EFFECT OF FOOD PROCESSES PESTICIDES IN CUCUMBER FRUITS

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Abstract

The effect of washing and peeling on the behavior and persistence of chlorpyrifos-methyl, diazinon and phenthoate in cucumber was investigated. The effect of insecticides on carbohydrate, chlorophyll and soluble protein contents as well as the activity of peroxidase and poly phenol oxidase were also studied.

After one hour from application, the residues on cucumber were 1.42, 1.71 and 0.53 ppm for chlorpyrifos –methyl, diazinon and phenthoate, respectively. The residues of half –life values (RL_{50}) for the same pesticides were 23.31, 18.71 and 17.85 in respect. Washing with tap water after one hour from the application removed 31.69 % of chlorpyrifos-methyl, 64.91 % of diazinon and 26.41 % of phenthoate. The corresponding values after peeling were 95.07 %, 76.02% and 94.32%, respectively.

The results revealed that all insecticides did not show any change in the total contents of carbohydrates, soluble sugars, reducing sugars, non-reducing sugars, cholorophyl, soluble protien, peroxidase and polyphenal oxidase activity. Phenthoate treatments significantly increased total car

bohydrate contents. Diazinon significantly decreased total soluble sugars, reducing and non reducing sugars, but increased significantly the contents of chlorophyl b. On the other hand, chlorpyrifos methyl significantly increased the contents of cholorophyl b.

INTRODUCTION

Organophosphorus insecticides are widely used on vegetables and fruits for the control of insect pests because of their fast action and prolonged protection. These chemicals are generally short persistence and do not accumulate in the animal tissue and environment. Pesticides residues after application on crops should be followed and the pre-harvest interval should be also determined to be sure that the residues

are below the maximum residue limits (MRL 'S) before marketing. Cucumber (*Cucumis sativus l)*, is an important crop in Egypt and widely used by consumers .

Organophosphours insecticides namely chloryrifos-methyl, diazinon and phenthoate are widely used in Egypt to control the economic pests as aphids (*Aphids gossypii)*, white fly (*Bemisia tabaci)*, and cotton leaf worm (*Spodopetra littorals)*.
The purpose of the present work is to study the behavior and persistence of the insecticide chlorpyrifos-methyl, diazinon and phenthoate in cucumber under field conditions. The effect of washing, balancing and peeling on the amount of residues remaining in the plant after one hour from application with the chemicals was investigated. The effect of the insecticides on the same chemical constituents of cucumber was further studied.

MATERIAL AND METHODS

This present study experiment included three sections. The first aimed to determine the residues of three tested insecticides on cucumber vegetable crop under normal field condition at Dakahlia Governorate, Egypt. The second aimed evaluate the role of some processes in removing the insecticide residues sprayed fruit after application. The third experiment studied the effect of the insecticide residues on some chemical constituents of treated fruit at the harvest.

1.Residues determination of tested insecticides on cucumber fruit

Insecticide used

a- Chlorpyrifos-methyl (Reldan E.C. 50%) .

O, O dimethyl O- (3, 5, 6- tri chloro-2 pyridyl) phosphorothioate.

b- Diazinon (Basudin E.C. 60%) .

O, O diethyl O-2 isopropyl-6- methyl pyrimidin-4 - yl phosphorthioat.

c- Phenthoate (Cidial E.C.50%).

5- α. ethoxy carbonyl benzyl O, O- dimethyl phosphorodithoate.

Experimental and insecticides treatments

Cucumber (*Curcumas sativas*) was planted in El-Dair village, Aga center, Dakahlia Governorate, Kaluobia Governorate, Egypt on April 1st 2000 under normal

field conditions. The soil used was sandy clay loam. The experimental area was divided according to the complete randomized block design including three replicates. The plot was 1/100 feddan. The northern plots were left as control. Cucumber was sprayed on June, 7th,2002,sprayed with the three tested insecticides. The insecticide formulation was diluted with water and applied using a knapsack sprayer equipped with one nozzle . The recommend rates 1L/ feddan (Ministry of Agriculture Recommendation 1997).

Sampling

Five kilograms samples were taken at random from each experimental plot. Sub-sampling was done at the laboratory, four replicates were taken 100, 100 and 50 g for cucumber fruits. The sample intervals were one hour after application (zero time), 1, 3, 7, 10 and 15 days. Clean new polyethylene bags were used for preservation of the collected samples. The samples were stored at - 20 ^{0}C in a deep freezer until analysis.

Analytical procedures

Extraction: Cucumber fruits were extracted according to Nasr and Hegazy (2002) which adapted to use methanol instead of acetone as a solvent for the extraction of three insecticides under study. Samples were cut into small pieces in a warring blender (100g), a constant amount of distilled methanol (200ml) was used for extraction. The sample was blended for three minutes at high speed and filtered through a dry pad of cotton into a graduated cylinder. A known volume of filtrate (100 ml) was taken and partitioned successively with 100, 50 and 50 ml of dichloromethane for water separating from methanol extract in a 500ml separatory funnel after adding 30 ml of sodium chloride saturated solution. The combined dichloromethane phase was dried by filtration through a pad of cotton and anhydrous sodium sulfate, then after evaporated to dryness on a rotary evaporator at 40 °C.

Clean-up procedure: The florisil column cleans up procedure of Nasr and Hegazy (2002) was used in cleaning the sample extract for the three insecticides in use. A18mm (i.d.) x 40 cm glass column chromatography was filled with 6 gm of activated florisil (60-100 mesh) and topped with anhydrous sodium sulfate and compacted

thoroughly. The column was pre washed using 50 ml n- hexane. The sample extract was dissolved in 10 ml of the same solvent and transferred to the column and then eluted with 200 ml eluate (50 % dichloromethane: 48.5 % n-hexane: 1.5% acetonitrill) at rate of 5 ml /min. The eluate was evaporated to dryness by rotary evaporator at 40°C and the residues were ready for chromatographic determination.

Gas liquid chromatography determination: Pye Unicam 4500 gas chromatography equipped with flame photometric detector operated in the phosphorus mode (526 nm) filter was used for determination of chlorpyrifos-methyl, diazinon and phenthoate. The column was PAS-1701 (25m x 0.32 nm x 0.52 Um). Temperature and gas flow rates were as follows:

Injector: 250°C

Detector: 250°C

Column: 230, 230 and 210 °C for chlorpyrifos-methyl, phenthoate and diazinon, respectively.

Gases flow were 60, 30 and 30 ml/min. for nitrogen, hydrogen and air.

Retention times for chlorpyrifos-methyl, diazinon and phenthoate under these conditions were 1.99, 1.99 and 3.14 mn. , respecively . Rates of recoveries of the insecticides on cucumber fruits were determined at the level of 1 ppm for the three insecticides under study. The average rates of recovery for the three insecticides in used on this crop were 96, 99, and 80 %, respecively.

The effect of washing and peeling on removing Chlorpyrifos-methyl, diazinon and phenthoate residues from cucumber fruits after application with the recommended rates was studied. Samples were collected after one hour and one day from application and were prepared as follows:

Washing with tap water: Cucumber samples were rinsed for three minutes with running tap water. Then drained on a clean paper for 30 minutes at room temperature until drying. Samples were kept in polyethylene bags under deep freezing until analysis.

Peeling of cucumber fruits: Cucumber fruits were peeled manually by a sharp knife and the samples were kept in polyethylene bags under deep freezing until analysis.

Effect Chlorpyrifos-methyl, diazinon and phenthoate resudies on chemical constituents of cucumber fruits and fractions was studied.

Determination of total hydrolysable carbohydrates content: Samples consist of 5 g of plant material were subjected to acid hydrolysis by adding 20 ml of hydrochloric acid 2N in a tube. The tubes were sealed and put in electrical oven over night at 90 °C. Then after samples were lifted to reach to room temperature and filtered on a filter paper. The filtrate made to a known volume by distilled water. The total hydrosable carbohydrates were determined with phenol-sulfuric acid method as described by El-Refahey (2003 as follow: One ml of phenol 5 % was added to 1 ml of sample extract. Then 5ml of concentrated sulfuric acid (98 % w/w) were added from a fast delivering pipette, then tubes were shaken gently. The color was measured after 15min, at wavelength 490 nm using Pye Unicam SP 1800 spectrophotometer. A standard calibration curve was made using glucose monohydrate to determine total hydrosable carbohydrates.

Determination of total soluble sugar contents: Total soluble sugars were extracted from the samples (2 g) in 80 % ethanol (20ml) overnight. A known volume was evaporated and dissolved in a known volume of distilled water. Soluble sugars were determined by phenol sulfuric acid as described above according to El-Refahey (2003)

Determination of reducing sugar contents: Reducing sugars were determined by picric acid methods (El-Refahey 2003) as follows: One ml sugar alcoholic extract was mixed with 1 ml sodium bicarbonate 20 % then 4ml picric acid were added (10g picric acid were dissolved in 100 ml sodium hydroxide 1% and completed to 250 ml using distilled water). The mixture was heated in water bath for 15 minutes and completed to 50 ml and then measured at the wave length 520 nm by using Pye Unicam sp 1800 spectrophotometer, in the presence of a blank and using glucose monohydrate as a standard.

Determination of non-reducing sugar contents: The non- reducing sugar contents were calculated by the following equation:

Non-reducing sugar = total soluble sugars - reducing sugar

Determination of chlorophyll contents: The fresh samples (5 g) were ground in a porcelain mortar with acetone in presence of little amount of calcium carbonate and

acid washed sand. The extract was filtered throughout filter paper, then the mortar residues were washed with acetone several times until the washing liquid was colorless. The extract and washing filtrate were made up to a known volume (50ml). The absorbance was measured at 665 and 649 nm for chlorophyll a and chlorophyll b, respectively, by using Pye Unicam Sp 1800 spectrophotometer. The chlorophyll was calculated from the following equation as indicated by Vernon (1960):

$$Chlorophyll\ a\ (mg / g) = \frac{11.63\ (A665)-2.18A(64)xV}{1000xW}$$

$$Chlorophyll\ b\ (mg / g) = \frac{11.63\ (A649)-2.18\ (A665)xV}{1000xW}$$

Total chlorophyll (mg l g) = Chlorophyll a (mglg) + Chlorophyll b (mg l g).

Where: V: is the final dilution volume ml.
W: weight of sample g.
A: absorbance at 665 and 649 nm for chlorophyll a and b, respectively.

Protein analysis

Extraction of enzyme fractions: Samples were extracted with sodium phosphate buffer (o.2 M, PH 7.9) at 4° C for one hour at the ratio 1:10 (w/v) as described by El-Refahey (2003) The homogenate was filtered through a triplicate layer of chess cloth and then the supernatant was used for enzyme assay.

Determination of soluble protein contents: Soluble protein fraction was estimated by using the comassie brilliant blue G-250 according to Bradford (1976), with bovine serum albumin as a standard.

Preparation of Bradford stock solution: 350 mg comassie brilliant blue G 250 were dissolved in 100 ml 95% ethanol then added to 200 ml ortho phosphoric acid 88 %.

Preparation of Bradford working solution: 30 ml Bradford stock solution was added to 425 ml distilled water then 15 ml ethanol 95% was added, mixing was carried out frist, then the mixture was completed to 500 ml by adding 30 ml ortho

phosphoric acid 88 %. The working solution filtered through whatman paper No.1and stored at room temperature in brown glass bottle. The reaction was done by adding 5 ml Bradford working solution to 0.1 ml protein extract, then the color was measured at wave length 595 nm by using Pye Unicam Sp 1800 spectrophotometer, in the presence of a blank and by using bovine serum albumin as a standard.

Determination of peroxides activity (POD): Peroxides were assayed by photochemical method as described by the modified method described by El-Refahey (2003).

Preparation of stock solution: 3.60 g Potassium dihydrogen phosphate were dissolved in bidstilled water and completed in volumetric flask up to 1000 ml.(solution 1) . 17.4189 g dipotassium hydrogen phosphate were dissolved in bidstilled water and completed in a volumetric flask up to 1000 ml.(solution 2).

Phosphate buffer PH 6.8: It was prepared by adding 50 ml from solution (1) to 50 ml from solution (2) and then, 100 ml bidstilled water were added to the mixture.

Pyrogallol 60 mmol (freshly prepared): 0.7566 g pyrogallol was dissolved in 100 ml bidstilled water.

Hydrogen peroxide (freshly prepared): 625 ul H_2O_2 30 % was diluted to 100 ml by using bidstilled water in a volumetric flask.

Procedure: The solutions were added at the following sequence to give the reaction mixture:

a) 1.5 ml phosphate buffer
b) 0.40 ml hydrogen peroxide
c) 1.00 ml pyrogallol
d) 0.10 ml sample extract

The increasing in absorbance at 430 nm was recorded against blank (with phosphate buffer instead of enzyme extract). One unit of enzyme activity was defined as the amount of enzyme, which cause change in the optical density at 430 nm per minute and 25° C under standard assay condition. Specific activity was expressed in units by dividing it on mg protein. The value of Σ at 430 nm for the reaction product of pyrogallol is 2.47 m M^{-1} CM^{-1}.

$$Specificactivity = \frac{\Delta Ab \times 1000 \times 1 \times V}{mg\,(protein) \times \Sigma \times 0.1}$$

Determination of poly phenol oxidase (PPO) activity: Polyphenol oxides were assayed by using photochemical method as described by El-Refahey (2003).

Procedure:

a) 2.6 ml sodium phosphate buffer (0.01 M PH 6.5).

b) 0.3 ml of 0.5M catechol.

c) 0.1 ml of enzyme extract.

the increasing in absorption at 420nm was measured by using Pye Unicam Sp 1800 spectrophotometer. One unit of enzyme activity is defined as the amount of the enzyme that causes increase of 0.001 absorbency unit per minute at 25°C.

3. Statistical analysis: Data were analyzed statistically using the complete randomized block design using the computer program sigma plot (Sendecor and Chachran 1967).

RESLUTS AND DISCUSSION

The insecticide chlorpyrifos-methyl, diazinon and phenthoate were sprayed on cucumber fruits under normal field conditions at the rate of 1 L/fed. The corresponding active ingredients used per fed. was 500 grams.

The samples were taken at different intervals 1 hour after application (zero time), then 1, 3, 7, 10 and 15 days post insecticides treatment. The samples were analyzed for insecticide residues. The effect of the pesticides on some chemical constituents and some enzyme activity in relation to washing and peeling on pesticide residues were studied.

1. Persistence of tested insecticides on and in cucumber fruits

Residues of chlorpyrifos-methyl, diazinon and phenthoate on and in cucumber fruits at different intervals after insecticides application are shown in Table 1. The data show that the concentrations of the initial deposits were 1.42, 1.71 and 0.53 ppm after one hour from application, respectively. These amounts decreased to 0.70, 0.65 and 0.19 ppm after one day from application, respectively. The residues were

dissipated to different rates with the elapsed time after 3, 7, 10 and 15 days from application to reach 0.16, 0.10, 0.08 and 0.02 ppm for chlorpyrifos-methyl, 0.31, 0.11 and 0.07 ppm for diazinon and 0.06 and 0.02 ppm for phenthoate,. No detectable amount was found from diazinon and phenthoate residues at 15 days after application. The data indicated the continuous loss of residues with elapse time. The percent loss rate amounted to 50.70, 88.73, 92.95, 94.36 and 98.59 % for chlorpyrifos-methyl, 61.98, 81.87, 93.56 and 95.90 % for diazinon and 64.15, 88.67, 96.22 % for phenthoate after 1, 3, 7, 10 and 15 days from insecticide treatment. The residues half-life values (RL_{50}) were 23.31, 18.71 and 17.85 hrs for the three insecticides. These results are in agreement with Hegazy *et al.* (1997) who found that the half-life value for chlorpyrifos-methyl on cucumber fruits was 17 hours. Thabit (2002) found the RL_{50} of malathion and fenitrothion were 13.8 and 14.4 hours in cucumber fruits. Nasr and Hegazy (2002) reported the RL_{50} of profenofos and pyrazophos on cucumber fruits were 14.4 and 18.22 hours, respectively.

Table 1. Residues of chlorpyrifos-methyl, diazinon and phenthoate in and on cucumber fruits.

Time after application (days)	Chlorpyrifos -methyl		Diazinon		Phenthoate	
	Ppm	Loss%	Ppm	Loss%	ppm	Loss%
Initial#	1.42	0.00	1.71	0.00	0.53	0.00
1	0.70	50.70	0.65	61.98	0.19	64.15
3	0.16	88.73	0.31	81.87	0.06	88.67
7	0.10	92.95	0.11	93.56	0.02	96.22
10	0.08	94.36	0.07	95.90	ND	ND
15	0.02	98.59	ND	ND	ND	ND
RL_{50} hrs	23.31		18.71		17.85	

: one hour after application ND: undetectable

According to Codex Alimentarius Commission (1997) the maximum residues levels (MRL'S) is 0.1 ppm for chlorpyrifos-methyl on cucumber fruits, 0.5ppm for diazinon and 0.02 ppm for phenthoate, respectively. The pre-harvest intervals (Safety period for consumption) were 7, 1 and 7 days for chlorpyrifos-methyl, diazinon and phenthoate, respectively, on cucumber fruits . The safe period for harvesting vegetables treated with organophosphorus insecticides ranged between 1 day and 12

days post treatment depending on the chemistry of the tested insecticide and kind of crops (Shokr 1997; Shady et al. 2000 ; Nasr and Hegazy 2002).

According to Bates (1979), data of pesticide residues in treated crops are required for premarket registration of pesticides and for setting maximum residue limits (toxicologically acceptable level) to protect the consumer against the possible health hazards of exposure to pesticides.

1. Removal of insecticide residues from treated vegetable crops by some processes

The frequent use of insecticides to control pests has polluted of the environment with toxic residues. The need for removing these residues becomes therefore important. In Egypt, consumer usually use water to wash vegetables and fruits before eating.

The efficiency of washing with tap water and peeling for removing chorpyrifos-methyl, diazinon and phenthoate residues from cucumber fruits after one hour and one day from treatment was evaluated .

A . The effect of washing with tap water on pesticide residues on cucumber fruits: The results in Table 2 show the levels in ppm and percentage of removal of insecticides after washing at one hour and one day of insecticides application. Chlorpyrifos-methyl, diazinon and phenthoate residues on and in cucumber fruits were 1.42, 1.71 and 0.53 ppm, respectively. These amounts were reduced to 0.97, 0.61 and 0.39 ppm , respectively by washing process. The corresponding percentage removal were 31.69, 64.91 and 26.4 % after one hour of application, respectively. The residues were 0.70, 0.65, 0.19 ppm for chlorpyrifos-methyl, diazinon and phenthoate after one day of insecticides application, respectively. These amounts were reduced to 0.48, 0.36 and 0.08 ppm after washing three minutes with tap water, corresponding percentage of removal were 31.42, 44.61 and 57.87 %, respectively. Hegazy *et al.* (1997) reported that the washing process removed 55.63 % from chlorpyrifos-methyl residues on cucumber fruits. Shokr (1997) reported that the washing process removed 53.79, 85.29, 84.34 % from pirimiphos-methyl, fenitrothion

and malathion on cucumber fruits. Thabit (2002) found that the washing process removed 33.3, 22 % from malathion and fenitrothion residues on cucumber fruits.

B - Peeling process in cucumber fruits: The results in Table 2 show the residue levels and the percentage of removal after peeling one hour and one day post application. The residues of chlorpyrifos-methyl, diazinon and phenthoate in cucumber fruits were 1.42, 1.71 and 0.53, respectively. The peeling process reduced these residues to 0.07, 0.41 and 0.03 ppm, respectively. The corresponding percentage of removal were 95.07, 76.02 and 94.37 % after one-hour from application. The residues were 0.70, 0.65 and 0.19 ppm for chlorpyrifos-methyl, diazinon and phenthoate, respectively. These amounts were reduced to 0.14, 0.25 and 0.07 ppm by the peeling process after one day for insecticide application, with the percentage of removal 80.80 , 61.53 and 63.15%, respectively. Hegazy *et al.* (1997) found that the peeling process of cucumber fruits removed 97.30 from chlorpyrifos-methyl residues. Shokr (1997) found that the peeling process of cucumber fruits removed 97.35, 86.22 and 97.47 from pirimiphos-methyl, fenitrothion and malathion residues, respectively.

Table 2. Effect of some processes on organophosphorous insecticide residues on and in vegetable crops, after one and 24 hours of spraying.

Time after application	Process	Chlorpyrifos -methyl		Diazinon		Phenthoate	
		Residues		Residues		Residues	
		ppm	%Loss	Ppm	%Loss	ppm	%Loss
Cucumber Fruits after one hour	Unprocessed	1.42	0.00	1.71	0.00	0.53	0.00
	Washed	0.97	31.69	0.61	64.91	0.39	26.41
	Peeled	0.07	95.07	0.41	76.02	0.03	94.32
Cucumber Fruits after one day	Unprocessed	0.70	0.00	0.65	0.00	0.19	0.00
	Washed	0.48	31.42	0.36	44.61	0.08	57.87
	Peeled	0.14	80.80	0.25	61.53	0.07	63.15

3.Effect of insecticides on the chemical composition of cucumber fruits

Pesticides may affect some biochemical constituent plants treated with insecticides. The effect of chlorpyrifos-methyl, diazinon and phenthoate on carbohydrate fractions contents, chlorophyll contents, soluble protein contents, peroxidase activity and polyphenol oxidase activity of cucumber fruits was investigated.

A- Carbohydrate contents

1- Effect on total carbohydrate contents in cucumber fruits: The results of chlorpyrifos-methyl, diazinon and phenthoate on carbohydrate contents are presented in Table 3 .

Table 3 . Effect of tested insecticides on total carbohydrate contents (mg/g fresh weight) on cucumber fruits.

Treatment	Control	Chlorpyrifos -methyl	Diazinon	Phenthoate
Initial#	65.26	64.29	71.03	68.31
1	60.36	60.83	56.15	67.29
3	62.79	65.31	54.14	65.46
7	77.11	72.86	70.07	91.71
10	64.74	48.69	68.01	84.47
15	62.43	62.08	67.12	63.57
Means±SD	65.45±5.97	62.34±7.89	64.42±7.37	73.49±11.64
T Value 0.05		1.13	0.39	-2.64*

One hour after application.

Each value is the average of three replicates.

*significant values.

The results show that the amount of total carbohydrate contents in cucumber fruits in control, chlorpyrifos-methyl, diazinon and phenthoate treatments were 65.45 , 62.35 , 64.42 and 73.46 mg/g fresh weight, respectively. The obtained results show no significant effect of chlorpyrifos-methyl and diazinon on total carbohydrate content on cucumber fruits compared with control treatment, while significant increase was found in case of phenthoate treatment. These results are in agreement with Thabit (2002).

2. Effect on total soluble, reducing and non reducing sugars in Cucumber fruits

Data in Table 4 reveal that the chlorpyrifos-methyl and phenthoate treatments did not show any significant effect on total soluble sugar contents in cucumber fruits. On the other hand, the diazinon treatm ent showed a significant decrease in this respect. The amounts of total soluble sugars were 10.82, 13.29, 6.95 and 10.88 mg/g fresh weight for control, chlorpyrifos-methyl, diazinon and phenthoate insecticides treatments, respectively.

This indicate that chlorpyrifos-methyl and phenthoate had no significant increase in reducing sugars content, but diazinon had significant decrease compared with control treatment. The amounts of reducing sugars were 5.28, 7.73, 3.35 and 7.08 mg/g for control, chlorpyrifos-methyl, diazinon and phenthoate, respectively. Also, show that diazinon and phenthoate treatments had a significant decrease on non-reducing sugars content in cucumber fruits, while chlorpyrifos-methyl did not show any significant differance. The amounts of reducing sugars on cucumber fruits were 5.55, 5.56, 3.62 and 3.80 mg/g for chlorpyrifos-methyl, diazinon and phenthoate treatments at all intervals studied.

B- Effect on chlorophyll contents: Table 5 indicates that Phenthoate did not show any significant effect on chlorophyll a, b and total chlorophyll compared with the control, while chlorpyrifos-methyl and diazinon significantly increased the chlorophyll b contents . The chlorophyll a, b, and total chlorophyll values were 6.08, 4.63 and 10.7 mg/g fresh weight for the control, 6.17, 6.54, 12.8 for chlorpyrifos-methyl, 5.50, 6.40 and 11.90 for diazinon and 5.10, 5.52 and 10.64 mg/g for phenthoate, respectively. El-Shahaat and Edrisha (1993) found that the total chlorophyll contents in fresh cabbage leaves were increased after application with pirimiphos-methyl and deltamethrin. Thabit (2002) reported that malathion and fenitrothion had no significant effect in chlorophyll a, b and total chlorophyll compared with the control.

C- Effect on peroxidase, polyphenol oxidase activities and soluble protein contents in cucumber fruits: Data in table 6 showed no significant effect of the insecticides on peroxidase, polyphenol oxidase activities and soluble protein contents. The mean values of peroxidase activity were 2347.92, 2419.84, 1748.21 and 2226.72

for the control, chlorpyrifos-methyl, diazinon and phenthoate treatments, respectively. Polyphenol oxidase activities were 106.94, 155.92, 109.50 and 98.29 for the control, chlorpyrifos-methyl, diazinon and phenthoate , respectively. The soluble protein contents were 9.40, 10.60, 10.86 and 9.84 mg/g fresh weight for control, chlorpyrifos-methyl, diazinon and phenthoate, respectively. The results are in agreement with Salem and El-Sherief (1998) and Thabit (2002).

Table 4. Effect of tested insecticides on total soluble sugars, reducing sugars and non-reducing sugars content on cucumber fruits (mg/g fresh weight).

Treatment (days)	Control			Chlorpyrifos -methyl			Diazinon			Phenthoate		
	Total Soluble sugar	Reducing sugar	Non-Reducing sugar	Total Soluble sugar	Reducing sugar	Non-Reducing sugar	Total Soluble sugar	Reducing sugar	Non Reducing sugar	Total Soluble sugar	Reducing sugar	Non Reducing sugar
Initial#	9.73	4.94		16.47	10.68	5.79	8.46	3.78	4.86	13.64	9.87	3.77
1	9.31	4.85	4.46	16.23	9.3	6.93	3.85	3.85	1.04	11.79	7.77	4.02
3	9.19	4.77	4.42	7.82	3.24	4.58	4.83	3.81	1.02	7.97	5.81	2.15
7	10.82	5.28	5.55	14.53	8.89	5.69	7.57	2.93	4.64	12.72	6.39	6.33
10	11.55	5.09	6.46	13.21	7.92	5.29	6.32	2.00	4.32	11.74	6.75	4.99
15	14.34	6.73	7.61	11.46	6.34	5.12	9.62	3.75	5.87	7.41	5.9	1.51
Means ±SD	10.82 ±1.95	5.27 ±0.73	5.55 ±1.27	13.29 ±3.27	7.73 ± 2.63	5.59 ± 0.79	6.95 ±1.94	3.35 ± 0.74	3.62 ±2.07	10.88 ±2.57	7.08 ±1.53	3.8 ± 1.77
T Value 0.05				-1.74	- 2.11	- 0.02	6.62*	4.70*	3.14*	- 0.03	-2.26	1.81

One hour after application.
Each value is the average of three replicates.
*Significant values.

Table 5. Effect of tested insecticides on chlorophyll contents (mg/g) fresh weight on cucumber fruits.

Treatment (days)	Control			Chlorpyrifos -methyl			Diazinon			Phenthoate		
	a	b	Total	a	b	Total	a	b	Total	a	b	Total
Initial#	4.80	4.63	9.43	5.71	6.67	12.4	6.02	6.33	12.4	5.32	6.01	11.3
1	6.36	4.24	10.6	7.90	7.50	15.5	6.21	6.98	13.2	6.90	6.76	13.7
3	5.97	4.69	10.7	6.43	6.71	13.2	5.05	5.82	10.9	4.89	4.87	9.76
7	7.35	5.83	13.2	3.29	4.53	7.82	5.58	6.87	12.5	4.32	4.85	9.17
10	4.94	4.04	8.98	6.14	6.61	12.8	3.99	4.89	8.88	4.36	4.76	9.12
15	7.08	4.35	11.4	7.66	7.24	14.9	6.13	7.99	14.1	4.89	5.88	10.8
Mean ± SD	6.08 ± 1.06	4.63 ± 0.63	10.71 ± 1.50	6.17 ± 1.66	6.54 ± 1.04	12.80 ± 2.71	5.50 ± 0.85	6.48 ± 1.06	11.99 ± 1.85	5.10 ± 0.95	5.52 ± 0.81	10.64 ± 1.73
T value 0.05				-0.12	2.84*	-1.34	1.40	- 4.07*	-1.89	1.4	-1.80	0.07

One hour after application.
Each value is the average of three replicates.
*Significant values.

Table 6. Effect of tested insecticides on specific activity of peroxidase and polyphenol oxidase and soluble protein content (mg/g fresh weight) on cucumber fruits.

Treatment (days)	Control			Chlorpyrifos -methyl			Diazinon			Phenthoate		
	Peroxidase activity	Poly phenol oxidase	Soluble protein	Peroxidase activity	Poly phenol oxidase	Soluble protein	Peroxidase activity	Poly phenol oxidase	Soluble protein	Peroxidase activity	Poly phenol oxidase	Soluble protein
Initial	1360.18	49.40	10.12	2332.52	205.77	9.72	1204.04	92.93	10.76	3282.25	126.64	9.87
1	1333.16	141.24	9.11	2196.9	96.89	12.9	2139.17	146.77	10.22	1371.03	49.71	10.04
3	4486.99	127.39	7.85	2105.27	75.00	10	1623.33	160.39	12.47	2973.77	131.16	9.53
7	1259.35	1156.2	8.68	1924.23	142.58	10.52	974.	87.49	12.47	931.6	71.9	10.43
10	2843.87	96.71	10.34	2678.64	212.67	10.58	3055.75	88.06	10.00	2811.51	115.73	8.64
15	2803.94	111.70	10.32	3281.53	202.63	9.87	1492.98	81.35	9.22	1990.15	94.53	10.51
Mean± SD	2347.92 ± 1232.18	106.94 ± 31.94	9.40 ± 1.02	2419.84 ± 492.21	155.92 ± 60.16	10.60 ± 1.18	1748.21 ± 753.49	109.50 ± 34.61	10.86 ± 1. 34	2226 ± 946.84	98.28 ± 32.43	9.8 ± 40.68
T value 0.05				- 0.14	- 1.39	- 1.73	1.12	- 0.20	-1.56	0.257	70.3	-0.08

[#] One hour after application.
Each value is the average of three replicates.
*Significant values.

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تأثير بعض المعاملات التصنيعية على متبقيات المبيدات في ثمار الخيار

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تـناول البحث دراسة بقاء ثلاثة مبيدات فسفورية و هي الكلوربيرفوس- ميثيل والديازينون والفينثويـت علـى و فـي ثمار الخيار و ذلك تحت الظروف الحقلية و تم اخذ العينات بعد ساعـة مـن المعاملة و١ و٣ و٧ و١٠ و١٥ يوما من المعاملة .

و يمكن تلخيص النتائج المتحصل عليها كالأتي :-

١ -تـبات متبقـيات الكلوربيريفوس مثيل و الديازينون و الفينثويت على ثمار الخيار كانت الكمية المتبقية من الكلوربيريفوس مثيل و الديازينـون و الفينثويت بعد ساعة من المعاملة ١,٤٢ و ١,٧١ و ٠,٥٣ جـزء في المليـون علـى التوالي وكانت فترة نصـف العمر لهذه المبيدات ٢٣,٣١ و ١٨,٧ و ١٧,٨٥ ساعة على التوالي. وكانت فترة الأمان للمستهلك ٧ و ١ و ٧ يوما يعد الرش.

٢- أوضحت الدراسة إن عملية الغسيل بماء الصنبور لثمـار الخيار أدت إلـى إزالة ٣١,٦٩ و ٦٤,٩١ و ٢٦,٤١ ٪ مـن متبقـيات الكلوربـيريفوس مثيل و الديازينون و الفينثويت بعد ساعة من المعاملة على التوالي و إزالة ٣١,٤٢ و ٤٤,٦١ و ٥٧,٨٧ ٪ من متبقيات هذه المبيدات بعد يوم واحـد من المعاملة على التوالـي . كما أدت عملية التقشـير لثمـار الخيار إلى إزالة ٩٥,٠٧ و ٧٦,٠٢ و ٩٤,٣٢ ٪ من متبقيات الكلوربيريفوس مثيل و الديازينون و الفينثويت بعد ساعة من المعاملة على التوالي. ٨٠,٨٠ و ٩١,٥٣ و ٦٣,١٥ ٪ من هذه المتبقيات بعد يوم واحد من المعاملة على التوالي.

٣- أوضـحت النتائج إن كل من المبيدات المستخدمة ليست ذات تأثيرات معنوية على محتوى ثمار الخـيار من الكربوهيدرات الكلية باستثناء معاملة ثمار الخيار بمبيد الفينثويت حيث أدت إلى حدوث زيـادة معنوية في كمية الكربوهيدرات الكلية . كذلك ليست لها تأثيرات معنوية على السكريات الكلية الذاتـية و المخـتزلة و السـكريات غير المختزلة في ثمار الخيار باستثناء معاملة ثمار الخيار بمبيد الديازيـنون أدت إلى حدوث نقص معنوي في محتوى الثمار من السكريات الكلية الذاتية و المختزلة والسـكريات الغـير المختزلـة. و لوحظ أن معاملـة ثمار الخيار بمبيد الكلوربيريفوس مثيل والديازينون أدت إلى حدوث زيادة معنوية في كمية الكلوروفيل ب في ثمار الخيار. و إن كل من المبـيدات المستخدمة ليست ذات تأثيرات معنوية على محتوى ثمار الخيار من البروتين الكلى الذائب وعلى نشاط إنزيم البروكسيديز ونشاط إنزيم البولي فينول اكسيديز في ثمار الخيار.