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INSECTICIDE PERSISTENCE

The Disappearance of Endrin Residues on Cabbage

L. R. MATTICK, D. L. BARRY, F. M. ANTENUCCI, and A. W. AVENS

New York State Agricultural Experiment Station, Cornell University, Geneva, N. Y.

An endrin formulation was sprayed on cabbage heads at rates of 0.8, 0.5, and 0.25 pound per acre. Samples were harvested and analyzed at intervals up to 21 days after spraying. A Barber Colman Model 10 gas chromatographic instrument was modified to analyze the samples by electron affinity detection. Endrin residue was 0.13 p.p.m. or less 21 days after spraying for all levels of application.

CURRENT METHODS for determination of endrin residues are the phenylazide (*1*), total chlorine (*7*), and infrared method (*3*). These methods are time consuming and require rigorous cleanup. They generally require 10 μg. or more of endrin, and, therefore, it is necessary to analyze large crop samples containing of the order of 0.1 p.p.m.

Recently, Lovelock and Lipsky (*5*) described a detector for gas chromatographic systems which is exceptionally sensitive to chlorine-containing compounds. Goodwin *et al.* (*4*) showed that this election affinity detector can be employed with pesticide residues, particularly chlorinated hydrocarbons. Clark (*2*) has also applied this technique to detection of chlorinated pesticides.

Endrin is widely used to control cabbage looper. No published data are available on the persistence or disappearance of this residue on cabbage.

Materials and Methods

Spraying, Sampling, and Extraction of Cabbage. An emulsified formulation of 1.6 pounds of endrin per gallon diluted to apply at rates of 0.8, 0.5, and 0.25 pound of actual pesticide per acre, was sprayed on maturing cabbage on August 29, 1961. A two-row, tractor-mounted sprayer was employed in the application of this pesticide. After being sprayed, cabbage heads were harvested from each plot at intervals of 0, 1, 3, 5, 7, 10, 14, and 21 days.

Upon arrival at the laboratory, the cabbage heads were finely chopped in a Hobart food chopper. A sample of 500 grams of chopped cabbage, 250 grams of ethanol, and 500 ml. of redistilled *n*-hexane was placed in a Waring Blendor, and the mixture macerated for 5 minutes. The mixture was then transferred to 250-ml. centrifuge bottles and centrifuged at 1500 r.p.m. for 10 minutes in a size D International centrifuge. The resulting supernatant hexane solution was decanted and dried over anhydrous sodium sulfate.

Gas Chromatographic Analysis of Endrin. A Barber-Colman Model 10 gas chromatographic instrument was employed in the analysis. The electrometer range switch was modified by the addition of 9×10^{10}-ohm Victoreen resistor to change the sensitivity from 10^{-9} to 3×10^{-10}-amp. full scale.

The normal high voltage power supply was disconnected from the cell, and a 67.5-volt dry cell battery with a wire-wound, 10,000-ohm potentiometer to vary the voltage between 0 and 67.5 volts was substituted. The battery was connected positive to ground. The polarity switch of the electrometer was used in the positive rather than the usual negative position as employed in β-ray detection.

A U-shaped column of heavy-walled, borosilicate glass tubing 5 mm. I.D. and 6 feet long was used. The partitioning medium employed was the ethyl acetate soluble fraction of Dow Corning high vacuum stopcock grease. The packing was prepared by dissolving 20 grams of the liquid partitioning agent to 250 ml. of chloroform. A slurry was made by adding this solution to 100 grams of Chromosorb W 80–100 mesh in a large evaporating dish. The chloroform was evaporated with constant stirring of the slurry. When the Chromosorb-partitioning agent appeared to be dry, the evaporating dish and contents was placed in an oven at 110° C. for 3 hours. The contents were cooled, and an aliquot portion was packed into the column with constant vibration. After being packed, the column was preconditioned by baking at 230° C. and a flow rate of 60 ml. of argon per minute. The progress of the baking was followed by employing the β-ray detection system (*9*). The baking procedure usually took 3 days.

Operating parameters employed were: column temperature, 200° C., cell temperature, 235° C.; flash heater, 265° C.; nitrogen pressure, 18 p.s.i.; flow rate of nitrogen, 60 ml. per minute. The detector employed was the Barber-Colman Model No. A-4071 detector containing 56 microcuries of Radium 226.

Optimum Voltage to Detector. A 1-μl. sample of a hexane solution of endrin containing 1 μg. per ml. was injected into the gas chromatographic

Table I. Recovery of Endrin from Cabbage by Gas Chromatography with Electron Affinity Detection

P.P.M. Endrin Added	P.P.M. Endrin Recovered	Per Cent Recovery
1.00	1.06	106
0.50	0.50	100
0.10	0.093	93
0.04	0.040	100
0.02	0.018	90
Check	0.000	..

Table II. Disappearance of Endrin Residue from Cabbage

Treatment	Days After Sprayed (P.P.M. Endrin)							
	0	1	2	5	7	10	14	21
0.8	4.17	4.79	2.36	2.08	0.81	0.95	0.30	0.13
0.5	2.26	2.45	1.06	0.48	0.32	0.18	0.17	0.10
0.25	..	0.72	0.50	0.34	0.21	0.10	0.09	0.004

system. The voltage across the detector was varied from 0 to 40 volts. The optimum voltage across the detector to give a maximum response to endrin was 26 volts.

The optimum voltage was determined for this specific detector under the operating conditions given. Another detector produced by the same manufacturer and bearing the same model number was subjected to the same determinations; the optimum voltage for this detector was 18 volts. The voltage on the detector for a given compound or class of given compounds will not only depend upon the electron affinity of the compound but also on the shape of the detector and the temperature and pressure of the gas within the chamber (*5*).

Results and Discussion

Recovery of Endrin from Cabbage. Following the determination of the optimum voltage to the detector, a standard curve was constructed with recrystallized endrin. When endrin was subjected to gas chromatography, two peaks resulted regardless of the type of detection. Phillips *et al.* (*6*) isolated and identified the compounds responsible for these two peaks. These investigators identified an isomeric ketone as the first emerging peak, and an isomeric aldehyde as the second peak. The formation of these compounds is due to the thermal isomerization of endrin on the column. This isomerization is rapid and essentially complete at the relatively high temperatures required on the flash heater and column during the analysis. This laboratory has duplicated the findings of Phillips *et al.* by injecting recrystallized endrin into a preparative gas chromatographic instrument, collecting the resulting two peaks, and identifying them by infrared and chemical methods.

Under the conditions of the analysis described, the ratio of the peak areas of the ketone and aldehyde was 2.25:1. This ratio held constant for the standard solution of endrin, the cabbage with endrin added, and the field-sprayed cabbage.

By measuring the first emerging peak, the isomeric ketone, by triangulation and correlating this area with the amount of endrin injected, a standard curve resulted. The standard curve was a straight line between 0 and 0.10 μg. having a standard error of estimate (*8*) of 7×10^{-4} μg. of endrin.

Cabbage known to be free of any residue was macerated, and known amounts of endrin were added to 500 grams of cabbage. The amount added corresponded to 1.0, 0.5, 0.1, 0.04, 0.02, and 0 p.p.m. The extracts of this cabbage were analyzed by the electron affinity gas chromatographic method, and the results are tabulated in Table I. The range of recovery was 90 to 106% with an average of 98%, and standard deviation of $\pm 7\%$.

Disappearance of Endrin Residue from Cabbage. Cabbage heads were harvested from sprayed plots as previously described. Five hundred grams of cabbage was extracted and analyzed for endrin by gas chromatography. Aliquots from 1 to 100 μl., depending upon the concentration of pesticide in the extract, were injected on the column. The area of the isomeric ketone peak was measured, and the endrin content calculated from the standard curve. Results are shown in Table II.

The amount of endrin in both 0.8 and 0.5 pound per acre samples showed a definite rise between 0 and 1 day after spraying. No explanation for this behavior can be advanced at the present time. The 0.25 pound per acre, 0-day sample was lost during laboratory preparation of the samples.

Following the initial rise at 1 day, endrin disappeared progressively until 21 days after spraying when the level of endrin was 0.13 p.p.m. or less in all trials attempted.

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