Effects of Washing, Trimming, and Cooking on Levels of DDT and Derivatives in Green Beans

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The effects of preparation procedures on levels of chlorinated hydrocarbon pesticides in market samples of green bean were determined by electron-capture gas chromatography. Washing, trimming, and cooking brought about a loss of *p,p'*-DDT, *o,p*-DDT, and *p,p'*-DDE, but *p,p'*-DDD and *o,p*-DDD increased. Pressure cooking for 3 minutes at 15 p.s.i. resulted in a greater decrease in total amounts of DDT and its derivatives than boiling for 12 minutes or cooking electronically for 6 minutes. Only traces of pesticides were found in the cooking liquid.

Most data on pesticide residues are based on samples of foods as obtained from the grower or from the market. These do not represent the levels of pesticides actually consumed. Several studies have been concerned with the influence of commercial processing on pesticide residues in foods. However, little attention has been given to the effects of home preparation procedures. Of course, the effects of both home preparation and commercial processing must be known in order to establish the probable amounts of pesticide actually ingested.

Carlin, Hibbs, and Dahm (*2*) evaluated the effects of simulated commercial canning or freezing on amount of residue of Guthion and DDT in snap beans. Colorimetric analysis indicated that residues of DDT were reduced to one half in frozen beans and to zero in canned beans. No residue was found in the brine in which frozen beans were cooked and only a trace in the liquid of the canned beans.

Anderson *et al.* (*1*) found that a standard commercial washing procedure removed 30% of Guthion from oranges, and the remaining residue was entirely in the peel. Both simple washing and rainfall were reported by Gunther and coworkers (*5*) to cause a marked decrease in nonpenetrating Guthion residues on lemons and oranges.

Koivistoinen *et al.* (*7*) applied organophosphate and carbamate pesticides as dips in an emulsion form to fruits and vegetables after harvest. The range for reduction of residues as a result of washing for 1 minute in running water was wide (0 to 79%). Approximate losses due to processing were: salting, pickling, jam preparation, or canning, 30 to 99%; pressing or steaming for juice, 70 to 90%; and drying at 75° C. for two days, 90 to 100%. Freezing at about −18° C. resulted in approximately 40 to 50% loss of pesticides. Freezing plus blanching increased losses of pesticide up to 95%.

Evaluation of varietal differences in absorption of pesticides from the soil by carrots was the main objective in the work of Lichtenstein, Myrdal, and Schula (*10*), but sites of storage and effects of boiling on stability of aldrin and heptachlor were measured also. From 14 to 30% of the absorbed insecticide was in the inner part of most varieties of carrots but was as high as 50% in one variety. Boiling the carrots for 30 minutes in a covered aluminum utensil caused a marked reduction in absorbed heptachlor. However, the cooking liquid became highly toxic for mosquito larvae. No such effects were observed for aldrin.

The insecticidal properties, the distribution, and the effects of boiling on persistence of indigenous 2-phenylisothiocyanate (mustard oil) in turnips and rutabagas grown on insecticide-free soil were investigated by Lichtenstein, Morgan, and Mueller (*9*). Sixty and 47% of the total amount of the compound were in the peelings of the turnips and rutabagas, respectively. After the turnips were boiled for 30 minutes, no insecticidal effects (for *Drosophila melanogastor* Meig) were demonstrated by the turnip tissue. Boiling for 5 minutes caused a slight reduction of these properties in the turnip tissue, and the water in which the tissue was cooked became toxic.

Mills (*11*), Williams (*15*), and Duggan, Barry, and Johnson (*3*) were interested in the level of pesticides in the total diet. Foods were obtained at intervals over a period of years from markets representing different geographical areas. The most common chlorinated pesticides detected in dairy products, meat, fish, and poultry, and leafy, legume, and root vegetables were DDT, DDE, and TDE. Also, dieldrin was detected in legume and root vegetables. DDT and lindane were the most common residues in cereal products.

Williams (*15*) indicated that preparation procedures had little or no effect on pesticide residue levels in foods. However, after the initiation of the study here reported, Duggan, Barry, and Johnson (*3*) stated that foods, ready for consumption, contained substantially lower levels of residues than the tolerances established for the specific pesticides. Evidently, more information is needed on the influence of preparation procedures on levels of pesticide residues in foods. The purpose of this study was to evaluate the effects of home preparation procedures on the chlorinated hydrocarbon (organo-

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chlorine) pesticide residue levels in market samples of green beans.

Experimental

Typical home procedures were used for preparing three market samples of green beans. For all treatments, except the control, the green beans were washed three times in 8 quarts of tap water followed by rinsing in 2 quarts of double distilled water. The distilled water rinse was included owing to the quantitative nature of the analyses. After being washed, the vegetables were blotted dry with cloth towels. The tips were removed, and the green beans were cut uniformly about 1 inch in length.

Cooking Procedures. Regardless of cooking method, 150 grams of green beans and 120 ml. of distilled water were used. Cooking utensils were rinsed with redistilled acetone prior to each use.

For boiling, a stainless steel 2-quart sauce pan with cover was the cooking utensil. Cooking time was 12 minutes from the time the water resumed boiling after the vegetable was added.

Pressure cooking was accomplished in a 4-quart aluminum sauce pan at 15 p.s.i. for 3 minutes.

For electronic cooking, the green beans and water were put in a borosilicate glass casserole (1½ quarts) and exposed to microwaves for 6 minutes. (Tappan electronic range, high setting, magnetron current 220 ma.)

Cooked samples were drained until no drop of the liquid formed after a 1-minute interval. The green beans and cooking liquid were analyzed separately.

Extraction and Cleanup Procedure. The extraction and cleanup procedure of Mills, Onley, and Gaither (*12*) as recommended by the Food and Drug Administration (*4*) was modified as follows:

Celite 545 in the acetonitrile extraction was omitted to increase recovery of pesticides.

An aliquot, approximately 250 ml., of the acetonitrile extract phase was used for analyses instead of the total amount. This shortened extraction time and minimized the difficulty of obtaining the same degree of dryness of the filter cake.

The weight of the total acetonitrile phase and the aliquot was determined and recorded for subsequent calculations.

$$\frac{\text{Wt. of 250-ml. aliquot}}{\text{Wt. of total acetonitrile phase minus sample dry wt.}}$$

Different cooking methods resulted in different water contents of the samples. The extent of volume contraction (acetonitrile-water) varied from sample to sample and had to be accounted for in each particular case.

The Florisil was partially inactivated just before use. It was heated at 130° C. overnight, then cooled in a desiccator. Just prior to use it was inactivated for 5 hours in an air-conditioned room (temperature 23° to 26° C.).

Purification of ethyl ether used in eluting mixtures was eliminated. Concentrated ethyl ether (200 ml. of ethyl ether reduced to near dryness and dissolved in 5 ml. of hexane) did not give any peaks by gas-liquid chromatography. If the ethyl ether in the eluting mixture is not completely dry, interfering substances appear in the eluates.

Gas Chromatography. A Barber-Colman Model Series 5000 gas chromatograph equipped with a tritium ionization detector, a 5-mv. Series 8300 recorder, and disk chart integrator Model 205 was operated with a detector cell temperature of 210° C., a detector cell current of 20-volt d.c., a flash heater temperature of 225° to 240° C., and a column temperature of 175° or 195° C. Purified nitrogen was the carrier gas with a flow rate of 40 or 80 ml. per minute, and an inlet pressure of 20 p.s.i. The column was a 180-cm. × 4-mm. glass U-tube. To obtain complete separation of the various pesticides and their degradation products and to confirm their identification, two types of columns were employed. One was packed with 60- to 80-mesh acid-washed Chromosorb W coated with 2.5% Dow 11, w./w. The other column was packed with equal weights of 5% QF 1, w./w., on acid-washed Chromosorb W and 5%, w./w., Dow 11 on acid-washed Chromosorb W (approximately 90 cm. each). The QF 1-coated Chromosorb W was placed in the first part of the column in the direction of the carrier gas flow, and the Dow 11-coated Chromosorb W was in the second part of the column (detector side). With the 2.5% Dow 11 column, *p,p'*-DDD appeared before *o,p*-DDT; however, *p,p'*-DDD was eluted after *o,p*-DDT on the combination column. Also, *o,p*-DDD was separated from *p,p*-DDE by the combination column.

Thin layer chromatography (TLC) was used for further verification of pesticides and their metabolites. Eastman chromatographic sheets (Type K 301R) coated with silica gel were spotted with the vegetable extracts and were developed in hexane–carbon tetrachloride, 7 to 3, v./v. Two chromogenic reagents were employed: 0.5% Rhodamine B in ethyl alcohol followed by 10% aqueous sodium carbonate (Eastman Chromogram System, Sheet 1065 C-213), and 1 gram of silver nitrate in 5 ml. of water plus 2.5 ml. of ammonium hydroxide made up to 100 ml. with acetone (developed in this laboratory).

Chromatograms were visualized with ultraviolet light.

Percentage recovery of pesticides from fortified samples of green beans were: lindane 87, heptachlor 80, aldrin 92, heptachlor epoxide 94, dieldrin 91, *p,p*-DDE 96, *p,p*-DDD 99, *o,p*-DDT 97, and *p,p*-DDT 98.

Results and Discussion

The means for chlorinated hydrocarbon pesticide residues found in three market samples of green beans are shown in Table I. Trace amounts of heptachlor epoxide, dieldrin, and endrin were present in addition to the residues listed in the table. The levels of pesticides in the control samples were within the tolerances set by the Food and Drug Administration as published in the summary of Registered Agricultural Pesticide Chemical Uses (*14*). The mean total of pesticides in control

Table I. Effects of Washing, Trimming, and Cooking[a] on Dissipation of Chlorinated Hydrocarbon Pesticides in Market Samples[b] of Green Beans

Sample Treatment	Pesticides Analyzed on 2.5% Dow 11 on Chromosorb W Column, P.P.M.			
	p,p'-DDT	*o,p*-DDT *p,p*-DDD	*p,p*-DDE *o,p*-DDD	Total pesticides
Control	0.46	0.20	0.01	0.67
Washed	0.44	0.19	0.01	0.64
Washed, trimmed	0.41	0.18	0.01	0.61
Washed, trimmed, boiled 12 min.[a]	0.22	0.13	0.01	0.36
Washed, trimmed, cooked 15 p.s.i., 3 min.[a]	0.09	0.14	0.01	0.25
Washed, trimmed, cooked electronically 6 min.[a]	0.23	0.11	0.01	0.35

[a] One hundred and twenty milliliters of distilled water. Only trace levels of pesticides found in liquid after cooking green beans. [b] Number = 3.

samples was 0.673 p.p.m. Each treatment—washing, trimming, boiling, pressure cooking, and electronic cooking—affected a reduction in total pesticide level (Figure 1). Samples of green beans from "organic gardeners," analyzed in this laboratory, were completely free from pesticide residues.

Effects of Washing and Trimming. Washing reduced the total pesticide residue in green beans by an average of 5.3% or 0.035 p.p.m. (Figure 1, Table I). Even though the washing procedure was more thorough than might be carried out in many homes, only surface residues could be removed. Apparently most of the residue detected in these studies had been absorbed into the vegetable.

Trimming had very little effect on pesticide level. Since only the tips of the beans were removed, no major change would be expected owing to this treatment. The two procedures, washing and trimming, caused a mean reduction of the total amount of pesticide of 9.2% or 0.062 p.p.m. The mean losses for *p,p'*-DDT and *o,p*-DDT were, respectively, 5.3 and 4.0% (Figure 1, Table I).

Apparently the usual home washing with water and

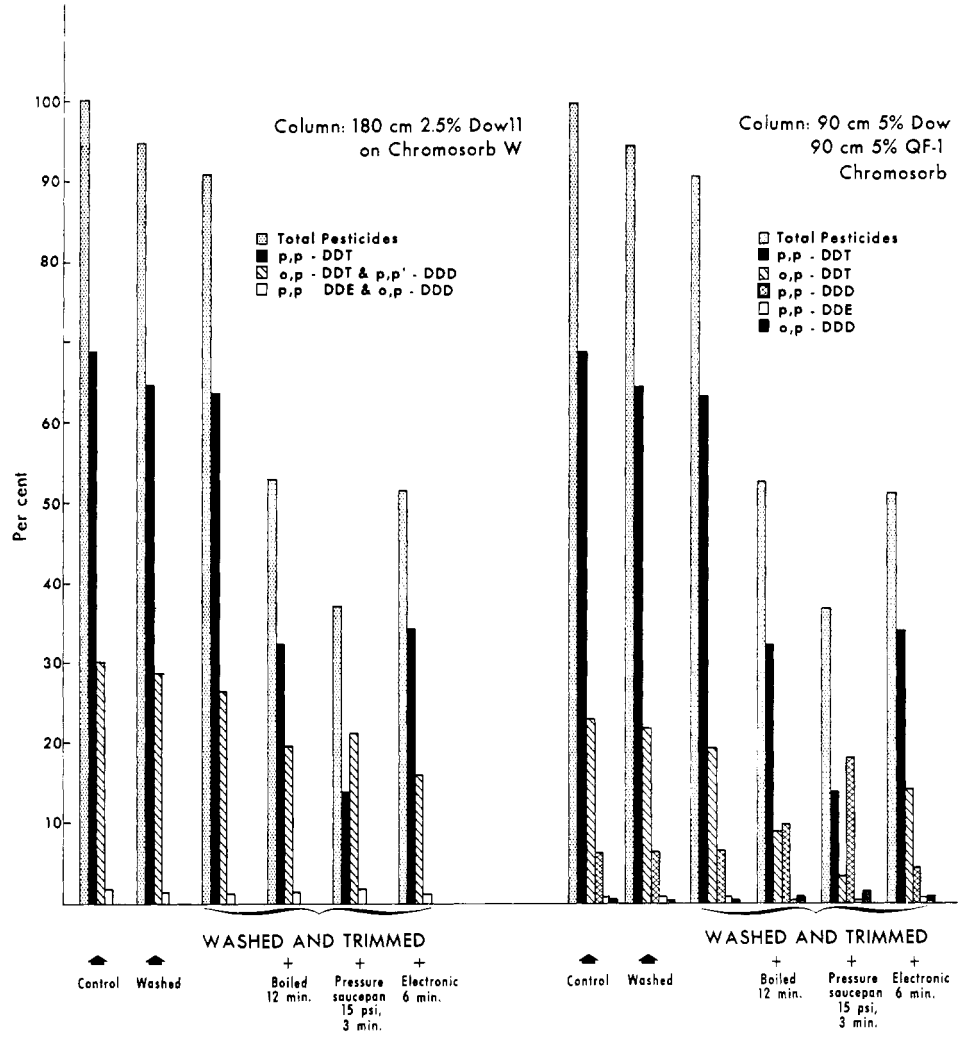

Figure 1. Effects of washing, trimming, and cooking on dissipation of chlorinated hydrocarbon pesticides in market samples of green beans ($n' = 3$)

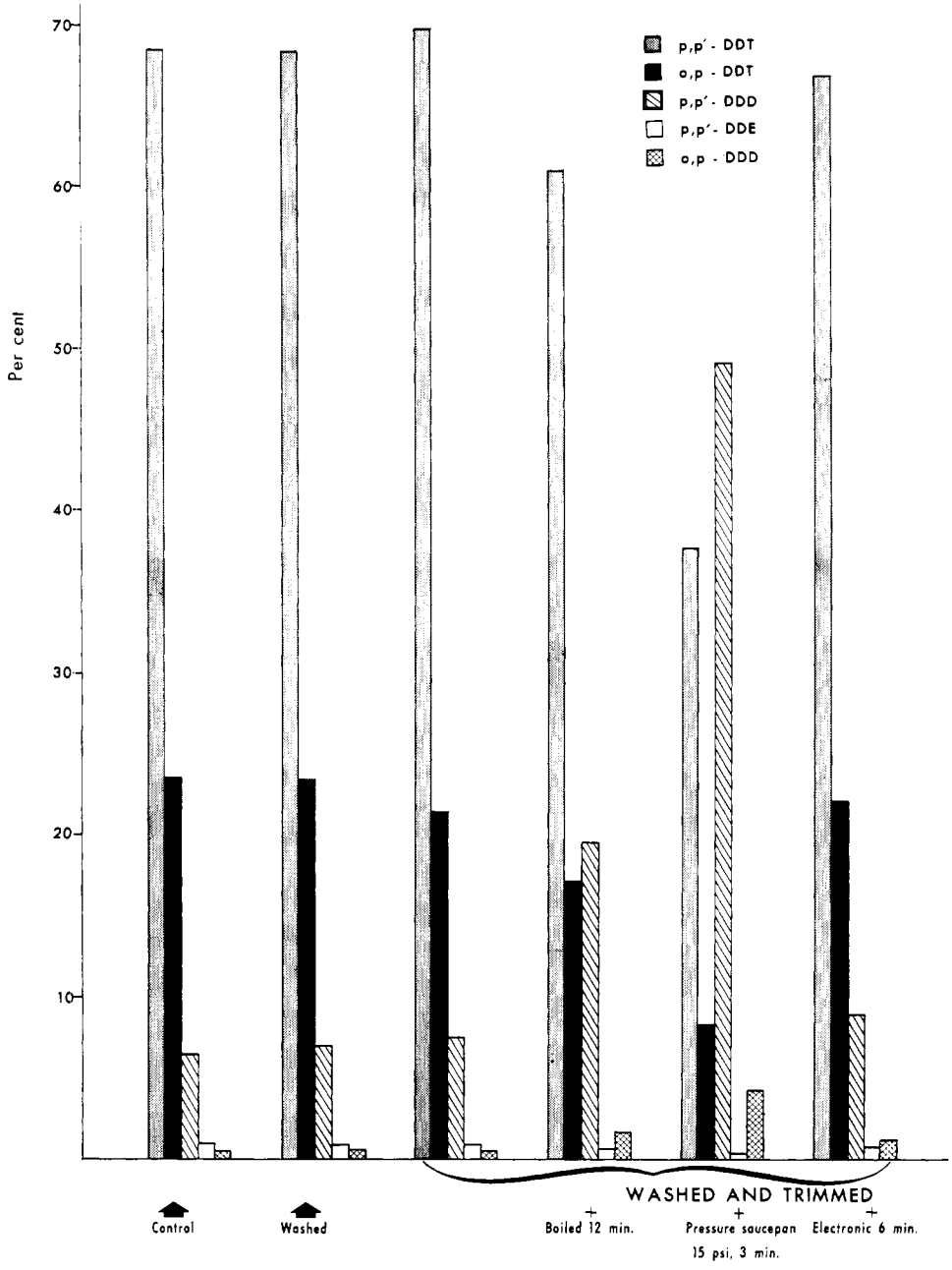

Figure 2. The relationship of one pesticide to another in green beans as affected by preparation procedures (total pesticides in each treatment represented as 100%)

trimming of green beans are relatively ineffective in reducing pesticide residues. Of course, surface treatments of this sort could not accomplish a major reduction in pesticide residue if the chemical were held in the inner tissue of the bean.

Effects of Cooking. The washing, trimming, and cooking of green beans reduced the mean total of pesticide residues by 47.1 to 62.9% (Figure 1). The greatest effect (62.9%) was observed in the pressure-cooked samples. This was the shortest cooking period, but cooking temperature was the highest, since at 15 p.s.i. the temperature would have been 250° F. The liquid of the electronically cooked sample began to boil within 3.5 minutes after exposure to microwaves was begun. Total time for the electronically cooked sample was one half that for boiling and total pesticide reduction was slightly greater (48.6%) than for the boiled beans (47.1%).

Only traces of pesticide were found in the liquid in which the beans were cooked. This is in agreement with the findings of Carlin, Hibbs, and Dahm (*2*), who stated that only traces of DDT remained in the liquid of canned beans and none in the brine in which beans were frozen and cooked. Therefore, the pesticide is deposited within the bean and not held on the surface.

Amounts of *p,p'*-DDT, *o,p*-DDT, and *p,p'*-DDE were always reduced by cooking. Apparently, *p,p'*-DDT was partially degraded to *p,p'*-DDD in the case of boil-

ing and especially in pressure-cooked green beans. The relationship of one pesticide to another as affected by preparation procedures is illustrated in Figure 2 where individual residues are represented as per cents of the total pesticide found in each treatment sample. There was a mean increase in *p,p'*-DDD of 11.8% over that of the control sample when pressure cooking was the method used, whereas a mean decrease of 54.7% in *p,p'*-DDT and 20.4% in *o,p*-DDT occurred with this method (Figure 1). This same trend was observed when individual standard pesticides (*p,p'*-DDT, *o,p*-DDT, and *p,p*-DDD) were boiled in water. Since an explanation of the losses and degradation entirely on a time-temperature relation was not possible, attention was turned to the influence of the composition material of the containers and a study of this factor has been initiated.

The observation of a possible container effect is supported by the recently published work of Carlin, Hibbs, and Dahm (*2*). In their study, container effect was mentioned in reference to the metal of the can in which beans were processed. The authors suggested that ferric ions from the can might have catalyzed decomposition of DDT. Previously, Ott and Gunther (*13*) suggested that reductive dechlorination or hydrogenolysis might occur owing to contact of DDT with the ferrous ions associated with a stainless steel chromatographic column. This hypothesis was supported by the work of Langlois, Liska, and Hill (*8*).

The conversion of DDT to DDD was illustrated by Kallman and Andrews (*6*). Their paper chromatograms of DDT labeled with C^{14} in the phenyl group showed that yeast has the ability to form DDD from DDT. Also, Langlois, Liska, and Hill (*8*) observed that sterilization of milk caused a change in *p,p'*-DDT residue to *p,p*-DDD. The degradation of DDT to DDE, DDD, and DDDE was confirmed by Ott and Gunther (*13*) by recycling a starting sample of pure DDT through a commercial chromatograph.

Acknowledgment

The authors appreciate the laboratory assistance of Ellis W. Brunton and Kay Gonnerman, graduate students.

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Received for review August 22, 1966. Accepted December 15, 1966. Contribution from the Missouri Agricultural Experiment Station. Journal Series No. 4075.