Removal of Gardona from Fruit by Commercial Preparative Methods

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Cherries, peaches, and pears were treated with Gardona [2-chloro-1-(2,4,5-trichlorophenyl)vinyl dimethyl phosphate] at recommended dosages and double the recommended dosage. The harvested fruit was processed using commercial processing methods. Gardona residues were determined on samples withdrawn at appropriate points in the processing. Sprays of Gardona at recommended dosages and spray schedules left residues of 4.3 (cherries) to 6.5 (peaches) ppm on raw fruit. Weathered Gardona residue contained a larger proportion of *trans* (low melting isomer) to *cis* (high melting) isomer than fresh residues. A canning process which did not include peeling (cherries) removed 95% of the Gardona residue. When hand peeling was included in the canning process (pears) 98.6% of the residue was removed. A lye peeling process (peaches) removed in excess of 99% of the Gardona residue.

Investigations of pesticide removal from crops by commercial and preparative processes were reviewed by Fahey *et al.* (1969) in their report of a study of the removal of Gardona and Azodrin from vegetable crops by commercial preparative methods. In 1969 a study of Gardona [2-chloro-1-(2,4,5-trichlorophenyl) vinyl dimethyl phosphate] residues in cherries, peaches, and pears was undertaken. This study included the magnitude of residues from normal spray applications, those from excessive sprays, and the effect of commercial preparative processes in the removal of these residues.

EXPERIMENTAL PLOTS AND SPRAY TREATMENTS

Spray treatments were applied with ground sprayers using single nozzle spray guns. Spray suspensions were prepared from a wettable powder formulation containing 75% Gardona. The spray dosages are expressed in lb of active insecticide per 100 gal of spray. The spray dosage on a per acre basis can be calculated from the rate per 100 gal, number of gal per tree, and number of trees per acre.

Cherries. Twenty Montmorenci cherry trees in the Tioga orchard at Monticello, Ind., were divided into five four-tree plots. One plot, separated from the other trees by two buffer rows, was left unsprayed and used as a control. Two plots were sprayed with Gardona at the rate of 0.4 lb per 100 gal and two plots were sprayed at the rate of 0.8 lb per 100 gal on June 23 and 28. On July 1 (3 days after spraying) cherry samples were collected from the control plot and from one of the plots treated with each spray dosage. On July 1, the two remaining plots were sprayed a third time at their respective dosages. On July 2, these two plots were sampled for study.

Peaches. Twenty peach trees in the Purdue University Horticulture Research Farm (1 mile west of Lafayette, Ind.) were divided into five four-tree plots. One plot, separated from the other trees by four buffer rows, was left unsprayed and used as a control. Two plots were sprayed with Gardona at the rate of 0.75 lb per 100 gal and two plots were sprayed at the rate of 1.5 lb per 100 gal on July 21, Aug 4 and 18. On Aug 25, samples were collected from the untreated and two of the treated plots (one at each spray level). The remaining plots (two) then received a final spray at their respective dosages and were sampled as soon as the spray had dried.

Pears. Twelve pear trees in the Purdue University Horticulture Research Farm were divided into three four-tree plots. One plot, about 200 ft from the other trees, was left unsprayed and used as a control. One plot was sprayed with Gardona at the rate of 0.75 lb per 100 gal and one plot at the rate of 1.5 lb per 100 gal on July 28, Aug 11 and 25, and Sept 8. On Sept 15, samples of pears were collected from the control plot and two treated plots. Heavy rains occurred on Sept 16 and 17, preventing immediate application of a final spray. On Sept 18, the plots received a final spray and were sampled as soon as that spray had dried.

SAMPLE PREPARATION

Cherries. Four gallons of cherries from each of four replicates (trees) of each treatment were selected for analysis. After picking, the sample fruit from each replicate was mixed and two 1-qt subsamples were taken for residue analysis (raw cherries). Two 500-g samples were placed in 0.5% sodium bisulfite solution (brined) and the remaining cherries were "plumped" in cool running water for 18 hr.

The brined cherries were set aside for analysis for approximately 90 days. After 90 days the cherries were placed in cold running water for 18 hr and washed twice in hot (90° C) water.

The "plumped" cherries were pitted and two 1-qt samples taken for analysis. Two 500-g lots were mixed with 100 g of sugar, placed in polyethylene bags, and frozen. In addition, three No. 303 cans were filled with the plumped-pitted cherries, covered with hot 88° C water and exhausted at 76.5° C. After sealing, the cans were processed at 100° C for 27 min.

Peaches. Samples of 1 bu were collected at random from each of four replicates (trees) of each treatment. After picking, a 10-fruit sample of each replicate was taken for analysis of residues on raw peaches. The remaining fruit was halved and the pits removed. The peach halves were warmed to 38° C in water and then placed in 3% lye (sodium hydroxide) solution at 82.5° C for 35 sec. The halves were then rinsed in cold water to remove the alkali and skin.

Samples of approximately 2 lb of peeled peach halves were taken for residue analysis. Three No. 303 cans were filled with halves (from each replicate), covered with sugar solution (20° Brix) at 82.5° C, and exhausted for 6 min at 93° C. The cans were sealed and heated for 20 min at 100° C.

Pears. Samples of 1 bu of pears were collected at random from each replicate of each treatment. Fifteen raw fruit were taken from each replicate for residue analysis. The remaining fruit was stored at 1° C until Oct 13 (28 days) and then trans-

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Table I. Recovery of Gardona Added to Fruit

Fruit	Stage of preparation	Gardona[a] Added μg	Added ppm	Found μg	% Recovered
Cherries					
	Raw	600	15.0	612	102.0
	Raw	200	5.0	206	103.0
	Washed	4	0.1	3.73	93.0
	Washed	40	1.0	39.4	98.5
	Canned	20	0.5	17.1	85.5
	Canned	10	0.25	8.3	83.0
	Canned	4	0.1	3.95	98.7
Peaches					
	Raw	600	15.0	584	97.3
	Raw	200	5.0	206	103.0
	Peeled	4	0.1	3.58	89.6
	Peeled	1	0.025	0.84	84.0
	Peeled	0.4	0.01	0.33	83.0
	Canned	1	0.025	0.978	97.8
	Canned	0.4	0.01	0.4	100.0
Pears					
	Raw	400	10.0	332	83.0
	Raw	200	5.0	195.4	97.7
	Raw	4	0.1	4.0	100.0
	Ripened	4	0.1	3.38	84.6
	Peeled	10	0.25	8.4	84.0
	Canned	4	0.1	3.85	96.4
	Canned	0.4	0.01	0.37	92.0

[a] Mean of two observations.

ferred to a ripening room at 24° C for 8 days. Samples of ripened pears were taken for analysis. The ripened fruit was hand peeled and about 500 g taken for analysis. Three No. 303 cans were filled with peeled pears from each replicate, covered with water at 88° C, and exhausted for 6 min at 94° C. The cans were sealed and heated for 20 min at 100° C.

ANALYSIS

Samples for analysis were taken from each of four replicates of each treatment. All fruit was blended for 3 min to give a uniform sample for analysis. Prior to blending, raw and brined cherries were pitted, raw peaches were quartered and opposite quarters blended, and the raw pears were chopped in a Hobart Mill. Forty grams of blended fruit was weighed into a 250-ml Erlenmeyer flask, 100 ml (80 g) of acetonitrile added, and shaken for 15 min. The sample was filtered, and 60 ml of the acetonitrile solution was placed in a separatory funnel with 290 ml of water and extracted three times with 100-ml volumes of hexane. The hexane extracts were combined and dried over anhydrous sodium sulfate. The sodium sulfate was removed and the hexane residue solution evaporated (rotary evaporator) under vacuum to about 10 ml.

A 20 mm column containing, bottom to top, 3 g sodium sulfate, 5 g 1 to 4 celite-Florisil containing 10% water, and 3 g sodium sulfate was washed with 50 ml hexane. The sample was added to the column and the flask rinsed with 20 ml of hexane. The column was eluted with 10 ml 25% ether-hexane and this eluate discarded. A clean flask was placed under the column and the Gardona residue recovered in 60 ml of 25% ether-hexane. The ether-hexane solvent was evaporated in a rotary evaporator and the volume adjusted with hexane for glc analysis.

Glc analysis was with a model 1200 Aerograph equipped with an EC detector (250 mc tritium). The following parameters were employed:

Column:	3 ft × 1/8 in. glass, containing 1 + 1 2% Reoplex 400 and 5% QF-1 on Gas chrom Q	
Temperatures:	Injector	220° C
	Column	200° C
	Detector	220° C
Carrier gas:	Nitrogen, 50 ml per min	

The *trans* (low melting) isomer of Gardona appeared as a shoulder on the peak resulting from the *cis* (high melting)

Table II. Ratio of *Cis* to *Trans* Isomers of Gardona in Residues on Fruit, 1969

Fruit	Stage of preparation	Ratio: *Cis*/*Trans* Isomers in Gardona Residue[a] Normal Schedule[b] X	Normal Schedule[b] 2X	Extra Spray[c] X	Extra Spray[c] 2X
Cherries					
	Raw	13.0	12.1	11.2	9.1
	Canned	5.7	5.4	4.7	4.4
Peaches					
	Raw	5.7	8.6	12.3	13.3
Pears					
	Raw	8.8	7.7	17.1	17.4
	Ripened	5.2	7.5	13.9	9.8

[a] Mean of four observations. [b] Cherries received two sprays at rates of 0.4 (X) and 0.8 (2X) lb per 100 gal, second spray 3 days before picking. Peaches (three sprays) and pears (four sprays) sprayed at rates of 0.75 (X) and 1.5 (2X) lb per 100 gal: last spray 7 days before picking. [c] Spray treatments same as given above (b) except that one extra spray was applied. Cherries received extra spray 24 hr before picking. Peaches and pears received extra spray 4 hr before picking.

Table III. Gardona Residues Found in Cherries, Peaches, and Pears

Fruit	Stage of preparation	PPM of Gardona[a]				Reduction[b] of Residue %
		Normal Sprays[c]		Extra Spray[d]		
		X	2X	X	2X	
Cherries						
	Raw	4.30	9.40	7.96	18.50	
	Plumped and pitted	0.95	2.11	1.85	3.31	78.6
	Frozen	0.81	1.88	1.52	3.71	80.49
	Canned	0.21	0.51	0.41	0.80	95.06
	Brined	...	...	0.15	0.33	98.2
Peaches						
	Raw	6.53	15.01	10.54	27.18	
	Peeled	0.04	0.05	0.04	0.05	99.7
	Canned	0.02	0.02	0.02	0.02	99.9
Pears						
	Raw	5.58	10.40	5.62	14.08	
	Ripened	3.48	9.36	3.89	9.15	28.4
	Peeled	0.22	0.62	0.24	0.57	95.5
	Canned	0.07	0.20	0.07	0.22	98.6

[a] Mean of analysis of four replicates. [b] Mean of four treatments. [c] Cherries received two sprays at rates of 0.4 (X) and 0.8 (2X) lb per 100 gal, second spray 3 days before picking. Peaches (three sprays) and pears (four sprays) sprayed at rates of 0.75 (X) and 1.5 (2X) lb per 100 gal: last spray 7 days before picking. [d] Spray treatments same as given above (c) except that one extra spray was applied. Cherries received extra spray 24 hr before picking; peaches and pears received extra spray 4 hr before picking.

isomer of Gardona under the conditions given above. Lowering the column temperature to 180° C separated the two isomers of Gardona. Because of the small quantity of the *trans* isomer of Gardona present, compared to the quantity of the *cis* isomer, it was not possible to analyze for both isomers with a single sample injection.

RESULTS

Table I shows the recovery of Gardona added to control samples at different stages in processing. Large residue of 200 to 600 μg per sample, as frequently found on raw test samples, may show recoveries in excess of 100%. This results from the necessity of diluting the residue solutions to attain the residue level of the analytical method and the resultant multiplication of small errors in quantitation. The recovery of Gardona added to samples, analyzed by the techniques given above, varied from 83 to 103%.

The two isomers of Gardona, *cis* (high melting) and *trans* (low melting), were found in samples of raw fruit and fruit that was not peeled in processing. Table II gives the ratio *cis* isomer/*trans* isomer in Gardona residues in cherries (raw and canned) and unpeeled peaches and pears. The ratio of *cis*/*trans* isomer in Gardona residues on cherries do not differ appreciably within a stage of preparation, regardless of the spray treatment. A possible explanation is that there was little difference in the age of residue (weathering period); one pair of treatments received a final spray 1 day before picking, and the other pair of treatments were sprayed 3 days before picking. The cherry canning process reduced the ratio of the *cis* isomer to *trans* isomer in Gardona residues, indicating that much of the *cis* isomer was removed or converted to *trans* isomer.

Gardona residues on peaches had a *cis*/*trans* ratio of 5.7 to 8.6 when three sprays were applied, and the final spray was 7 days before picking. When an additional spray was applied, 4 hr before picking, the ratio of *cis* to *trans* isomer increased to 12.3 and 13.3, indicating that there was an increase in the *trans* isomer in the aged residue. A similar relationship is shown with pears. The weathered Gardona residue (final spray 7 days before picking) contained 7.7 to 8.8 times as much *cis* as *trans* isomer and the fresh residue contained 17.1 to 17.4 times as much *cis* as *trans* isomer. Aging of the residue on pears, in the ripening room, decreased the ratio of *cis* to *trans* isomer.

Table III shows the results of analysis of Gardona residues in processed cherries, peaches, and pears. The Gardona residue on cherries sprayed twice with 0.4 lb Gardona per 100 gal, with a final spray 3 days before harvest, was 4.3 ppm. When the spray dosage was doubled or an extra spray applied and the fruit sampled 24 hr after treatment, there was a proportional increase in Gardona residue. After plumping and pitting, the cherries contained 0.95 to 3.31 ppm of Gardona, a reduction of 78% of the raw fruit residue. Freezing had no additional effect on the residue. Canned cherries contained 0.21 to 0.80 ppm of Gardona, a residue reduction of 95% by the unit canning process. Brined cherries (maximum residue only) contained 0.15 to 0.33 ppm of Gardona, a residue reduction of 98%.

Raw peaches contained 6.53 to 27.18 ppm of Gardona when harvested. The lye peeling process removed 99.7% of the residue present at harvest. The residues in canned peaches were only 0.02 ppm. Pears at harvest contained 5.58 to 14.08 ppm of Gardona. Afer being held in a ripening room for 33 days, the residue decreased to 3.48 and 9.36 ppm, a loss of 28%. Hand peeling reduced the residue in the pears by 95.5%. The residue remaining may have been transferred to the flesh from the pear surface during peeling. Canned pears contained 0.07 to 0.22 ppm of Gardona, a loss of 98.6% of the harvest residue.

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