water. The colorimetric procedure originally described by George (*2*) as modified by Waldron (*7*) was used to determine amounts of dimethoate present. This method involved the hydrolysis of dimethoate and subsequent development of a pale red color with 1-chloro-2,4-dinitrobenzene in 3A alcohol, the absorbance of which was read at 505 mμ. A standard curve was made as described (*7*), producing a slope of 150 ± 8 μg. per 1.000 absorbance unit, against which all sample readings were compared. Since it was established that the oxygen analog is removed in the present cleanup procedure, the results are indicative of the parent compound only.

Results and Discussion

Table I presents data showing the persistence of dimethoate residues found in Valencia orange peel and pulp at various time intervals following a single field treatment. Table II presents similar data for applications 18 days apart. The persistence residue half-life (RL_{50}) of dimethoate on and in the peel is approximately 19 days when computed by the procedure of Gunther (*4*). At the bottom of each table are the results of analyses of peel from fruits washed with a dilute solution of Triton X-100. Comparison of the residue values of the washed fruit with the unwashed fruit sampled the same date (April 8) indicates that no measurable insecticide was removed by the detergent washing.

Table III presents data showing the amount of residue in laboratory-processed citrus pulp cattle feed dried to two levels of moisture content. Optimum water content for this type of cattle feed is considered to be approximately 11%, but technical difficulties cause some variation in commercial practice. The two moisture levels presented herein cover the range most likely to be encountered in commercial preparations. Results demonstrate that dimethoate can be removed from citrus peel being made into cattle feed by extending the heating period sufficiently to lower the water content to 1%. This experiment was not designed to elucidate exact conditions, but rather to show if such a reduction of dimethoate residues is possible.

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