TECHNOLOGICAL PROCESSES AFFECTINGON REDUCTION OF DICOFOL RESIDUES ON STRAWBERRY AND CANTALOUPE

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ABSTRACT

The effect of both home preparations and some technological processes on dicofol residues applied on strawberry and cantaloupe were investigated using gas-liquid chromatography with electron capture detector (ECD). Data revealed that washing with tap water reduced 22.3% and 10.6% from dicofal residues found on strawberry fruits and 17.3% and 12.3% of residues on cantaloupe immediately after treatment and after 15 days of treatment. Adequate washing removed 34.2% and 29.5% of residues from strawberry and 32.1% and 28.6% from cantaloupe fruits immediately after treatment and after 15 days of treatment to be within the established maximum residue limits (MRLs) of Dicofol. Extraction of strawberry and cantaloupe juices reduced 22.3% and 34.9% of residues on strawberry and 35.8% and 50.4% on cantaloupe after treatment and after 15 days later, also peeling of cantaloupe fruits reduced 27.2% and 39.5% of residues at the same mentioned period. Pasteurization, sterilization of strawberry and cantaloupe juices and manufacturing of jam and compote from washed fruits minimized the dicofal residues to be lower than the MRLs to be safe for human consumption. Obtained data showed that freezing of experimental fruits has low effect on reduction of residues, but storage of preserved products for three months reduced the residue levels with a high percent to be very safe for public health without any serious side effect.

INTRODUCTION

Nowadays the number and amount of different agrochemicals and other environmental toxicants in our food are increasing. Pesticides as one of serious agrochemicals especially their remaining residues or metabolites, can find their way into the food chain from several sources. Without continues surveillance, some of those that persist in our food could endanger the public health. Man undoubtedly still would consume contaminated foods which contained various levels of different pesticide residues. Therefore, it is of great important to minimize such levels of these residues remaining on or in plant food to be within or below the acceptable daily intake and lower than the safety tolerance level for protecting the human health to avoid any hazardous effects. Most countries have introduced laws governing not only the use of pesticides, but also setting up limits for pesticides residues which

may be tolerated in food stuff. Therefore, regulatory agencies, both national and international are seeking to limit the human intake of pesticides residues throughout the consumption of food, have established systems of "tolerances" or Maximum Residue Limits (MRLs) in food (**Polen 1971, Trichilo and Schmitt, 1989**). It is of great important to make sure that at the time of food consumption, the residue levels of any agrochemicals should be within or below the established MRLs to avoid their hazardous effects on human beings and domestic animals (**Elkins, 1989, and Bessar *et al.* 1989, 1990 and 1994a**). Organo chlorine pesticides were almost prohibited from use in Egypt since 1980 according to their long persistence tendency to accumulate in fat tissues impact on the environment and hazards to human health. In spite of that certain organo chlorines still have restricted use to control harmful pests. Dicofol (Kelthane) is one of these compounds which have short persistence in comparison to others. However, it was found to be indispensable in controlling the red spider mites investing many vegetable and fruit crops. According to Environmental Protection Agency (EPA) dicofol considered as a carcinogenic pesticide which make it necessary for studying to know all the factors affecting its residue reduction.

The present work was achieved to study the effect of technological factors, also role of washing either with tap water or with detergent on reduction of dicofol residues on strawberry and cantaloupe and in their products after different period of treatment and after storage period for three months for preserved products. Strawberry and cantaloupe were chosen for this study because they produced and consumed throughout many countries, they have a short storing time after harvesting. Also the meeting of the Pesticide Residues Committee (PRC) 2002 revealed that strawberry contains dicofol residues.

MATERIALS AND METHODS

1. Treatment of Plant Foods.

At the farm near Rashid area Behira 4 pots from strawberry plants (*Fragaria ananassia Duch* Var. *Camaroza*) were randomized selected, labeled and sprayed with dicofol 18.5% EC at the rate of one liter/400L water/Fadden. At the same area 4 pots from cantaloupe (Musk melon) plants (*Cucumis melo* Var. *reticulates*) were labeled and treated with the same previous rate of dicofol 18.5% EC. Another one pot from both strawberry and cantaloupe plants were kept without treatment to serve as control checks. Random representative treated samples of strawberry and cantaloupe fruits were collected after one hour of application (represent the initial deposit of dicofol), after 7 days and after 15 days of treatment for residues analysis.

2. Home Preparations and Processing.

Control and treated samples of strawberry and cantaloupe collected at zero time, 7 and 15 days post application were washed with tap water only and with 0.5% Pril detergent and rinsed with tap water again, washed fruits with tap water of strawberry were processed using pasteurization, sterilization of juice and manufacturing of jam, washed cantaloupe fruits were peeled and processed using pasteurization, sterilization of juice and manufacturing of compate and cantaloupe jam. Washed strawberry (500 g) and peeled, cutted cantaloupe (500 g) were put in polyethylene bags and frozen at -5°C. Extraction of strawberry and cantaloupe juices, pasteurization of juices at 85°C for 1 min, sterilization at 100°C for 20 min, manufacturing of compate and jam were done according to **Saad *et al.* (1989)**.

3. Analysis of Dicofol Residues.

3-1. Reagents: Dicofol (2,2,2 trichloro-1, 1-bis (4-chlorophenyl)-trichloromethyl benzenemethanol) technical grade material is specified to be 99.9% pure acetone pure, benzene pure, dichloromethane (Merck No. 0650), n-hexane (Merck No. 9688). Elution mixture (10:2:2) dichloromethane-benzene-acetone, charcoal pure, (AR), (No. 2186), Cillite 545 (C. Roth Karlsruhe), silica gel 0.05-0.2 mm (Merck No. 7734). Sodium chloride (AR) and anhydrous sodium sulphate.

3-2. Equipment: A Hewlett-Packard model 5730/A gas-liquid chromatograph equipped with a liner Ni^{63} electron capture detector (18713/A) and 2 cm stainless steel transfer line from the column to the detector was used for dicofol assays. A 1.5 mm (i.d.) 1.8m glass column packed with 1.95% OB-17 on 100-120 mesh Chromosorb was used under the following conditions: Carrier gas 5% methane in argon at 60 cm^3 min^{-1} flow, injection port 250°C, oven temperature 270°C, detector temperature 3000°C, starting temperature 200°C, speed of heating 2°C min^{-1} and initial holding time 2 min. Injection of 1 µl using 10-µ Hamilton syringe equipped with change adapter.

3-3. Extraction and purification: Dicofol residues are extracted from treated fruits (50 g sample) with 200 ml acetone and the extract filtered. Then, 50 ml of the filtrate were diluted with 200 cm^3 of water and dichloromethane (1:1) for partitioning dicofol residues. The extract was dried with anhydrous sodium sulfate and the dichloromethane layer was kept. The dichloromethane layer was removed by charcoal-silica gel purification column with the elution mixture (dichloromethane-benzene-acetone = 10:2:2). Then, the solvent mixture was evaporated and dicofol

residues were dissolved again in 10 ml of n-hexane and diluted 6-times in n-hexane for chromatographic determination (**Dogheim *et al.*, 1993**).

3-4. Recovery value of dicofol: The efficiency of the gas liquid chromatographic method for residue determination of dicofol was achieved by adding 100 µg dicofol per g sample to a portion of untreated fruit sample which then was put through the extraction, purification and residual determination processes as followed in the used methods. Then, the recovery value was calculated as follows:

$$\text{Recovery value} = \frac{\text{µg Dicofol per g sample found}}{\text{µg Dicofol per g sample added}} \times 100$$

The average recovery values for dicofol in strawberry were 89% and 93% and these values were used to correct all the obtained results of dicofol.

RESULTS AND DISCUSSIONS

1. Reduction of dicofol residues by home preparation procedures.

Elimination of pesticide residues from plant foods by washing controlled with many factors, such as chemical and physical properties of applied pesticide, nature of fruit surface, duration of the time that pesticide has been in contact with the plant food, formulation in which the pesticide was applied and weather conditions (**Elkins, 1989**).

Data of Table (1) show the effect of washing with tap water (simple washing) or with detergent (adequate washing) and extraction of strawberry and cantaloupe juices on dicofol residues, immediately after treatment, after 7 days of application and after 15 days later. The results indicated that simple washing removed 22.3%, 13.2% and 10.6% from strawberry and 17.3%, 16.9% and 12.4% from cantaloupe immediately after application, after 7 days and after 15 days post treatment, respectively.

As well as adequate washing removed 34.2%, 28.7% and 29.5% of dicofol residues from strawberry fruits and 32.1%, 31.1% and 28.6% of residues found in cantaloupe after the same mentioned waiting periods, respectively. Extraction of strawberry and cantaloupe juice after simple washing reduced 22.3%, 28.0% and 34.9% of dicofol residues found on washed strawberry and reduced 35.8%, 46.3% and 50.4% of residues found in washed cantaloupe at the same previously mentioned waiting periods.

From the presented data we have noted that waiting period after application for one week caused a reduction in dicofol residues with 26% after 7 days of application on strawberry and with 24% on cantaloupe, also waiting period for 15 days later reduced the residues with 36% on strawberry and with 54% on cantaloupe. This reduction means that simple

washing reduced the dicofol residues to be within the Maximum Residue Limit (MRL) for dicofol (1.0 mg/kg. **CCPR 1993**). As for adequate washing the residue levels were reduced to be safe for human consumption. These results are in harmony with **Bessar (1984, 1992), Bessar *et al.* (1990a, 1991a & b, 1994 a & b), Dogheim *et al.* (1993) and Tag El-Din (1990, 1993).**

Table (1) : Role of home preparation procedures on reduction dicofol residues

Home Preparative Procedures	Immediately after treatment		Seven days after treatment		Fifteen days after treatment	
	Mean ± SD	R%	Mean ± SD	R%	Mean ± SD	R%
	Strawberry					
Unwashed fruits (initial)	1.84 ± 0.11	-	1.36 ± 0.13	-	1.22 ± 0.15	-
Simple washing[a]	1.43 ± 0.14	22.3	1.18 ± 0.14	13.2	1.09 ± 0.13	10.6
Adequate washing[b]	1.21 ± 0.08	34.2	0.97 ± 0.06	28.7	0.86 ± 0.08	29.5
Fresh juice	1.11 ± 0.13	22.3	0.85 ± 0.03	28.0	0.71 ± 0.04	34.9
	Cantaloupe					
Unwashed fruits (initial)	1.96 ± 0.23	-	1.48 ± 0.11	-	1.29 ± 0.15	-
Simple washing	1.62 ± 0.16	17.3	1.23 ± 0.09	16.9	1.13 ± 0.06	12.4
Adequate washing	1.33 ± 0.09	32.1	1.02 ± 0.04	31.1	0.92 ± 0.08	28.6
Peeling	1.18 ± 0.11	27.2	0.76 ± 0.07	38.2	0.65 ± 0.09	39.0
Fresh juice	1.04 ± 0.07	35.8	0.66 ± 0.05	46.3	0.56 ± 0.09	50.4

a– Simple washing: Washing with tap water.
b– Adequate washing: Washing with detergent.

$$R\% = \text{reduction percent} = \frac{\text{Initial residues} - \text{found residues}}{\text{Initial residues}} \times 100$$

2. Effect of technological processes on dicofol residues in strawberry and cantaloupe products.

Thermal technological processes play an important role in degradation and reduction of pesticide residue levels. Pasteurization and sterilization of strawberry and cantaloupe juice manufacturing of compote and jam mainly shared in degradation of dicofol residue levels as indicated in Table (2). It has been noted that the pasteurization of strawberry juice reduced 21.2% and 25.3% of dicofol residues found in fresh juice after 7 days post application and 15 days post treatment, as well as, pasteurization of cantaloupe juice reduced 22.7% and 30.4% of residue levels at the same mentioned periods. Sterilization of strawberry and cantaloupe juice was more effective in degradation of dicofol residues than pasteurization. Data in Table (2) also showed that the manufacturing of strawberry and cantaloupe jam has similar effect on reduction of dicofol residues with that of juice sterilization. Table (2) also indicated that manufacturing cantaloupe compote reduce the residue levels with 21.9% after 7 days of application and with 23% after 15 days later. From the data presented in Table (2) it has been noted that low temperature had a lower effect on pesticide degradation which ranged from 16.8% to 19.3% in frozen strawberry and from 11.4% to 15.4% in frozen cantaloupe.

Table (2): Effect of technological processes on dicofol residues in strawberry and cantaloupe.

Procedures	Immediately after treatment		Seven days after treatment		Fifteen days after treatment	
	Mean ± SD	R%	Mean ± SD	R%	Mean ± SD	R%
	Strawberry					
Fresh juice	1.11 ± 0.10	-	0.85 ± 0.06	-	0.71 ± 0.08	-
Pasteurized juice	1.43 ± 0.12	22.5	0.67 ± 0.08	21.2	0.53 ± 0.09	25.3
Sterilized juice	0.67 ± 0.09	39.6	0.54 ± 0.04	36.5	0.45 ± 0.06	36.6
Strawberry jam	0.59 ± 0.08	58.7	0.48 ± 0.03	59.3	0.36 ± 0.07	66.9
Frozen strawberry	1.19 ± 0.08	16.8	0.98 ± 0.06	16.9	0.88 ± 0.09	19.3
	Cantaloupe					
Fresh juice	1.04 ± 0.06	-	0.66 ± 0.09	-	0.56 ± 0.06	-
Pasteurized juice	0.81 ± 0.04	22.1	0.51 ± 0.06	22.7	0.39 ± 0.04	30.4
Sterilized juice	0.61 ± 0.07	41.3	0.38 ± 0.04	42.4	0.28 ± 0.03	50.0
Compote	1.17 ± 0.09	27.7	0.96 ± 0.03	21.9	0.87 ± 0.02	23.0
Cantaloupe jam	0.56 ± 0.06	65.4	0.37 ± 0.03	69.9	0.24 ± 0.03	78.8
Frozen cantaloupe	1.37 ± 0.08	15.4	1.09 ± 0.04	11.4	0.99 ± 0.06	12.4

The obtained data confirmed that in spite of the residue levels of dicofol, were below its MRL (1 mg/kg) in fresh juice after 7 days of treatment, we have noted that processing minimized dicofol residues to be mere traces and very safe for human consumption without any hazardous effects on human beings. These results are in agreement with those of **Newsome (1980), Ripley (1978) and Bessar (1984, 1992 and 1996), Archer (1973) and Tag El-Din (1996).**

3. Influence of storage for three months on degradation of dicofol residues in preserved products of strawberry and cantaloupe.

Data presented in table (3) shows the influence of storage for three months on dicofol residues in some preserved products of strawberry and cantaloupe. It has been noted that the storage of strawberry products which processed after dicofol application reduced 40.6%, 41.8%, 45.8% and 31.9% of residue levels in pasteurized, sterilized juice, strawberry jam and frozen strawberry respectively. As well as 50.7%, 51.9%, 60.4% and 35.7% of residues after one week and 50.9%, 51.1%, 55.5% and 34.1% of residues after two weeks of application were decreased in the same mentioned products respectively. Storing cantaloupe products decreased the residues of dicofol with 42%, 47.5%, 37.6% 48.2% and 35.7% in the products processed immediately after treatment and with 39.2%, 36.8%, 36.5%, 59.5% and 30.3% in the products processed after 7 days of treatment and 53.8%, 53.6%, 33.3%, 42.1% and 21.3% of residue levels after 15 days later in pasteurized sterilized juice, compote, cantaloupe jam and frozen cantaloupe respectively. These results are in harmony with those of **Iwata *et al.* (1982), Bessar (1992) and Bessar *et al.* (1990).**

Table (3): Influence of storage period for three months on degradation of dicofol residues in stored products of strawberry.

Procedures	Immediately after treatment		Seven days after treatment		Fifteen days after treatment	
	Mean ± SD	R%	Mean ± SD	R%	Mean ± SD	R%
	Strawberry					
Pasteurized juice	0.51 ± 0.08	40.6	0.33 ± 0.05	50.7	0.26 ± 0.07	50.9
Sterilized juice	0.39 ± 0.06	41.8	0.26 ± 0.04	51.9	0.22 ± 0.06	51.1
Strawberry Juice	0.32 ± 0.06	45.8	0.19 ± 0.06	60.4	0.16 ± 0.07	55.5
Frozen strawberry	0.82 ± 0.11	31.9	0.63 ± 0.11	35.7	0.58 ± 0.09	34.1
	Cantaloupe					
Pasteurized juice	0.47 ± 0.05	42.0	0.31 ± 0.07	39.2	0.18 ± 0.03	53.8
Sterilized juice	0.32 ± 0.03	47.5	0.24 ± 0.04	36.8	0.10 ± 0.04	53.6
Compote	0.73 ± 0.07	37.6	0.61 ± 0.05	36.5	0.58 ± 0.04	33.3
Cantaloupe juice	0.29 ± 0.03	48.2	0.15 ± 0.03	59.5	0.11 ± 0.04	42.1
Frozen cantaloupe	0.88 ± 0.01	35.7	0.76 ± 0.08	30.3	0.68 ± 0.08	31.3

$$R\% = 1 - \frac{\text{Residues after storage}}{\text{Residues before storage}} \times 100$$

CONCLUSION

The present study indicates that washing, peeling and juice extraction play an important role in minimizing dicofol residues found on strawberry and cantaloupe fruits after one week of application to be within MRLS, as well as technological processing and storage for preserved products of strawberry and cantaloupe which processed immediately after treatment or after 7 and 15 days of application reduced the residue levels to be under MRLS and became very safe for human consumption.

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الملخص العربي

العمليات التكنولوجية المؤثرة على اختزال مبيد الديكوفول بالفراولة والكانتلوب

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فـــي هـــذا البحث تم دراسة تأثير كل من العمليات التجهيزيه الأولية وكذلك بعض العمليات التكنولوجية على اختزال متبقيات مبيد الديكوفول فى ثمار الفراولة والكانتلوب باستخدام جهاز التحليل الغازي الكروماتوجرافى

وأوضحت النتائج المتحصل عليها الاتي :

١- أن عملية الغسيل باستخدام الماء العادي اختزلت ٢٢,٣٪ و ١٠,٦٪ من المبيد الموجود في ثمار الفراولة بعد المعاملة مباشرة وبعد ١٥ يوم من المعاملة على التوالـــي واختزلت أيضاً ١٧,٣٪ و ١٢,٣٪ من متبقي المبيد الموجود في ثمار الكانتلوب على نفس الفترات الزمنية السابقة.

٢- أدى الغســـيل باستخدام منظف مسموح به إلى اختزال المبيد بنسبة ٣٤,٢٪ و ٢٩,٥٪ من المتبقي الموجود في ثمار الفراولة وبنسبة ٣٢,١٪ و٢٨,٦٪ بالنسبة لثمار الكانتلوب بعد المعاملة مباشرة وبعد ١٥ يوم من المعاملة على التوالي.

٣- استخلاص عصير الفراولة والكانتلوب أدى إلى اختزال ٢٢,٣٪ و ٣٤,٩٪ من متبقـــى المبيد في ثمار الفراولة و ٣٥,٨٪ و ٥٠,٤٪ من المتبقي الموجود في ثمار الكانتلوب بعد المعاملة مباشرة وبعد ١٥ يوم من المعاملة.

٤- أوضحت النتائج أيضاً أن عملية تقشير الكانتلوب اختزلت ٢٧,٢٪ ٣٩,٥٪ من متبقي المبيد على نفس الفترات السابقة.

٥- عملـــية البســـترة والتعقيم لعصير الفراولة والكانتلوب وكذلك تصنيع المربى والكمـــبوت مـــن ثمار الفراولة والكانتلوب المغسولة أدى إلى اختزال متبقيات المبيد لتصبح أقل من الحد المسموح به.

٦- تجميد ثمار الفراولة والكانتلوب لها تأثير قليل على اختزال متبقيات المبيد بينما تخـــزين المنـــتجات المصنعة السابقة الذكر لمدة ثلاث شهور اختزلت متبقيات المبـــيد بنســـبه كبيرة لتصبح أكثر أماناً لصحة المستهلك بدون حدوث أي آثار جانبية أخرى.