Removal of Gardona and Azodrin from Vegetable Crops by Commercial Preparative Methods

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Tomatoes, sweet corn, and green beans were treated with Gardona and green beans were also treated with Azodrin, applied within 24 hours of crop harvesting. The harvested crops were canned by commercial methods. Pesticide residues were determined on samples withdrawn at appropriate points in the canning process. Approximately 99% of the residue on corn ears was removed in the husking process; canned corn contained less than 0.1 p.p.m. of Gardona. Washing removed nearly 50% of the Gardona residue from tomatoes. Tomato juice, heated at 100° C. for 30 minutes, contained residues of 0.03 to 0.09 p.p.m. of Gardona, while canned tomatoes, heated at 100° C. for 45 minutes, contained 0.01 to 0.03 p.p.m. of Gardona. A cold wash and hot blanching of green beans removed 90% of the Gardona residue and canned beans contained less than 0.01 p.p.m. of Gardona. The cold wash and blanching removed 33 to 53% of the Azodrin residue from green beans. Canned green beans contained 0.01 to 0.28 p.p.m. of Azodrin.

Removal of pesticide residues from crops in commercial and home processing has received varying degrees of attention since the 1920's. The removal of lead arsenate in commercial processing of fruit was recorded in many early publications. Some studies of the effect of washing and processing on residues of DDT in fruit and vegetables were reported between 1946 and 1957 (Bohm *et al.*, 1950; Brittin and Fairing, 1950; Haller and Carter, 1950; Lamb *et al.*, 1948, 1950; Manalo *et al.*, 1946; Tressler, 1947; and Walker, 1949). Carter (1948) reported the effect of cooking on DDT residues in beef. More recently Koivistoinen *et al.* (1964a,b,c, 1965a,b,c) reported on the stability and persistence of organophosphorus and carbamate pesticide residues in commercially processed fruit and vegetables. Ralls *et al.* (1967) studied the transformation products of diazinon and the effects of food preparation methods on its removal. The efficiency of commercial and home processing in the removal of DDT, malathion, and carbaryl from green beans was reported by Elkins *et al.* (1968) and from tomatoes by Farrow *et al.* (1968). The removal of DDT, parathion, and carbaryl in processing of spinach was reported by Lamb *et al.* (1968b), and Lamb *et al.* (1968a) reported the removal of DDT from potatoes in commercial and home processing. Farrow *et al.* (1966) reported the converson of DDT to DDE in canned spinach.

The studies reported here described the effect of commercial processing methods on residues of Gardona [2-chloro-1-(2,4,5-trichlorophenyl) vinyl dimethyl phosphate] in green beans, sweet corn, and tomatoes and residues of Azodrin (dimethyl phosphate, ester with *cis*-3-hydroxy-*N*-methylcrotonamide) in green beans. Gardona and Azodrin are promising chemicals for control of vegetable insects which have not been labeled for use on green beans, sweet corn, and tomatoes, the principal commercial cannery crops grown in Indiana.

INSECTICIDE TREATMENTS

Plots of sweet corn, green beans, and tomatoes were planted on the Purdue-O'Neal farm near Lafayette, Ind. As the crops approached maturity, they were sprayed with a tractor-mounted sprayer using two nozzles per row. The spray rate of 100 gallons per acre was obtained by adjustment of pressure and tractor speed. The following treatments were applied:

Plots 1 and 2. Gardona, 75% wettable powder, 0.45 kg. (1 lb.) per acre of active ingredient.

Plots 3 and 4. Gardona, 75% wettable powder, 0.90 kg. (2 lb.) per acre of active ingredient.

Plots 5 and 6. Azodrin, 1.45 kg. (3.2 lb.) per gallon of emulsion concentrate, 0.36 kg. (0.8 lb.) per acre of active ingredient.

Plots 7 and 8. Azodrin, 1.45 kg. (3.2 lb.) per gallon of emulsion concentrate, 0.72 kg. (1.6 lb.) per acre of active ingredient.

Odd-numbered plots (1, 3, 5, and 7) received 2 sprays: green beans Aug. 20 and 29, sweet corn Aug. 30 and Sept. 9, and tomatoes Sept. 6 and 16. The even-numbered plots received a single spray, applied on the last spray date. Green beans were harvested Aug. 29, sweet corn Sept. 10, and tomatoes Sept. 17. Double rate treatments of each compound were obtained by spraying plots twice. No rain fell during the treatment period for green beans; however, sweet corn received 0.55 inch of rain and tomatoes received 0.16 inch of rain.

Untreated plots of sweet corn, green beans, and tomatoes grown 400 yards from the nearest treated crop were used as controls or untreated checks.

SAMPLES FOR ANALYSIS AND PROCESSING

Sweet Corn. Fifty ears from each of four replicates from each treatment were collected and processed on Sept. 10. At the processing laboratory, the corn was husked by hand, washed, and cut from the cob. The kernels from each individual replicate were mixed and a 500-gram portion of raw corn was withdrawn for analysis. The remainder of the sample was placed in No. 303 size cans, filled hot with a solution of 5% sugar and 0.5% salt, sealed, and heated to 121° C. (250° F.) (15 p.s.i.) for 25 minutes.

The factory waste (husks, cobs, and silks) was chopped and mixed. Samples of raw kernels and factory waste were frozen and held at −15° C. until analyzed.

Beans. Samples of 9 kg. (20 pounds) of beans from each replicate were collected and processed on Aug. 29. The sample was mixed and 500 grams were taken for analysis as raw beans. The remainder was washed and cut and a second

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Table I. Recovery of Gardona and Azodrin Added to Vegetable Crops

Crop or Plant Part	Chemical Added	No. Obsd	Added, μg.	Added, P.P.M.	Found, μg.	Recovery, %
Green beans						
Raw	Azodrin	2	250	5.0	240	96.0
Blanched	Azodrin	2	100	2.0	99	99.0
Canned	Azodrin	2	25	0.5	25.4	101.6
Green beans						
Raw	Gardona	2	5	0.10	4.8	96.0
Canned	Gardona	2	2.0	0.04	1.85	97.5
Sweet corn						
Raw	Gardona	4	5.0	0.1	5.20	104.0
Canned	Gardona	4	2.0	0.04	1.59	79.7
Corn factory waste	Gardona	2	30.0	0.6	2.50	83.3
Tomato						
Raw	Gardona	2	50.0	1.0	50	100.0
			100.0	2.0	111	111.0
Washed	Gardona	1	20.0	0.4	18.4	92.0
		1	50	1.0	50.0	100.0
Canned	Gardona	2	1.0	0.02	.975	97.5
		2	2.0	0.04	2.00	100.0
Juice	Gardona	2	1.0	0.02	1.12	112.0
		2	4.0	0.08	4.00	100.0

500-gram lot was taken for analysis as washed beans. The beans were blanched 1½ minutes at 90° C. (194° F.) and 500 grams of the blanched beans taken for analysis. The remainder of the sample was placed in cans, filled hot with 8% salt brine, sealed, and heated at 115.5° C. (240° F.) (12 p.s.i.) for 20 minutes. The samples of raw, washed, and blanched beans were frozen and stored at −15° C. until analyzed.

Tomatoes. Samples of 9 kg. (20 pounds) of tomatoes from each replicate were selected and processed on Sept. 17. Ten raw unwashed tomatoes were quartered and the opposite quarters were blended, frozen, and stored at −15° C. until analyzed. The remaining tomatoes were washed with cold water and 10 fruits were sampled as above. Tomatoes for canning were blanched and peeled and were then placed in No. 303 cans and a 30-grain salt tablet was added. The cans were filled hot with cover juice, sealed, and heated at 100° C. (212° F.) for 45 minutes.

Tomatoes for juicing were washed and extracted. The juice was heated to 88° C. (190° F.) and placed in No. 303 size cans with a 30-grain salt tablet. The cans were sealed and heated to 100° C. (212° F.) for 30 minutes.

Samples of tomato pomace were also blended and frozen until analyzed.

RECOVERY OF RESIDUES FROM CROPS

Gardona. The sample was chopped and mixed with 1 to 4 times its weight of anhydrous sodium sulfate and then blended with a 3:1 mixture of hexane and isopropyl alcohol (4 ml. of mixed solvent per gram of crop) for 10 minutes. The extract was recovered from the crop maxtrix and the isopropyl alcohol removed by washing with water. The hexane solution was separated and dried over anhydrous sodium sulfate. The canned products (tomatoes, green beans, and sweet corn) were blended with a Waring blender before the weighed aliquot was taken for analysis.

Azodrin. Only beans were analyzed for Azodrin residues. Samples were chopped with anhydrous sodium sulfate and then blended with chloroform (4 ml. of chloroform per gram of plant material). The blended plant material was filtered and the chloroform residue solution dried over anhydrous sodium sulfate.

Table I shows the recovery of Gardona and Azodrin residues from crops by the preparation procedure and analytical methods outlined. The recovery of Azodrin from green beans approximated 100% (96 to 101.1%). The recovery of Gardona from vegetable samples varied from 79.7% in canned sweet corn to 112.0% in tomato juice and averaged 97.9%.

ANALYTICAL METHODS

Gardona. Aliquots of residue solution were cleaned up for gas–liquid chromatography (GLC) analysis by liquid–solid chromatography on a Florisil–Celite column (Shell Chemical Co., 1967). The column, 20 mm., was packed with a 1-cm. layer of anhydrous sodium sulfate, 5 grams (approximately 3 cm.) of a 4:1 mixture of Florisil (60/80 mesh)–Celite deactivated by addition of 10% water and capped with 1-cm. anhydrous sodium sulfate. The column was wet with 25 ml. of hexane, an aliquot of the sample added and rinsed into the column with 10 ml. of hexane. The column was eluted with 75 ml. of 25% ether–hexane; the first 10 ml. of eluate were discarded and the last 65 ml. collected in a clean flask. The activity of the Florisil–Celite absorbent will vary and should be calibrated as suggested in the Shell Chemical Co. method (1967). The solvent was evaporated and the residue made to a convenient volume with hexane. Final quantitation was made by GLC using an Aerograph model 1200 chromatograph with an electron-capture detector. The parameters employed were:

Column, 150 cm. × 2 mm.; 5% SE-30 on Chromasorb W; 200° C.
Injector, glass 235° C.
Detector, tritium 250 mc, 225° C.
0.2 nonogram gave a 42% scale deflection.

Azodrin. Chloroform extract of plant materials was dried over anhydrous sodium sulfate and analyzed without further cleanup. Aliquots of the chloroform extract were evaporated to dryness on a rotary evaporator and made to a convenient volume with hexane. Quantitation with GLC was carried out using the flame photometric detector of Brody and Chaney (1966) in the phosphorus mode with an Aerograph Model 2000 chromatograph. The parameters employed were:

Column, 120 cm. × 3 mm.; 1:1 mixture of 5% QF-1 and 2% Reoplex 400 on Gaschrom Q; 190° C.

Table II. Gardona Residues on Sweet Corn, Green Beans, and Tomatoes

Vegetable Treatment	P.P.M. of Gardona[a] Plot 1	Plot 2	Plot 3	Plot 4	Reduction[b] of residue, %
Sweet corn					
Factory waste	19.41	6.56	24.13	19.80	
Raw, kernels	0.07	0.07	0.24	0.08	
Canned corn	<0.01	<0.01	<0.01	<0.01	100
Tomatoes					
Raw, unwashed	1.22	0.95	2.37	1.79	
Raw, washed	0.64	0.45	1.40	0.80	49
Pomace	1.68	1.09	1.90	1.25	
Juice	0.03	0.03	0.09	0.08	96.5
Canned	0.03	0.01	0.03	0.02	98.6
Green beans					
Raw, unwashed	5.68	5.35	10.89	7.21	
Raw, washed	1.72	3.07	4.23	4.24	54
Blanched	0.31	0.39	0.79	0.64	93
Canned	<0.01	<0.01	<0.01	<0.01	100

[a] Mean of analysis from four replicates.
[b] Mean of four plots.

Table III. Azodrin Residues on Green Beans

Treatment	P.P.M. of Azodrin[a] Plot 5	Plot 6	Plot 7	Plot 8	Reduction[b] of residue, %
Green beans					
Raw, unwashed	4.31	4.14	7.25	6.03	
Raw, washed	2.51	2.15	6.56	5.55	27
Blanched	2.44	1.94	4.90	4.05	40
Canned	0.01	0.02	0.22	0.28	98

[a] Mean of analysis from four replicates.
[b] Mean of four plots.

Injector, 200° C.
Detector, 210° C.
2.0 nanogram gave a 40% scale deflection.

RESULTS AND DISCUSSION

Table II shows the results of analysis for Gardona residues. Analysis of the corn waste showed appreciable residues of Gardona—6.56 p.p.m. from one spray at 1 lb. per acre to 24.13 p.p.m. from two sprays at 2 lb. per acre. The raw kernels contained 0.07 to 0.24 p.p.m. of Gardona. This residue may have been transferred from the husks to the kernels in the processes of husking, washing, and cutting. The canned corn after heat processing did not contain measurable Gardona residues (greater than 0.01 p.p.m.).

The raw tomatoes at harvest contained from 0.95 (plot 2) to 2.37 (plot 3) p.p.m. of Gardona, varying according to treatment. The tomato pomace contained from 1.09 (plot 2) to 1.90 (plot 3) p.p.m. of Gardona. Cold-washed tomatoes contained from 0.45 to 1.40 p.p.m. of Gardona or approximately 50% of the residue found on raw tomatoes. Tomato juice samples contained from 0.03 to 0.09 p.p.m. of Gardona. The canned whole tomatoes contained from 0.01 p.p.m. (minimum detectable residue) to 0.03 p.p.m. Gardona.

The raw beans contained from 5.35 to 10.89 p.p.m. of Gardona. Washing (cold water) reduced the residue to 1.72 to 4.24 p.p.m. Blanching the beans further reduced the Gardona residue to 0.31 to 0.79 p.p.m. The canning process, heating at 240° F. for 20 minutes, destroyed any Gardona remaining on the beans (residue less than 0.01 p.p.m.).

The Azodrin residues found on bean samples are given in Table III. Raw beans contained 4.31 to 7.25 p.p.m. of Azodrin. Washing in cold water reduced the residue to 2.15 to 6.56 p.p.m. Blanching further removed the residue to a range of 1.94 to 4.90 p.p.m. The canning process reduced the Azodrin residue level to 0.01 to 0.02 p.p.m. for beans treated with 0.8-lb. dosage and 0.22 to 0.28 p.p.m. for beans treated at the 1.6-pound level.

SUMMARY

Sweet corn, green beans, and tomatoes were treated with Gardona at rates of 1 and 2 pounds per acre. Two spray applications were made at 10 days and 24 hours before harvest. With sweet corn, most of the insecticide residue was removed in husking. It is suggested that the small residue found on raw corn kernels may have been transferred from the husks to the kernels in the process of removing the husk. No residue was found in the canned corn. The study of residues on beans shows that the processes of washing, blanching, and canning each remove significant Gardona residues. No residue exceeding 0.01 p.p.m. of Gardona was found in canned beans. Azodrin was more resistant to removal by processing than Gardona. Canned green beans contained 0.01 to 0.28 p.p.m. of Azodrin. The juice made from washed tomatoes contained from 0.03 p.p.m. to 0.09 p.p.m. of Gardona; the tomatoes canned after blanching and peeling contained 0.01 to 0.03 p.p.m. of Gardona.

LITERATURE CITED

Bohm, R. O., Lamb, F. C., Lewis, L. D., White, D. G., "Insecticide residue studies on raw and canned green beans," National Canners Associaion, Research Report No. 13600-C, Feb. 14, 1950.
Brittin, W. A., Fairing, J. D., *J. Assoc. Offic. Agr. Chemists* **33,** 599 (1950).
Brody, S. S., Chaney, J. E., *J. Gas Chromatog.* **4,** 42 (1966).
Carter, R. H., *Science* **107,** 347 (1948).
Elkins, E. R., Lamb, F. C., Farrow, R. P., Cook, R. W., Kawai, Margaret, Kimball, J. R., J. AGR. FOOD CHEM. **16,** 962 (1968).
Farrow, R. P., Elkins, E. R., Cook, R. W., J. AGR. FOOD CHEM. **14,** 430 (1966).
Farrow, R. P., Lamb, F. C., Cook, R. W., Kimball, J. R., Elkins, E. R., J. AGR. FOOD CHEM. **16,** 65 (1968).
Haller, M. H., Carter, R. H., *Proc. Am. Soc. Hort. Sci.* **56,** 116–21 (1950).
Koivistoinen, P., Karinpaa, A., Kononen, M., J. AGR. FOOD CHEM. **12,** 555 (1964a).
Koivistoinen, P., Karinpaa, A., Kononen, M., Roine, P., J. AGR. FOOD CHEM. **12,** 551 (1964b).
Koivistoinen, P., Karinpaa, A., Kononen, M., Roine, P., J. AGR. FOOD CHEM. **13,** 468 (1965a).
Koivistoinen, P., Kononen, M., Karinpaa, A., Roine, P., J. AGR. FOOD CHEM. **12,** 557 (1964c).
Koivistoinen, P., Koskinen, A., Schulman, M., Karinpaa, A., Roine, P., Salonen, A., J. AGR. FOOD CHEM. **13,** 463 (1965b).
Koivistoinen, P., Vanhanen, L., Koskinen, E. H., J. AGR. FOOD CHEM. **13,** 344 (1965c).
Lamb, F. C., Farrow, R. P., Elkins, E. R., Cook, R. W., Kimball, J. R., J. AGR. FOOD CHEM. **16,** 272 (1968a).
Lamb, F. C., Farrow, R. P., Elkins, E. R., Kimball, J. R., Cook, R. W., J. AGR. FOOD CHEM. **16,** 967 (1968b).
Lamb, F. C., Lewis, L. D., Bohm, R. O., "Insecticide Residue Studies on Raw and Canned Apricots," National Canners Association, Research Report No. 13400-C, May 9, 1950.
Lamb, F. C., Lewis, L. D., Lee, S. K., "Studies on Removal of Insecticide Residues from Apricots," National Canners Association, Research Report No. 12441-A, Oct. 7, 1948.
Manalo, Gloria D., Hutson, R., Miller, E. J., Benne, E. J., *Food Packer* **27,** No. 13, 64–8 (1946).
Ralls, Jack, Gilmore, D. R., Cortes, Antoni, Shutt, S. M., Mercer, W. A., *Food Technol.* **21,** 1030 (1967).
Shell Chemical Co. Agricultural Chemical Div., 110 W. 51st St. New York, N.Y., 11020, Analytical Method PMS-G-905/67, Dec. 26, 1967.
Tressler, C. J., *J. Assoc. Offic. Agr. Chemists* **30,** 140 (1947).
Walker, K. C., *J. Agr. Res.* **78,** 383–7 (1949).

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