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Residues of Four Ethylenebis(dithiocarbamates) and Their Decomposition Products on Field-Sprayed Tomatoes

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Ethylenebis(dithiocarbamates) and their decomposition products ethylenethiuram monosulfide, ethylenebis(isothiocyanate), and ethylenethiourea were determined on tomatoes after field spraying with four different formulations. The highest residues were found on crops treated with the manganese-containing products. After 14 days, 24–37% of the initial ethylenebis(dithiocarbamate) remained. The heating of homogenates of the treated crop material resulted in a 38–48% conversion to ethylenethiourea.

In a previous study of the dissipation of maneb and its decomposition products on two crops (Newsome et al., 1975), it was found that significant levels of all compounds remained 2 weeks after application. It was also observed that the residues of maneb were excellent precursors of ethylenethiourea (ETU) when subjected to heat.

The present investigation was initiated to provide residue data for other ethylenebis(dithiocarbamates) (EBDC's) as compared to maneb and to determine the extent to which these residues were converted to ETU under conditions of cooking. In addition, data were sought on the levels of ethylenebis(isothiocyanate) (EBI) present after treatment with various EBDC's, since there was previous chromatographic evidence that it existed on tomatoes treated with maneb (Engst et al., 1968).

EXPERIMENTAL SECTION

Tomato Plots. Tomato plants (Ottawa 78 variety) were grown at the Ottawa Research Station, Agriculture Canada during the summer of 1975. Five plots were planted, four of which were treated with different EBDC's and one of which was sprayed with water as a control. A plot consisted of two 30-ft rows, each containing 10 plants. Each treated area was separated from the others by a 4 ft high polyethylene vapor barrier to prevent contamination by drift. Total rainfall during the test interval was 5.82 in.

Treatment with EBDC's. The EBDC's used in this experiment were purchased from a local supplier and consisted of: Manzate D, an 80% maneb formulation; Dithane M-45, a product containing 80% mancozeb; Polyram 80-W, containing 80% metiram; and Zineb 75W, containing 75% zineb. All products were applied at the maximum rates recommended by the manufacturers which were as follows: Manzate D, 3 lb (2.4 lb of active ingredient (AI))/acre; Dithane M-45, 3 lb (2.4 lb of AI)/acre; Polyram 80-W, 2 lb (1.6 lb of AI)/acre; and Zineb 75W, 3.25 lb (2.4 lb of AI)/acre. Seven treatments of each fungicide were applied as aqueous suspensions at intervals of 7 days.

The sprayer was an E.R.S. self-propelled plot sprayer developed by Gary Hergert, Engineering Research Service, Agriculture Canada for the application of spray solutions to small areas in a manner simulating commercial low-pressure sprayers. The apparatus consisted of a chassis containing a 5-gal reservoir, pump, pressure regulator, and drop tubes for three Spraying Systems no. 6508 nozzles mounted on a spray boom. The sprayer was operated at a constant forward speed of 2 mph and a pump pressure of 30 psi, resulting in a 103 gal/acre output. The EBDC's were maintained in suspension during spraying by agitation provided by by-pass liquid from the pressure regulator.

Sampling. Samples were collected immediately after the final application of fungicide and at intervals up to 14 days thereafter. Each plot was divided into 6 sampling areas from which approximately 500 g of tomatoes was removed after each interval. Immediately upon receipt at the laboratory each sample was homogenized without prior washing or peeling and subsamples removed for ethylenethiuram monosulfide (ETM) and EBI analysis. The remaining homogenate was frozen at −18 °C for later analysis of the parent EBDC's and ETU.

Heat Treatment. Tomato homogenate (5 g) was heated to boiling in a 125-ml flask connected to a reflux condenser. The elapsed heating time was 10 min. After cooking, the samples were cooled and extracted with ethanol for the determination of ETU.

Analytical Methods. EBI (Newsome, 1976) and ETM (Newsome, 1975) were determined by gas–liquid chromatography exactly as described. ETU was determined by gas–liquid chromatography of the trifluoroacetylated *S*-benzyl derivative (Pecka et al., 1975) on a 6-ft column of 2% butanediol succinate on Chromosorb W, HP. The EBDC's were analyzed by hydrolysis and gas–liquid chromatography of the resulting ethylenediamine (Newsome, 1974).

RESULTS AND DISCUSSION

The dissipation of the various EBDC's with time is given in Table I. Residues left by the manganese-containing

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Table I. Residues[a] of Ethylenebis(dithiocarbamates) on Tomatoes at Various Intervals after Application by Spraying

Elapsed time, days	Dithane M-45	Manzate D	Polyram 80-W	Zineb 75W
0	8.83 ± 0.49	12.5 ± 1.82	4.56 ± 0.19	4.78 ± 0.13
1	10.7 ± 0.55	9.06 ± 0.89	4.88 ± 0.39	3.68 ± 0.26
2	9.09 ± 0.59	8.01 ± 0.84	5.07 ± 0.45	4.00 ± 0.17
3	9.01 ± 0.39	6.03 ± 0.56	3.59 ± 0.14	5.24 ± 0.12
6	4.02 ± 0.32	2.97 ± 0.27	2.02 ± 0.15	1.50 ± 0.06
10	3.86 ± 0.13	3.68 ± 0.16	1.84 ± 0.13	1.83 ± 0.15
14	3.24 ± 0.17	3.08 ± 0.13	1.10 ± 0.06	1.27 ± 0.06
Control 0.136 ± 0.014 (as maneb)				

[a] Values (in parts per million) are the means ± standard error of six samples and are expressed in terms of the active ingredient applied. Seven treatments were made at intervals of 7 days.

Table II. Residues[a] of Ethylenethiuram Monosulfide and Ethylenebis(isothiocyanate) on Tomatoes Treated with Ethylenebis(dithiocarbamates) in the Field

Elapsed time, days	Dithane M-45	Manzate D	Polyram 80-W	Zineb 75W
		Ethylenethiuram Monosulfide Found, ppm		
0	0.019 ± 0.009	0.066 ± 0.018	0.008 ± 0.002	0.009 ± 0.002
1	0.032 ± 0.003	0.041 ± 0.005	0.020 ± 0.004	0.008 ± 0.001
2	0.035 ± 0.001	0.025 ± 0.001	0.012 ± 0.002	0.014 ± 0.004
3	0.017 ± 0.001	0.027 ± 0.001	0.007 ± 0.002	0.003 ± 0.001
6	0.019 ± 0.001	0.020 ± 0.001	na[b]	na[b]
Control 0.004 ± 0.002				
		Ethylenebis(isothiocyanate) Found, ppm		
0	0.009 ± 0.002	0.011 ± 0.001	0.007 ± 0.0	0.002 ± 0
1	0.016 ± 0.002	0.016 ± 0.003	0.006 ± 0.001	0.003 ± 0.001
2	0.013 ± 0.001	0.015 ± 0.001	0.002 ± 0.001	0
3	0.014 ± 0.002	0.013 ± 0.001	0.005 ± 0.001	0
6	0.003 ± 0.001	0.016 ± 0.001	na[b]	na[b]
Control 0.002 ± 0				

[a] Values are the means ± standard errors of six samples. Seven treatments were made at intervals of 7 days. [b] Not analyzed.

Table III. Effect of Cooking on Ethylenethiourea Residues[a] in Tomatoes Sprayed with Ethylenebis(dithiocarbamates)

Time after spraying, days	Dithane M-45	Manzate D	Polyram 80-W	Zineb 75W
		Uncooked		
0	0.036 ± 0.004	0.033 ± 0.004	0.025 ± 0.005	0.033 ± 0.005
1	0.065 ± 0.015	0.018 ± 0.002	0.085 ± 0.015	0.024 ± 0.003
3	0.036 ± 0.009	0.026 ± 0.003	0.006 ± 0.003	0.007 ± 0.001
6	0.017 ± 0.004	0.015 ± 0.001	0.039 ± 0.004	0.006 ± 0.003
14	0.011 ± 0.001	0.008 ± 0.001	0.009 ± 0.002	0.011 ± 0.006
Control 0.001 ± 0.001				
		Boiled 10 min		
0	1.14 ± 0.080	1.11 ± 0.138	0.217 ± 0.026	0.772 ± 0.144
1	1.33 ± 0.134	1.42 ± 0.162	0.754 ± 0.162	0.950 ± 0.117
3	1.08 ± 0.140	0.945 ± 0.173	0.584 ± 0.052	0.535 ± 0.080
6	1.03 ± 0.127	0.462 ± 0.051	0.174 ± 0.016	0.206 ± 0.005
14	0.935 ± 0.142	0.519 ± 0.049	0.184 ± 0.015	0.110 ± 0.007
Control 0.020 ± 0.002				

[a] Values (in parts per million) are the means ± standard error of determinations on six samples.

products were significantly higher than those of Polyram or zineb. With all compounds, 24–37% of the initial residue remained 14 days after application. The rate of decline of maneb is similar to that found previously (Newsome et al., 1975) although the levels are lower than those obtained by manual application of the fungicide. Compared to maneb, there appears to be little change in the amounts of the other EBDC's over the first 3 days. In all treatments, free ethylenediamine values did not exceed twice the control level of 0.033 ± 0.005 ppm.

The amounts of the decomposition products ETM and EBI found at various intervals after spraying are shown in Table II. The highest levels of these residues are associated with those treatments which resulted in the highest levels of parent EBDC. In all treatments there is a gradual decline of ETM. The amounts of EBI found were less than those of ETM, and in the case of zineb treatment were not significantly greater than the control value.

The relatively low levels of ETU present on the uncooked samples agree with an earlier study with maneb (Newsome et al., 1975) and are in contrast to those found after boiling as shown in Table III. The amount of ETU formed on boiling reflects the level of parent compound on the crop. The mean percentage yield (molar basis) of ETU from each EBDC is as follows: Dithane M-45, 48.8; Manzate D, 37.7; Polyram 80-W, 47.2; and Zineb 75W, 40.2. Thus, the extent of conversion is similar for each EBDC and agrees with the values found in fortification studies (Watts et al., 1974).

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Changes of Thiofanox Residues in Potatoes Resulting from Storage and Cooking

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Dacamox, the 5–15% granular formulation of thiofanox (P), 3,3-dimethyl-1-(methylthio)-2-butanone *O*-[(methylamino)carbonyl]oxime, was applied to potato crops in furrow at planting as an insecticide in the U.S. and Canada. Less than 0.5 ppm of the anticholinesterase carbamate residues derived from P was found in the tubers harvested from plots treated at the 3 lb (active ingredient) rate in the U.S. and Canada. These residues in potatoes may be reduced significantly by three mechanisms: (1) storage of the tubers at room temperature for 10–20 weeks reduced 48 to 97% of these residues through metabolic degradation; (2) baking and frying potatoes reduced the initial residues 50–90% due to hydrolysis of these residues; and (3) boiling potatoes reduced 30–60% of the initial residues due to water extraction.

Thiofanox (P), 3,3-dimethyl-1-(methylthio)-2-butanone *O*-[(methylamino)carbonyl]oxime, a potent systemic and contact insecticide, effectively controls a wide range of insects which attack potato plants and other crops (Schauer, 1976). Cholinesterase-inhibiting residues were determined in the tubers harvested from P-treated potato plants in different locations of the U.S. and Canada. Metabolic studies indicated that a two-step oxidation of P is the primary mode of degradation in plants (Whitten and Bull, 1974; Holm et al., 1975), animals (Tallant and Sullivan, 1974), and soils (Duane, 1974). The present paper reports the qualitative and quantitative changes of the residues derived from P in potatoes during storage and cooking.

EXPERIMENTAL SECTION

Reagents. Besides the parent material P, the following derivatives of P were prepared as standards: the sulfoxide (P_1), 3,3-dimethyl-1-(methylsulfinyl)-2-butanone *O*-[(methylamino)carbonyl]oxime; the sulfone (P_2), 3,3-dimethyl-1-(methylsulfonyl)-2-butanone *O*-[(methylamino)carbonyl]oxime; the three hydrolytic products of P, P_1, and P_2: (O), 3,3-dimethyl-1-(methylthio)-2-butanone oxime, (O_1), 3,3-dimethyl-1-(methylsulfinyl)-2-butanone oxime, and (O_2), 3,3-dimethyl-1-(methylsulfonyl)-2-butanone oxime, respectively; and the ketone (K_2), 3,3-dimethyl-1-(methylsulfonyl)-2-butanone. Radioactive analogues of the three carbamates were also prepared with radioactive carbon-14 at the methyl carbon attached to the sulfur atom (Wolfe and Magee, 1975). The specific activities were from 19.1 to 21.7 mCi/g. All the standards were greater than 99% pure.

Methods. For residue analysis, potato plants were treated with different rates of Dacamox (5–15% granule P) in furrow at planting in different locations. The P and P_1 residues in the potato samples were first oxidized to P_2 and the total anticholinesterase carbamate residues derived from thiofanox (P_t, $P_t = P + P_1 + P_2$) were determined in the form of total P_2 (Chin et al., 1975). For studying the relative quantities of P, P_1, P_2, and O_2 in potatoes, some samples with high P_t levels were selected from the 1972 and 1973 treatments for the determination of these residues individually.

The distribution of P_t residues in tubers was studied by determining the P_t residues in different parts (skin, outer part, and inner part) and sizes (small, medium, and large) of the tubers. From a 200-g fresh sample, 150 g of potato juice and 35 g of dry matter were obtained and the P_t residues in the juice were determined.

For studying the changes of P_t residues during storage, tubers from two plots of a treatment were analyzed immediately after harvest. The samples were stored in the dark at room temperature in paper boxes and analyzed at the 10th week for P_1 and P_2. Starting from the 11th week, sprouts began to emerge and one-half of the tubers were set out on a lab bench and exposed to standard fluorescent light for an average of 8 h per day. The remaining tubers were retained in the paper boxes. At the 20th week, both the tubers and sprouts were analyzed.

To study the thermostability of P in water and oil solutions, two test tubes (15 mm i.d. × 150 mm) containing 2 ml of water were set in water baths maintained at 45 and 100 °C. Approximately 25000 dpm of [^{14}C]P in 5 μl of 10^{-3} N HCl was mixed with the water in the tubes. After the mixture was allowed to stand for 60 min, the radioactivity was extracted with 2 × 20 ml of $CHCl_3$ for subsequent analysis by TLC (Holm et al., 1975). In a third test tube, the same amount of [^{14}C]P was mixed with 2 ml of vegetable oil maintained at 200 °C in an oil bath. After standing for 10 min, the radioactivity was extracted with 3 × 20 ml of 0.2 N HCl. Radioactive components in the aqueous extract were then extracted (3 × 20 ml of $CHCl_3$) for TLC analysis. The thermal influence on P under these

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