Residues of Iprodione in Fresh and Canned Peaches after Pre- and Postharvest Treatment

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Iprodione at an application rate of 0.05% active ingredient (ai) was applied once on clingstone peach trees. The fruits were collected 15 days postapplication and were subjected to washing or postharvest treatment (dipping in a 0.05% ai solution), cold storage, chemical peeling, and canning. Samples from each situation were analyzed to determine the residue concentration. The mean concentration in field-treated fruits was 1.23 mg/kg, while in washed fruits it fell to 0.61 mg/kg. Postharvest treatment resulted in a residue concentration of 3.04–5.05 mg/kg. Cold storage for up to 20 days did not affect residues. Chemical peeling removed 82.5–95% of the residues. In canned peaches the concentration of iprodione was low (0.01–0.10 mg/kg).

Keywords: *Iprodione; Rovral; fungicides; peaches; residues; canned fruit*

INTRODUCTION

Clingstone peaches destined to be canned with the addition of sugar syrup are usually stored for several days in cold rooms so that they can be processed gradually, according to the capacities of canning factories. During storage, fruits suffer from postharvest decay due to the fungi *Monilla cinerea*, *Botrytis cinerea*, and *Rhizopus stolonifer*. Trials have been carried out in the field (preharvest application) and in the laboratory (postharvest application) to study the efficacy of various fungicides against the above pathogens. Within the framework of this project the residues remaining on and in the fruits after treatment and handling were determined. This paper reports the results on the residues of one fungicide tested, dicarboximide iprodione. The available literature gives some information on the residues of iprodione in cold-stored fruits, but it refers to grapes (Scrano et al., 1991) and kiwi fruit (Moras and Nicolas, 1987). Some residue data from supervised trials are summarized in the evaluations of the FAO/WHO Joint Meeting on Pesticide Residues (JMPR) (FAO/WHO, 1978, 1981).

MATERIALS AND METHODS

Chemicals. All solvents and chromatographic adsorbents were of high purity and suitable for pesticide residue analysis. Iprodione standard of 99.4% purity was kindly provided by Rhone Poulenc Agrochimie.

Preharvest Fungicide Application. The site for this project was located in the north of Greece, where the bulk of clingstone peaches are produced and where most of the canning factories are situated. Four experimental plots were established in a 12–13-year-old peach grove of cultivar Andros (clingstone variety) belonging to the Pomology Institute of the National Agricultural Research Foundation. Two plots were treated with iprodione, and two received no treatment (control plots). Each plot had four replicates of three trees each. Iprodione was applied by using common orchard spraying equipment. One application was made, on August 24, using the commercial preparation Rovral 50% WP of Rhone Poulenc Agrochimie at an application rate of 0.05% active ingredient (ai). The harvest was made 15 days postapplication. The fruits of each tree were collected manually and packed separately into large plastic boxes, of the type commonly used for the packing of clingstone peaches. From those fruits, 12 samples (three from each plot) of 18 fruits each (6 fruits from each tree) were collected in accordance with FAO/WHO recommendations (FAO/WHO Codex Alimentarius Commission, 1987). These samples were transported to the laboratory for residue analysis. The remaining fruits were forwarded to the Laboratory of Technology of Agricultural Products and were subjected to postharvest handling and treatment.

Postharvest Handling and Treatment. Some of the fruits from each of the four field plots were dipped for 3 min into tap water. These fruits were used as control samples by the mycologists for observations concerning the biological activity of the fungicide after postharvest use. They also were analyzed for iprodione to ascertain the effect of this type of washing on the level of residues. To that end nine samples were collected from the washed fruits after drying under an air stream at 28 °C. These samples again consisted of 18 fruits each and represented the two plots field-treated with iprodione and the control plot. The remaining fruits were dipped for 3 min in an aqueous suspension of Rovral at a concentration of 0.05% ai (500 ppm). Four samples of 15 fruits each representing the four field plots were collected after drying for residue analysis. The remaining fruits were stored in a cold room of 90–95% relative humidity at a temperature of 4 °C. After 15 days of storage, the fruits were canned by specialists of the Institute of Technology of Agricultural Products using a simulated industrial technique. The stones were removed with a knife, and the peaches were peeled by alkali and heating (2% NaOH at 95 °C for 50 s). Samples of peeled peach parts, weighing ca. 1 kg each, were collected. The peeled fruits were canned with the addition of sugar syrup, and the cans were stored in the laboratory. Samples of cans (two for each replicate of two cans each) were randomly taken after 8 months of storage in the laboratory and analyzed for iprodione residues. The contents of cans (fruit plus syrup) were homogenized, and the analysis was carried out on the homogenized material.

In the following year, a small-scale trial was conducted to assess the effect of cold storage on iprodione residues. Peaches collected from trees not treated at all with iprodione were dipped into an aqueous suspension of Rovral of the same concentration as that of the previous year. Three samples of 15 fruits each were collected after drying, and the remaining fruits were stored in a cold room under the same conditions as those of the previous year. Three samples of 15 fruits each were collected after 15 days of storage and three similar samples after 20 days of storage and analyzed for iprodione.

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Table 1. Residues of Iprodione on and in Clingstone Peaches after Preharvest Treatment and Postharvest Handling

	concentration (mg/kg)					
	14 days postapplication		after washing[b]			
field plots[a]	in the pulp[c]	in the whole fruit[d]	in the pulp[c]	in the whole fruit[d]	in pulp peeled after storage[e]	in cans[f]
A	1.23 ± 0.10[g]	1.16 ± 0.11	0.53 ± 0.12[g]	0.50 ± 0.13	0.10[h]	0.02[i]
B	1.37 ± 0.07[g]	1.29 ± 0.08	0.70 ± 0.09[g]	0.66 ± 0.11	0.10[h]	0.01[i]
av ± SD	1.30 ± 0.12	1.23 ± 0.11	0.61 ± 0.14	0.57 ± 0.13	0.10	0.015
C	NA[j]	NA	NA	NA	NA	NA
D	0.61 ± 0.12[g]	0.58 ± 0.10	0.42 ± 0.10[g]	0.39 ± 0.12	0.05[h]	<0.01

[a] A, B = one preharvest treatment in the field with iprodione at 0.05%. C, D = no treatment (control plots). [b] Washing by dipping for 3 min in tap water. [c] Pulp = flesh + skin. [d] Pulp + stone. [e] Storage for 15 days at 4 °C, 90–95% relative humidity, chemical peeling by alkali (2% NaOH) at 95 °C for 50 s. [f] Analyzed after 8 months of storage in the laboratory. [g] Mean ± standard deviation of three samples of 18 fruits each. [h] One representative sample weighing ≈ 1 kg. [i] Mean of two samples of two cans each. [j] NA, not analyzed.

Analysis of Iprodione in Peaches and Cans. Before analysis, the weight of each sample was taken. The stones were removed with a knife and their weights noted. In this way it was possible to calculate the concentration in the whole fruit (pulp plus stone) from the concentration determined in the pulp (flesh plus peel) of the fruits. This was necessary because the maximum residue limits set by international organizations apply to whole fruits (FAO/WHO Codex Alimentarius Commission, 1986; EEC, 1990), not to only the edible parts. (In the text the term pulp means the unpeeled flesh of the peaches, unless otherwise stated.) Fruits were quartered, and opposite quarters from each peach were collected and homogenized. Samples prepared in this way were kept in a freezer (−20 °C) until analysis. The method used for the determination of iprodione residues was basically that of Laurent and Buys, described by Lacroix et al. (1980), with some minor modifications concerning the analytical sample size (20 g instead of 100–200 g) and the volumes of solvents used (proportionally reduced). According to this method, the analytical sample is extracted in an Omni-Mixer with acetone in the presence of Hyflo Super Cel. The extract is filtered under vacuum through a Büchner funnel fitted with a Whatman paper filter. The solvent is removed by rotary evaporation, and the remaining aqueous extract is partitioned with dichloromethane. The organic phase is concentrated, and cleanup takes place on a Florisil 60–100 mesh (activated at 180 °C and deactivated with 2% water) column, using dichloromethane as the eluting solvent.

Recovery Efficiency Studies. Known quantities of iprodione dissolved in acetone were added to 20 g samples previously tested to be iprodione free. As discussed below, the control plot samples were found to be contaminated with iprodione, which meant that they could not be used for recovery checking. Thus, fruits from another field were used, fortified at the 0.02, 0.05, 0.5, and 5 mg/kg levels. Three samples for each fortification level were extracted as above and analyzed.

Gas Chromatographic Conditions. A Varian Model 3700 gas chromatograph equipped with a ^{63}Ni electron capture detector was used: column, borosilicate glass of 0.65 m length × 2 mm × 1/4 in. i.d. packed with 10% OV-101 on Chrom WHP 80/100 treated with 6% Carbowax M; injector temperature, 210 °C; detector temperature, 250 °C; oven temperature, 210 °C; carrier gas and flow, nitrogen at 30 mL/min. The column length was relatively short because, during the initial evaluation of the method, it was noted that iprodione decomposes and gives two peaks if longer (>1 m) columns are used. The extracts, and especially those from postharvest treated fruits, were greatly diluted, because the detector response was linear only over the range 0.1–1.0 ng. The concentration of 0.01 mg/kg was estimated to be a reliable limit of determination. Under these working conditions the retention time of iprodione was 2.04 min. The analysis of extracts of canned peaches was impeded by the presence of an interference peak at approximately the same retention time as iprodione. This problem was overcome by using a column (1 m × 2 mm) of different polarity (2% DEGS on Chrom WHP 80/100 mesh) under the following conditions: injector temperature, 230 °C; detector temperature, 250 °C; oven temperature, 200 °C; carrier gas and flow, nitrogen at 20 mL/min. In this way satisfactory resolution was achieved and the limit of determination was again 0.01 mg/kg. However, the retention time was much longer (≈30 min). All analyses were carried out in duplicate.

RESULTS AND DISCUSSION

Recovery Efficiency. Recoveries at the levels tested varied from 90 to 110%. The mean recovery of 12 analyses was 98%, and the coefficient of variation was 7. The selection of suitable columns, namely the use of a support fully deactivated with Carbowax, permitted a low limit of determination to be achieved.

Residues after Preharvest Treatment. The residues determined on and in peaches harvested 15 days postapplication ranged between 1.10 and 1.48 mg/kg in the pulp (mean concentration of the two iprodione-treated plots 1.30 mg/kg) and between 1.04 and 1.39 mg/kg in the whole fruit (pulp plus stone), average 1.23 mg/kg (Table 1). Control samples contained on the average 0.61 mg/kg iprodione in the fleash (0.58 mg/kg in the whole fruit), due to unavoidable contamination by drifting. Thus, as already mentioned, these control samples were not used for the preparation of fortified samples for the assessment of the analytical method. The residues resulting from the preharvest treatment were lower than the limit of 10 mg/kg set by Codex Alimentarious as the maximum admissible concentration (FAO/WHO, 1994) and also lower than the European Union's maximum residue level (MRL) (5 mg/kg) (EEC, 1993). However, Codex limits are set intentionally high to accommodate residues resulting from postharvest use, given that the recently (1992) established Acceptable Daily Intake for Man (0.2 mg/kg of body weight) allows for such maximum permissible concentrations (FAO/WHO, 1993). The MRLs refer to iprodione only, because, from the metabolism data submitted, the FAO/WHO and European Union experts agreed that the residue definition should be restricted to the parent compound only.

Residues in Washed Fruits. As shown in Table 1, the washing of fruits, in the way described above, removed a large part of the residues, estimated on the average to be approximately 50% of the residues present before washing. The mean concentration in washed samples from field-treated plots was 0.61 mg/kg in the pulp compared to 1.30 mg/kg in unwashed samples.

Residues after Postharvest Treatment. The fruits pre- and postharvest treated contained 5.35 mg/kg

Table 2. Residues of Iprodione on and in Clingstone Peaches after Pre- and Postharvest Treatment and Canning

	concentration (mg/kg)			
	after postharvest treatment[b] (time 0)		in pulp	
field plots[a]	in the pulp[c]	in the whole fruit[d]	peeled after storage[e]	in cans[f]
A	5.30[g]	5.00	0.30[h]	0.07[i]
B	5.40[g]	5.13	0.40[h]	0.10[i]
av	5.35	5.06	0.35	0.08
C	3.20[g]	3.04	NA[j]	NA
D	5.20[g]	4.94	0.32[h]	0.10[i]

[a] A, B = one preharvest treatment in the field with iprodione at 0.05%. C, D = no preharvest treatment (control plots). [b] Dipping for 3 min in a suspension of 500 ppm iprodione. [c] Pulp = flesh + skin. [d] Pulp + stone. [e] Storage for 15 days at 4 °C, 90–95% relative humidity, chemical peeling by alkali (2% NaOH) at 95 °C for 50 s. [f] Analyzed after 8 months of storage in the laboratory. [g] 15 fruits representative of the plot analyzed as a sample. [h] One representative sample weighing ≈ 1 kg. [i] Mean of two samples of two cans each. [j] NA, not analyzed.

Table 3. Residues[a] of Iprodione on and in Pulp of Clinstone Peaches after Postharvest Treatment[b] and Cold Storage[c]

time 0	time 15 days	time 20 days
3.70 ± 0.35	3.74 ± 0.25	3.70 ± 0.17

[a] Milligrams per kilogram. Mean of three samples of 15 fruits each. [b] Dipping for 3 min in a suspension of 500 ppm iprodione. [c] 4 °C, 90–95% relative humidity.

iprodione on the average in the pulp (5.06 mg/kg in the whole fruits). Fruits treated only postharvest contained 3.20–5.20 mg/kg in the pulp (3.04–4.94 mg/kg in the whole fruits) (Table 2). The concentrations detected were lower than the Codex Alimentarius MRLs but slightly higher in some cases than the MRLs of the European Union.

Residues in Cold-Stored Fruits. Residues on and in the pulp of fruits after cold storage for 15 or 20 days were not different from those determined before storage. Residues in the pulp of fruits before storage ranged from 3.35 to 4.05 mg/kg (mean concentration 3.70 mg/kg), while after cold storage for 15 days they ranged from 3.50 to 4.00 mg/kg (mean concentration 3.74). After 20 days of storage, they ranged from 3.60 to 3.90 mg/kg (mean concentration 3.70 mg/kg) (Table 3). The above results indicate that no reduction of iprodione residues occurs during cold storage for this time period. The same conclusion was reached by Scrano et al. (1991) for iprodione on grapes field-treated and cold-stored for 20 days.

Residues in Peeled Pulp. As shown in Tables 1 and 2, considerable reduction of residues was observed after chemical peeling of the fruits. The percentage reduction ranged between 82.5% for field-treated fruits washed before peeling and 95% for pre- and postharvest-treated fruits. These results, supported by the results on the effect of washing on the magnitude of residues, show that most of the residue remains on the skin and that there is limited translocation of the fungicide into the interior of the fruit. Studies with unlabeled iprodione and with ^{14}C-phenyl-labeled products, carried out by the producer company and summarized by JMPR (FAO/WHO, 1978), showed that iprodione does not appreciably penetrate through the plant cuticle.

Residues in Cans. Canned fruits produced from fruits having received postharvest treatment contained higher residues of iprodione (0.07–0.10 mg/kg) than those in cans produced from fruits only field-treated (0.01–0.02 mg/kg). Control samples contained no detectable (<0.01 mg/kg) residues. Given that the total net weight of each can was ≈450 g and that of this 200–250 g (225 g on the average) was the weight of fruits and 190–250 g (220 g on the average) was the weight of syrup, a 50% reduction of the residue concentration was caused by dilution. When this dilution is taken into account, it is clear that the amount of iprodione in the homogenized can's content was smaller than the initial amount present in the peeled fruits, suggesting that metabolism of the compound took place. Data on the fate of iprodione during processing are lacking and were requested by the 1980 JMPR (FAO/WHO, 1981). However, according to information provided by the manufacturer of the product, the degradation of iprodione to its major metabolite, 1-[(3,5-dichlorophenyl)carbamoyl]-3-isopropylhydantoin (FAO/WHO, 1978), is accelerated by the presence of water and becomes more important under anaerobic conditions.

CONCLUSIONS

The analytical method used permitted reliable determination of iprodione residues higher than 0.01 mg/kg. Residues in fruits treated once in the field at the recommended application rate and collected 15 days postapplication were lower than FAO/WHO Codex Alimentarius and European Union MRLs. Residues in postharvest-treated fruits were lower than Codex Alimentarius MRLs. Washing of field-treated fruits removed a great part of the residue, while cold storage for up to 20 days did not affect the residue concentration. Chemical peeling reduced the residues considerably, and in canned peaches the fungicide was degraded, leading to low final concentrations after 8 months of storage.

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LITERATURE CITED

EEC. Council Direactive 90/642/EEC on the fixing of maximum levels for pesticide residues in and on certain products of plant origin, including fruit and vegetables. *Off. J. Eur. Communities* **1990**, *No. L 350*, 71–79.

EEC. Council Directive 93/58/EEC of 29 June 1993 amending Annex II to Directive 76/895/EEC relating to the fixing of maximum levels for pesticide residues in and on fruit and vegetables and the Annex to Directive 90/642/EEC relating to the fixing of maximum levels for pesticide residues in and on certain products of plant origin, including fruit and vegetables, and providing for the establishment of a first list of maximum levels. *Off. J. Eur. Communities* **1993**, *No. L 211*, 6–39.

FAO/WHO. *Pesticide Residues in Food, 1977 Evaluations*; FAO: Rome, 1978; pp 305–311.

FAO/WHO. *Pesticide Residues in Food, 1980 Evaluations*; FAO: Rome, 1981; p 254.

FAO/WHO. *Pesticide Residues in Food, 1992 Evaluations, Part 2, Toxicology*; FAO: Rome, 1993; pp 211–232.

FAO/WHO Codex Alimentarius Commission. Portion of commodities to which Codex Maximum Residue Limits apply and which is analyzed. CAC, Rome, 1986; Vol. XIII, 2 ed.

FAO/WHO Codex Alimentarius Commission. Report of the ad hoc working group on development of residue data and sampling. Alinorm 87/24A/appendix IV; FAO, Rome, 1987; pp 1–5.

FAO/WHO Codex Alimentarius Commission. Codex Committee on Pesticide Residues. Status of Codex Maximum Residue for pesticides in food and animal food. FAO, Rome, 1994; CX/PR 2-1994.

Lacroix, L.; Laurent, M.; Buys, M. Iprodione. In *Analytical methods for pesticides and plant growth regulators. Vol XI: Updated general techniques and additional pesticides*; 1980; pp 247–261.

Moras, P.; Nicolas, J. Kiwi storage: Influence of several postharvest factors and storage conditions on the shelf-life of the fruits. *Infos (Centre technique interprofessionnel des Fruits et Legumes)* **1987**, *35*, 25–30.

Scrano, L.; Faretra, F.; Cariddi, C.; Antonacci, E.; Bufo, S.; Evaluation of dicarboximide residues in cold-stored grapes exposed to field and post-harvest treatments. *Pestic. Sci.* **1991**, *31*, 37–44.

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