Residues of Sevin on and in Lemons and Oranges

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The insecticide Sevin shows promise against several pests of citrus. Lemons field-treated with 1 or 2 pounds of a 50% wettable powder per 100 gal. had 12-day residues of 2.2 and 4.5 p.p.m., respectively, and Valencia oranges similarly treated carried 14-day residues of 1.0 and 2.5 p.p.m., respectively. Corresponding residue half-life values for the two varieties were 28 and 42 days, respectively. Analysis before and after washing showed that the residues on oranges are largely cuticular. Hydrolytic breakdown of Sevin in situ to 1-naphthol was undetectable. Under storage conditions, Sevin is stable in methylene chloride solution in the presence of a typical citrus extractive.

THE INSECTICIDAL COMPOUND 1-naphthyl *N*-methylcarbamate, commonly known as Sevin, has been shown in this laboratory to be promising for the control of several scale insects and orangeworms on citrus in California. A study of the persistence of Sevin residues on and in lemons and Valencia oranges field-treated with this compound in a commercial manner is presented.

A previously described (*4*) colorimetric analytical procedure designed to respond to microquantities of Sevin is based on the coupling of *p*-nitrobenzenediazonium fluoborate with the phenolic hydrolysis product of Sevin, 1-naphthol. None of the available modifications (*2, 3, 5*) of this basic procedure provided adequate cleanup when used with citrus extractives; the present modified total procedure included chromatography on Florisil, hydrolysis to 1-naphthol, extraction of this naphthol into cold aqueous alkali, then into methylene chloride for concentration and color development as above. A simultaneous determination of free 1-naphthol residues was also performed by elimination of the hydrolysis step.

Materials and Method

Application. Mature lemon trees were treated on March 23, 1960, with a mixture of either 1 or 2 pounds of a 50% wettable powder formulation of Sevin with 1 pound of a 25% wettable powder formulation of the acaricide Tedion (*p*-chlorophenyl-2,4,5-trichlorophenyl sulfone) per 100 gal. of water. Mature Valencia orange trees were treated similarly on June 22, 1960, but without Tedion. Applications were made as conventional high-pressure sprays, with manually operated spray guns, at the rate of approximately 1500 gal. per acre to the lemon trees and 2500 gal. per acre to the orange trees (90 trees per acre).

Sampling. Mature lemon fruits for assay of residues were collected before treatment and 5, 12, 19, 26, 33, 47, and 75 days after treatment. Mature Valencia orange fruits were collected before treatment and 2, 7, 14, 26, 40, 61, and 90 days after treatment. Four fruits (one from each quadrant) were collected in the standard manner (*1*) from each of eight trees in each plot, and each resulting 32-fruit sample was processed as a unit. Fruit samples from the triplicated plots for each treatment were processed separately.

Processing. The unwashed fruits were peeled; peel and pulp (edible portion) were processed separately with redistilled methylene chloride as previously described (*1*) to afford final stripping solutions. Replicate samples from Valencia oranges treated at the higher dosage were hand-scrubbed in a dilute Triton X-100 solution, rinsed with water, and air-dried before being processed as above to assess penetration of Sevin into the waxy and oily portions of the fruit rind.

Analysis. A 50-ml. aliquot of a methylene chloride stripping solution was allowed to percolate through a 20 × 35 mm. column of Florisil previously wet with chloroform; the column was then washed with 100 ml. of chloroform and the volume of the combined chloroform–methylene chloride solution was determined. Half of this solution was treated at room temperature with 4 ml. of a 0.4*N* methanol solution of potassium hydroxide for exactly 10 minutes in order to hydrolyze Sevin to 1-naphthol. Both the hydrolyzed and the non-hydrolyzed portions of the sample were analyzed for naphthol.

To the chloroform–methylene chloride solution, 50 ml. of ice-cold 0.5*N* potassium hydroxide solution were added and thoroughly shaken for 15 seconds. The lower organic phase was discarded; the remaining aqueous solution was washed with 50 ml. of methylene chloride, then acidified with 10 ml. of 6*N* hydrochloric acid solution. This aqueous acid solution was extracted with three 50-ml. portions of methylene chloride which were combined and filtered through a bed of anhydrous sodium sulfate into a Kuderna-Danish evaporative concentrator (*1*) containing 10 ml. of a 10% diethylene glycol solution in methylene chloride as "keeper." This mixture was then concentrated in the usual manner to 2 ml.

To the above residual solution in the Kuderna-Danish tube, 2 ml. of a 0.2*N* methanol solution of potassium hydroxide and 1 ml. of freshly prepared *p*-nitrobenzenediazonium fluoborate solution were added at room temperature and mixed thoroughly; the resulting blue color was allowed to develop for 10 minutes. Then 5 ml. of methanol were added, and the absorbance at 590 mμ was determined, using a reagent blank to zero the instrument. Typical standard curves prepared from purified Sevin and 1-naphthol read 5.9 and 4.0 μg., respectively, per 0.1 absorbance unit.

Results

Residues. Residue values for Sevin on and in the peel of field-sprayed lemons as determined by this colorimetric procedure are presented in Table I. No determinable amounts of free 1-naphthol (less than 0.6 p.p.m.) were

Table I. Residue Values (P.P.M.) for Sevin[a] on and in Peel of Field-Sprayed Lemons and Valencia Oranges[b]

Days after Treatment	Dosage 50% W.P.[c] 1 lb./100 gal.	2 lb./100 gal.		Control[cd]
		LEMONS		
5	11.8, 6.9, 9.7	15.4, 15.1, 21.0		1.8, 0.9, n.d.
12	7.5, 8.0, 6.5	16.8, 13.1, 16.7		n.d., n.d., n.d.
19	5.6, 7.2, 5.6	14.7, 15.3, 9.4		2.7, 2.3, 1.1
26	5.6, 3.7, 2.4	13.9, 7.2, 9.5		2.4, 1.2, 1.8
33	3.0, 3.6, 4.2	4.4, 5.0, 6.7		n.d., n.d., n.d.
47	2.6, 2.3, 3.0	4.5, 6.7, 9.6		2.2, 1.6, 1.6
75	2.0, 0.8, 0.7	2.9, 3.8, 3.6		1.9, 0.9, 1.5
		ORANGES		
		Unwashed	*Washed[d]*	
2	9.4, 10.1, 7.8	16.7, 18.2, 14.9	...	n.d., n.d., 1.2
7	4.4, 6.8, 6.8	14.1, 18.9, 18.4	2.9, 3.4, 1.5	n.d., 1.1, n.d.
14	5.7, 4.4, 5.1	13.5, 12.4, 12.0	...	n.d., n.d., n.d.
26	5.0, 5.2, 5.8	12.2, 10.3, 11.3	6.4, 7.3, 7.3	n.d., 0.7, n.d.
40	3.5, 3.7, 4.6	8.3, 6.9, 7.1	...	0.7, n.d., n.d.
61	2.9, 2.6, 2.2	3.5, 7.2, 4.8	5.6, 5.5, ...	n.d., 1.0, n.d.
90	3.0, n.d., 1.6	4.3, 6.2, 5.9	n.d., n.d., n.d.	n.d., n.d., n.d.

[a] No determinable amounts of 1-naphthol, the hydrolysis product of Sevin, were found (recovery, 81% and 78%; background, <0.6 p.p.m.).

[b] Based on weight of peel only (mature lemons have 30.0 ± 8.5 weight % peel from 632 measurements; mature Valencia oranges 18.7 ± 6.3 weight % peel from 297 measurements). All values corrected for averaged daily recovery (71% and 86%) and, except for controls, appropriate averaged daily backgrounds. Values of n.d. means less than 3 μg. of Sevin was found; aliquots represented from 2.5 to 5.0 grams of peel.

[c] Sevin-treated and control plots were both treated with 1 pound of a 25% W.P. formulation of the acaricide Tedion per 100 gal. of water. W.P., wettable powder.

[d] Hand-scrubbed with dilute Triton X-100 solution before processing. Values of n.d. means less than 3 μg. of Sevin was found; analytical aliquots represented from 2.5 to 5.0 grams of peel.

Table II. Storage Stability of Sevin in the Presence of Lemon Extractives in Methylene Chloride Solution at 10° C.

Storage Interval, Months	Sevin, P.P.M. Added	Sevin, P.P.M. Found[ab]	1-Naphthol, P.P.M. Added	1-Naphthol, P.P.M. Found[ab]
0	0.0, 0.0, 0.0	n.d., n.d., 0.7	0.0, 0.0, 0.0	n.d., n.d., n.d.
0	4.0, 4.0, 4.0	3.9, 4.1, 4.2	0.0, 0.0, 0.0	n.d., n.d., n.d.
8	0.0, 0.0, 0.0	n.d., n.d., 0.7	0.0, 0.0, 0.0	n.d., n.d., n.d.
8	4.0, 4.0, 4.0	3.9, 4.0, 4.2	0.0, 0.0, 0.0	n.d., n.d., n.d.

[a] All values corrected for average recoveries (Sevin, 71%; 1-naphthol, 81%) and backgrounds shown in Table I.

[b] Values of n.d. means less than 3 μg. of Sevin per 12.5 grams of peel and less than 8 μg. of 1-naphthol per 12.5 grams of peel.

found on or in any of the peel samples, and no determinable amounts of Sevin (less than 0.2 p.p.m.) or 1-naphthol (less than 0.1 p.p.m.) were found in the pulp portion of any of the fruit samples.

Residue values of Sevin on and in the peel of field-sprayed Valencia oranges are also presented in Table I. As with lemons, no determinable amounts of Sevin were found in the pulp portion of any of the fruit samples, and no determinable amounts of 1-naphthol were found in either peel or pulp samples.

Storage Stability. Since the duration of this field program was 8 months, it was necessary to establish the storage stability of Sevin in the presence of citrus extractives in solution in methylene chloride. All fruit samples were processed and stripped within 24 hours after receipt in the laboratory; then stripping solutions were stored at 10° C. awaiting analysis. Aliquots of the peel stripping solutions from the three pretreatment lemon samples were fortified to contain 4.0 p.p.m. of Sevin; half of each aliquot was analyzed at once and the other half was analyzed after 8 months at 10° C. Both Sevin and 1-naphthol were determined. Results are shown in Table II.

Discussion

Analytical Procedure. Methylene chloride, used in the ratio of 2 ml. of solvent to 1 gram of substrate, was the stripping solvent of choice. This ratio gave 12% better efficiency than 1 ml. per gram, and 44% better efficiency than hexane used at 2 ml. per gram, although Sevin has a solubility in *n*-hexane of 295 μg. per ml. at 28° C.

The elution efficiency of the chromatographic step as described is 81% for 1-naphthol and 95% for Sevin. Thus, the naphthol is only poorly eluted in the methylene chloride, but the remainder largely comes through in the chloroform with the Sevin.

Hydrolysis of Sevin to 1-napthol using 4 ml. of 0.4*N* potassium hydroxide solution in methanol, in 150 ml. of chloroform–methylene chloride solution, is complete in 10 minutes. Additional exposure to hydrolytic conditions results in increasing losses of the naphthol.

The extraction efficiency of 1-naphthol from chloroform–methylene chloride into 0.5*N* potassium hydroxide solution, then re-extraction into methylene chloride from acidified solution is 93%. Use of only 0.1*N* potassium hydroxide solution provides 81% efficiency. Sevin lost by hydrolysis under these conditions is less than 2%.

By use of the Kuderna-Danish evaporative concentrators and of diethylene glycol keeper, evaporative losses of 1-naphthol were less than 2%.

Residue Evaluation. Calculation (*1*) of RL_{50} or half-life values for Sevin residues on and in lemons from the data in Table I results in an average value of 28 days; from the data in Table I, an average RL_{50} or half-life value for Sevin on and in Valencia oranges is 42 days. Data in Table I also show that in situ hydrolytic breakdown of residual Sevin is not evident on citrus fruits. The rate of penetration of Sevin into the oily or waxy portions of oranges is very slow, as shown in Table I, suggesting that partial removal of Sevin residues in the normal packing house washing and scrubbing operations is feasible for at least 30 days after treatment.

Sevin in methylene chloride solution in the presence of lemon extractives is stable for at least 8 months at 10° C.

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