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ACARICIDE RESIDUES

Persistence of Residues of 2, 4, 5, 4'-Tetrachlorodiphenylsulfone in Florida Citrus Fruits

J. J. McBRIDE, Jr.
University of Florida, Citrus Experiment Station, Lake Alfred, Fla.

Residues of 2,4,5,4'-tetrachlorodiphenylsulfone, a compound effective in controlling the citrus red mite [*Metatetranychus citri* (McG.)] have been determined in all major varieties of Florida citrus fruits at varying times after application. Tedion is absorbed into the peel of citrus fruits and persists in the peel for longer than three months after application. Absorption into the pulp and juice, when it occurs, is extremely low.

THE COMPOUND 2, 4, 5, 4'-tetrachlorodiphenylsulfone (Tedion) has been found to be an effective acaricide for the citrus red mite [*Metatetranychus citri* (McG.)] in Florida (3). A project has been carried out in these laboratories to determine the amounts of Tedion residues at various times after application in the major varieties of citrus fruits grown in Florida and furnished in the fresh-fruit market.

Analytical Procedure

Tedion residues were determined by the method of Fullmer and Cassil (2), except that benzene was used throughout in place of chloroform and no keeper was used (it was found unnecessary).

Tedion was extracted from the samples by first thoroughly macerating the peel or pulp-juice portion of the fruit in a Waring Blendor and then tumbling the macerate with benzene for one hour. For peel samples 150 grams of peel and 200 ml. of benzene were used. For pulp-juice samples 200 grams of pulp-juice, 200 ml. of benzene, and 60 grams of anhydrous sodium sulfate

Table I. Recovery of Tedion from Citrus Fruits

Variety	Tedion, γ		Recovery, %
	Added	Found	
Valencia orange Peel	8.0	6.8	85
	24.0	20.0	83
	37.0	36.7	99
Pulp-juice	8.0	7.9	99
	24.0	26.3	109
	40.0	35.4	89
Grapefruit Peel	8.0	7.5	94
	16.0	17.6	110
	32.0	35.9	112
Pulp-juice	8.0	7.8	98
	20.0	20.4	102
	36.0	32.9	91
Tangerine Peel	8.0	8.2	102
	16.0	18.3	114
	32.0	33.9	106
Pulp-juice	8.0	7.7	96
	16.0	14.3	89
	24.0	25.5	106

were used. Aliquots taken for analysis varied from 20 to 50 ml., depending on the Tedion content.

Recoveries. Recoveries were good from both the peel and the pulp-juice of

all varieties. Recovery samples were prepared by adding a standard solution of Tedion in chloroform to the macerate prior to extraction with benzene. Table I shows some representative recoveries.

Residues. Sprays were applied with a hand pressure sprayer to the point of runoff which is a more thorough coverage than is generally obtained in commercial applications. Fruit was sampled at intervals after application until the Tedion content became constant or decreased. All fruit was washed with a detergent by thorough hand brushing, using a stiff-bristled brush to remove surface deposits. Table II shows Tedion residues in major varieties of citrus fruits at varying intervals between application and harvest.

Discussion

Inspection of Table II shows that Tedion is absorbed into the peel of citrus fruits in significant amounts and is extremely persistent. No attempt was made to determine the distribution of the Tedion residues in the peel. Varietal differences are slight. Tangerine peel shows slightly higher Tedion content than other varieties. In gen-

eral, the Tedion content in the peel increases during the first 2 to 3 weeks after application and then remains relatively constant for at least 8 weeks. [This is in accord with the findings of Cassil and Fullmer that surface residues of Tedion "diminish largely as a result of fruit growth and not by decomposition" (7)]. Penetration into the pulp and juice in measurable amounts occurred in only two varieties and in these cases the amounts found were about 1% of the peel content.

Acknowledgment

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Table II. Tedion Residues^a, P.P.M., in Citrus Peel, Pulp-Juice, and Whole Fruits

(Whole fruit basis calculated from peel content and peel to whole fruit weight ratio)

Days after Application	Date Sprayed									
	9-17-57	9-17-57	11-19-57	9-23-57	9-25-57	11-12-57	1-27-58	11-14-57	1-27-58	
	Pineapple Oranges	Hamlin Oranges	Valencia Oranges ^a	Temple Oranges	Marsh Grapefruit	Tangerines	Tangelos	Limes ^b	Lemons	
Peel										
0	0.3	0.4	0.0	0.3	0.1	0.3	0.3	0.1	0.3	
3	0.5	0.5	0.2 ^c	0.4	0.2	0.4 ^c	
7	0.8	0.9	0.3	0.7	0.4	1.2	0.6	0.4	0.6	
14	1.0	1.4	0.4	1.0	0.6	1.9	
21	1.5	1.3	0.5	1.0	0.4	1.7	0.8	0.8	0.9	
28	1.0	1.3	0.4	0.7	...	1.8	...	0.9	...	
35	1.0	1.3	0.4 ^d	0.8	0.4	2.1	0.7	...	0.7	
62	1.0	1.1	...	1.0	0.5	1.5 ^e	1.1 ^e	...	1.2 ^e	
90	0.4	1.1	0.5	1.1	1.2	...	1.0	
112	1.0	1.0	0.4	0.8 ^f	0.5 ^g	0.7	
Pulp-Juices										
0	0.01	h	h	h	0.02	h	
3	0.02	h	h	h	h	h	
7	0.02	h	h	h	0.1	h	h	...	h	
14	0.02	h	h	h	h	h	
21	h	h	h	h	h	h	
28	h	h	...	h	...	h	
36	h	h	...	h	...	h	h	...	h	
Fruits										
0	0.05	0.1	0.0	0.05	0.03	0.08	0.05	0.02	0.1	
3	0.1	0.1	0.05	0.1	0.05	0.1	
7	0.2	0.2	0.1	0.1	0.1	0.3	0.1	0.1	0.2	
14	0.2	0.3	0.1	0.2	0.2	0.5	
21	0.3	0.3	0.1	0.1	0.2	0.4	0.1	0.2	0.4	
28	0.2	0.3	0.2	0.1	0.1	0.4	...	0.2	...	
35	0.2	0.3	0.1	0.2	0.1	0.5	0.1	...	0.3	

^a Valencias sprayed at the rate of 1/2 lb. Tedion 25% W.P./100 gal.; all others at 1 lb./100 gal. ^b Pulp-juice residues not determined; calculated on assumption of no Tedion penetration through peel. ^c 2 days. ^d 42 days. ^e 49 days. ^f 135 days. ^g 127 days. ^h Nil.

INSECTICIDE RESIDUES

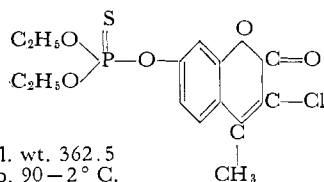
Photofluorometric Method for Determination of Co-Ral Residues in Animal Tissues

CHARLES A. ANDERSON, JAMES M. ADAMS, and DANIEL MacDOUGALL

Chemagro Corp., Kansas City, Mo.

This work was carried out to develop a highly sensitive method for the determination of traces of Co-Ral and/or its oxygen analog in a wide variety of animal tissues. The method has a sensitivity of 0.02 p.p.m. based on a sample of 50 grams and a final solution volume of 5 ml. Cleanup procedures for meat and fat have been developed.

THE COMPOUND *O*-(3-chloro-4-methylumbelliferone) *O,O*-diethyl phosphorothioate (Bayer 21/199, more recently Co-Ral) has been registered recently in the United States and Canada for the control of cattle grubs, screw-worms, horn flies, lice, and ticks. The compound possesses the following properties:



A survey of possible approaches to the determination of Co-Ral residues in animal tissues revealed several colorimetric methods for the estimation of low concentrations of coumarin derivatives in various types of biological material. In two cases, procedures of this type have been applied to Co-Ral (1, 2). However, in no case could the desired degree of sensitivity (0.01 to 0.02 p.p.m.) be obtained without the use of large samples of tissue and involved extraction and concentration procedures.

Fluorescence has been used extensively for the determination of trace amounts of various types of organic compounds—

e.g., thiamine, riboflavin—in biological material (77). Although this method has not been used for the determination of pesticide residues, it has been used extensively for naturally occurring coumarins (3, 4, 10). Hornstein (5) has reported on the fluorescence of several pesticides.

Co-Ral is a highly fluorescent compound; however, its fluorescence is much less than that of 3-chloro-4-methyl-7-hydroxycoumarin. As this latter compound or a related coumarin derivative can be formed from Co-Ral by hydrolysis, the possibility of obtaining a very sensitive residue method presented itself.