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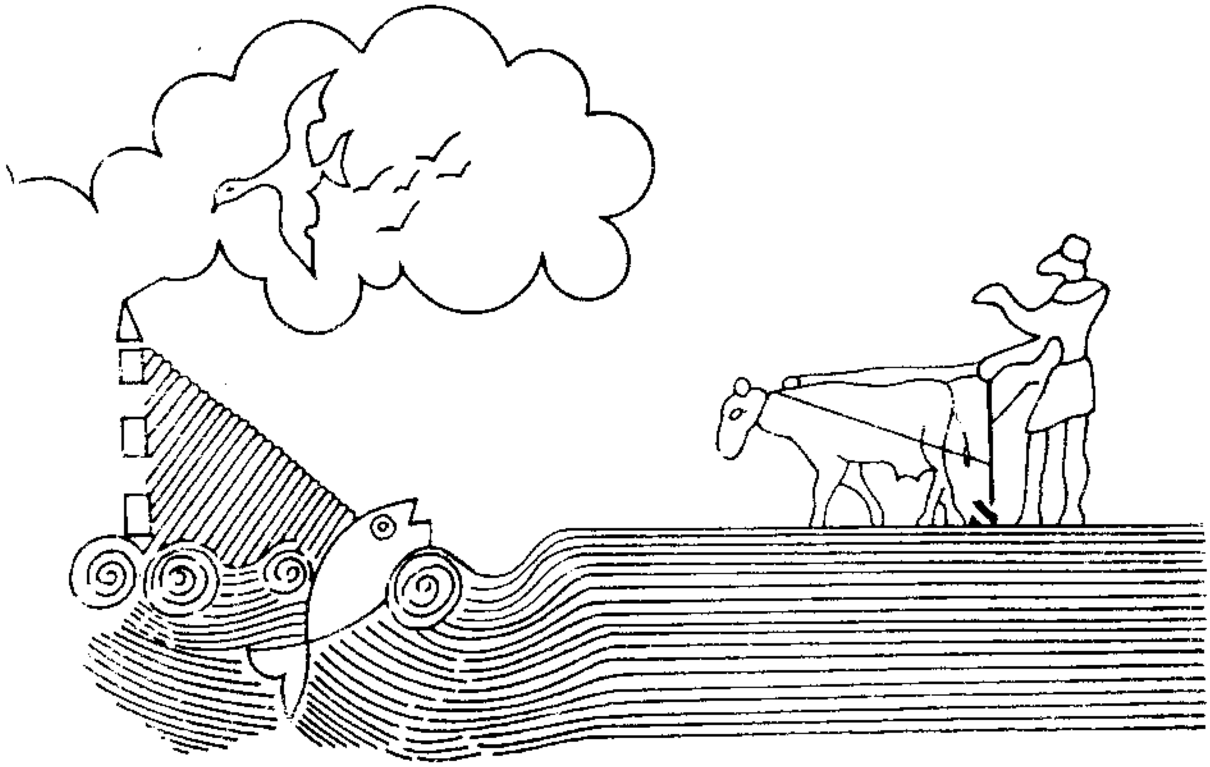

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Residues of pirimiphos-methyl and fenitrothion in grapes, their effect on some quality properties and their dissipation during the removal and processing methods

By

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ABSTRACT

The persistence patterns of the two organophosphorus insecticides; pirimiphos-methyl and fenitrothion in leaves and fruits of grapes in relation to their effects on some internal quality properties were studied. In addition, the elimination of the two insecticide residues contaminating grapes through the use of washing or home processing methods was also investigated. The results showed that waiting period of 21 days after application on grapes is enough to reduce the pirimiphos-methyl or fenitrothion residues to below the maximum residue limits (MRL). However, pirimiphos-methyl appeared longer persistent with $t_{1/2}$ of 5.4 and 4.4 days than fenitrothion with $t_{1/2}$ of 3.2 and 2.8 days for fruits and leaves, respectively. Results also showed that washing treated fruits with any of the tested washing of solutions removed considerable amounts of such residues. Blanching of grape leaves, removed 77.19% and ~ 100% of the initial residues of pirimiphos-methyl and fenitrothion, respectively. Grape processing into raisins or juice caused almost complete residue reduction (~100% removal for each insecticide). As for the internal quality parameters of grape fruits, the tested insecticides had significantly increased total soluble sugars. Pirimiphos-methyl significantly increased % acidity,decreased pH of the grape juice and did not produce any significant effect on the % fatty acids. On the other hand, fenitrothion significantly decreased % acidity and also did not cause any effect on the tested fatty acids except linoleic acid in grape fruits which was increased.

Keywords: Pirimiphos-methyl, fenitrothion, insecticides, grapes, fruit quality, removal.

INTRODUCTION

Grapevines are attacked by a number of insects and diseases that require frequent use of pesticides to control those pests. A variety of organophosphorus contact insecticides are used to control insects and their use is therefore important in grape production. Therefore, assessment of insecticide residues in grapes and in their processed products such as juice and rasins is of great concern. However, studies on insecticide residues in grape and their fate during processing are quite limited. (Cabras *et. al.,* 1995, Dagher *et al.*, 1999 and Cabras and Angioni, 2000) and more are required. Also, knowledge of the effect of insecticide residues on grape quality parameters is quite needed.

Pirimiphos-methyl and fenitrothion are organophosphorus insecticides widely used to control various insect pests including grape moth, leaf worms, aphids, leafhoppers, white flies and thrips on grapes. There is lack of published data in Egypt for the fate of these insecticides in grapes and in the processed products.

Therefore, the present work was carried out in an attempt to: (1) study the persistence of pirimiphos-methyl and fenitrothion in grapes (fruits and leaves). (2) evaluate the influence of different washing solutions or some home preparative procedures on the removal of such residues from treated grapes. (3) investigate the effect of the two tested insecticide residues on some quality parameters of grapes.

MATERIALS AND METHODS

Insecticides used: Pirimiphos-methyl; *O*- (2-diethyl-amino-6-methyl pyrimidin-4-yl) *O*, *O*-dimethyl phosphorothioate with acute oral LD_{50} of 1180 mg/kg for rats, technical grade sample with the purity of 99.8% provided by ICI PLC, Plant Protection Division, U.K. and fenitrothion; *O, O*-dimethyl-*O*- (3-methyl-4-nitrophenyl) phosphorothioate with acute oral LD_{50} of 250 mg/kg for rats, technical grade with the purity of 96.5% obtained from American Environmental Protection Agency (US.EPA) were used for GLC standardization in the present study. The emulsifiable concentrate (50%) from each insecticide was employed in the field experiment.

Field experiment and sampling: A field trial of vineyard (*Vitis vinifera* L.) var. Thompson seedless was carried out in a randomised block design during 1999 at Abees area, Alexandria Governorate, Egypt. Separate test plots of grapes were designed with three replicates (the area of each plot was 100 m^2, with 20 vines). Common cultural and fertilization practices for grape production were followed. The vines were sprayed with the insecticide, pirimiphos-methyl 50% or fenitrothion 50% emulsifiable concentrate at the rate of 300 cm^3/feddan (recommended field application rate). The amount of formulated insecticide was diluted with 200 liters of water per feddan, and a knapsack-sprayer (Cp-3) equipped with one nozzle was used. The untreated control plots were sprayed with an equal amount of water. Plots were isolated from each other by a one file of vines between plots in order to prevent cross contamination. Each insecticide was applied once at four weeks before harvesting time. A sample of three clusters and large quantities of leaves were collected randomly from each replicate, in duplicate soon after one hour and then at 1, 3, 5, 7, 10, 14, 21 and 28 days after insecticide application. The samples were brought to the laboratory in plastic bags and frozen at –18 °C until ready for analysis.

Extraction and clean up: For extraction of pirimiphos-methyl or fenitrothion residues, the chopped grape fruits samples (50 gm subsamples) were extracted with acetone (150 ml) for three minutes followed by partitioning using dichloromethane (Bowman, 1980). Grape leaves (25 gm/sample) treated with each insecticide were extracted with chloroform-acetone (130 + 20 ml, v/v) solvent system followed by partitioning using chloroform and sodium chloride (Antonious and Abdel-All, 1988). The resulted extracts were evaporated to near dryness using rotary evaporated at 35 °C. The concentrate was taken in 1 ml n-hexane for clean up. The extracts from either fruits or leaves were cleaned-up on silica gel column amended with 1 gm activated charcoal using 20% acetone in n-hexane as an eluting solvent according to the method of Bowman and Leuck (1971).

To examine the efficacy of extraction and clean-up, three samples from each grape fruits or leaves were spiked with known concentration (2 mg/kg) of the pure insecticide standard solution. Extraction and clean-up were performed as described earlier and the average recovery rates were found to be 89.20%

and 79.60% for grape fruits and leaves treated with pirimiphos-methyl, respectively, as well as 86.40% and 77.10% for the corresponding samples treated with fenitrothion, respectively. Results were corrected according to the average of recovery.

Residue determination: Determination of pirimiphos-methyl and fenitrothion residues were performed on a Shimadzu 4 CM (PFE) GC-FPD with an analytical glass column (2m x 3 mm i.d) packed with 4% SE-30 + 6% OV-210 on 80/100 Chromosorb W. The operating temperatures (°C) for both insecticides tested were maintained as follows: Column 220 isothermal, injector 270, detector 270 and gas flow rate (ml/min) were: Nitrogen 40, hydrogen 80 and air 100; the limits of detection under these conditions were 0.30 and 1.4 ng for piripimhos-methyl and fenitrothion, respectively. Identification of each tested insecticide residues was accomplished by retention time (t_R) and compared with known standard at the same conditions. The quantities were calculated on peak height basis. Using these conditions,the retention times of pirimiphos-methyl and fenitrothion were 8.6 and 7.2 minutes, respectively.

Removal of insecticide residues from treated grapes: Removal tests were also carried out on the 14th day treated grape samples either by different washing solutions (fruits) or by some home preparative procedures (fruits and leaves) to evaluate their effectiveness on removing such residues. The fruit samples were dipped into jar filled with any of the following solutions (tap water, soap solution (1%), potassium permanganate solution (0.01%), sodium hydroxide solution (0.1%), sodium chloride solution (1%), acetic acid solution (2%) and sea water) for one minute. The washed samples were allowed to dry on a clean paper before packing. In another part of treated fruits, samples were subjected to two different processing methods:(1) raisins: The treated fruits were boiled in water for 5 minutes then allowed to dry on a clean paper and left in sunlight (10 hours/day) for 3 days. (2) juice: Grape juice was obtained by crushing the fruits in a strainer and receiving the juice in an another cattle free from remnants. Juice obtained was subjected to incubation at room temperature for one month. On the other hand, only blenching method was carried out on grape leaves (rainsed in boiling water for 5 minutes). The samples were prepared for analysis as described before.

Determination of some internal quality parameters: Analytical determination for the studied chemical quality parameters was made on treated and untreated grape fruits to evaluate the side effect of the tested insecticide residues on quality of grape fruits. These chemical parameters included total soluble sugars, pH, T.S.S., total acids and fatty acids content.

Total soluble sugars: Total soluble sugars were extracted by blending 5 gm of grapes with 100 ml of 80% ethanol, together with charcoal (0.5 gm) for one minute. The mixture was filtered and determined colourimetrically by picric acid method as described by Thomas and Dutcher (1924).

pH value: The pH of the grape juice was determined according to the AOAC methods (1984) by digital pH meter.

Total soluble solids (T.S.S): T.S.S were recorded by using hand – referactometer.

Total acids: This was determined in terms of % citric acid by titration with 0.01 N sodium hydroxide in the presence of phenolphthaline indicator (AOAC, 1970).

Fatty acids content: This was determined according to Radwan (1978), by using GC after the conversion of fatty acid into fatty acid methyl esters. The analysis of the tested fatty acids was matched versus their standard mixture.

Statistical analysis: Statistical significance of the data was determined by using the analysis of variance with LSD method at the probability of 0.05 (Steel and Torrie, 1980).

RESULTS AND DISCUSSION

Insecticide residues: Grapes were sprayed at fruiting stage with pirimiphos-methyl or fenitrothion at the recommended field rate to study the persistence of such insecticides at different intervals. Results in Table (1) showed that the initial deposits

Table (1): Residues of pirimiphos-methyl and fenitrothion in grape fruits and leaves at periodic intervals.

Samplig days	Residue[a] [ug.g^{-1} (% dissipation)]			
	Pirimiphos-methyl		Fenitrothion	
	Leaves	Fruits	Leaves	Fruits
0 (1h)[b]	17.08	6.54	24.12	10.71
1	15.19 (11.06)	5.88 (10.09)	21.80 (9.62)	8.25 (22.97)
3	13.41 (21.49)	3.88 (40.67)	13.20 (45.27)	6.20 (42.11)
5	7.22 (57.73)	2.77 (57.65)	4.60 (80.93)	3.02 (71.80)
7	5.92 (65.34)	2.51 (61.62)	2.47 (89.76)	2.07 (80.67)
10	2.23 (86.94)	2.39 (63.46)	1.60 (93.37)	1.51 (85.90)
14	1.61 (90.57)	1.16 (82.26)	0.57 (97.64)	0.75 (92.99)
21	0.22 (98.71)	0.22 (96.64)	0.17 (99.30)	0.11 (98.97)
28	nd (~ 100)	Nd (~100)	nd (~ 100)	nd (~ 100)

[a] Mean of three replicates, [b] Initial deposits of the insecticide
nd = not detectable

of pirimiphos-methyl were greater on grape leaves (17.08 ppm) than fruits (6.54 ppm), one hour after application. The amount of residues decreased to reach 0.22 ppm on grape leaves and fruits at 21 days after spraying. On the other hand, the initial deposits of fenitrothion were 24.12 and 10.71 ppm on grape leaves and fruits, respectively. These figures decreased gradually until reached 0.17 and 0.11 ppm in leaves and fruits, respectively after 21 days of application. No residues of pirimiphos-methyl or fenitrothion could be detected after 28 days following application for grape leaves and fruits.

The calculated half-life values of pirimiphos-methyl were 4.4 and 5.4 days for grape leaves and fruits, respectively. The corresponding half-lives of fenitrothion were 2.8 and 3.2 days, respectively (Table, 2).

Table (2): The value of apparent rate constant (k) and half-life time ($t_{1/2}$) of tested insecticide residues on grapes using GC methods.

Insecticide	Grape Sample	Apparent rate constant (k)*	Half-life time ($t_{1/2}$) (day)**
Pirimiphos-methyl	Fruits	0.13	5.4
	Leaves	0.16	4.4
Fenitrothion	Fruits	0.22	3.2
	Leaves	0.25	2.8

*K = $^1/t$ Ln a/m, where k = apparent rate constant, a = initial concentration, m = concentration after t, and t = time in days,

** t ½ = Ln(2)/k = 0.693/k

From the present results of insecticide residues on grape leaves and fruits, it could be concluded that pirimiphos-methyl or fenitrothion revealed faster disappearance in grape leaves than that in the fruits, however, the initial deposit of such insecticides on grape leaves was higher than that on the fruits.

The high levels of initial deposits of such insecticides on treated grapes (fruits and leaves) mainly due to many factors, the ratio of surface to mass area, the character of treated surface (smooth or rough and waxy or non-waxy), physicochemical properties of the insecticide, high wax content of fruit surface and hydrophilic-lipophilic balance of investigated insecticides controlled the penetrability of applied agrochemicals into plant tissues (Cabras *et al.*, 1988).

It could be also concluded that waiting period of 21 days after application on grapes is enough to decline pirimiphos-methyl or fenitrothion residues to be within the maximum residue limits (MRLs) established by Codex Alimentaries Commission which were 1mg/kg for pirimiphos-methyl and 0.5 mg/kg for fenitrothion (Anonymous, 1999) and to be valid for safe consumption without any hazardous side effects on human health.

The present results of pirimiphos-methyl and fenitrothion residues on fruits and leaves of grapes are comparable to those reported by the following authors; small amounts of pirimiphos-methyl (0.05 and 0.56 ppm) were detected on tomato and okra fruits, respectively, after 15 days of application (Ramadan, 1991), while it was undetectable in the whole pods of cowpea after 10 days (Soliman, 1994). The level of pirimiphos-methyl residues on broad bean fruits was found to be below the MRLs after 5 days of application, while it exceeded that level on tomato fruits after the same time of application (Radwan *et al.*, 1995). Also, fenitrothion treated cucumber, pepper or tomatoes must not be marketed before 12-14 days from application, whereas pirimiphos-methyl showed moderate pre-harvest interval with sprayed vegetables being 7.5, 8.8 and 7.83 days for cucumber, pepper and tomatoes, respectively (Zidan *et al.*, 1996).

More recently, Cabras and Angioni (2000) reviewed the residues obtained in the 1990's from research on the behaviour of pesticide residues on grapes, from treatment to harvest, and their fate in drying, wine making and alcoholic beverage processing. They stated that the decay rate of the organophosphorus insecticides e.g. chlorpyrifos, phoaslone and dimethoate was very fast with $t_{1/2}$ ranging between 0.97 and 3.84 days.

Removal of pirimiphos-methyl and fenitrothion residues from treated grapes: When the preharvest intervals between treatments and harvest are not respected by the farmers, the risk of having higher pesticide levels is not negligible. In this case, the higher levels of pesticides can involve considerable economic losses if the maximum residue limits established by FAO/WHO are surpassed. So, the effect of washing by different solutions or after using some home preparative processing methods in removing the pesticide residues from plants may be a solution to overcome this problem.

- **Intentional removal of the tested insecticide residues:**

The effect of washing by different solutions in the removal of pirimiphos-methyl and fenitrothion residues from grape fruits is shown in Fig.(1). This figure declared that washing with any of the tested solutions decreased the residues in fruits when mpared with that of unwashed fruits. Washing grape fruits by sea water gave percent removal of 86.63 and 91.10 % for pirimiphos-methyl and fenitrothion, respectively.

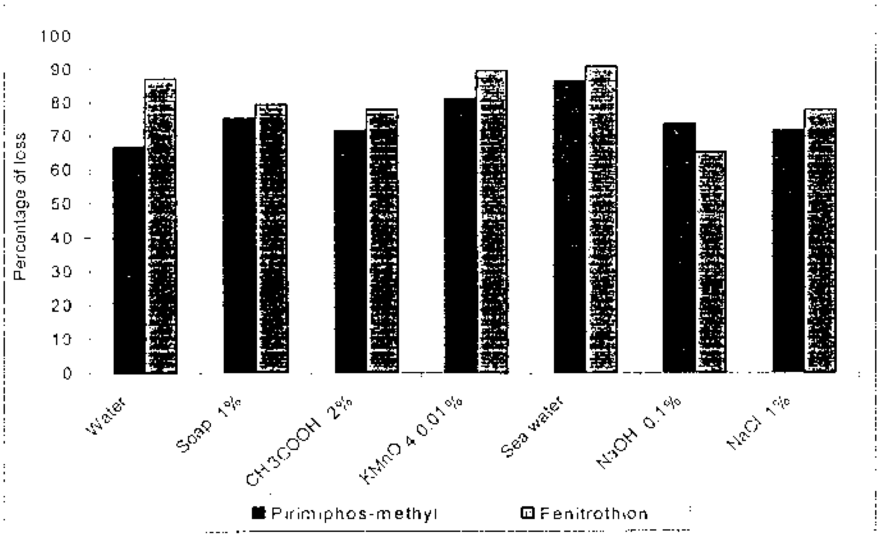

Fig. (1): Percentage of loss of pirimiphos-methyl and fenitrothion from grape fruits by different washing solutions

Using potassium permenganate as washing solution, gave 81.28 and 89.83 % removal for pirimiphos-methyl and fenitrothion, respectively. The corresponding percent removal when used soap solution were 76.47 and 79.66 % respectively. Also, tap water washing reduced the initial residues of fenitrothion by 87.28 %, but it was the lowest removing method in the case of pirimiphos-methyl.

- **Home preparative processing:**

As regards to the effect of some home preparative processing methods on reducing pirimiphos-methyl or fenitrothion residues in/on treated grapes (fruits and leaves), the results showed that residues of pirimiphos-methyl and fenitrothion were reduced to 77.19 % and ~ 100 % of the initial concentration after blanching of grape leaves. No detectable residues of such insecticidal treatment (~100 % removal) was shown in grape fruits after raisins or juice making. In general blanching of leaves, raisins of fruits or juice reduced the level of such residues in grape fruits and leaves to below the Maximum Residue Limits (MRLs) as mentioned before. These results are in agreement with findings of Rao *et al.*, 1987; Elkins, 1989 and Yoshikawaet.. *al.*, 1996. They stated that washing and subsequent processing steps resulted in a great reduction of pesticide residues from treated vegetables and fruits and the residue levels in final products became lower than the MRLs.

Effect of pirimiphos-methyl and fenitrothion residues on some internal quality parameters of grape fruits: Pesticide residues may interfere with the biochemical and physiological processes in plants, retarding the growth of the plant and then the yield. Also, it may lower its food quality and may even prevent its use as food by affecting its quality characteristics (Bartholomew *et. al.*, 1951). So, the possible effect of pirimiphos-methyl and fenirtothion residues on the chemical characteristics of grape fruits was determined and recorded in Tables 3 and 4.

Results in Table (3) clearly indicated that both of the tested insecticide residues had increasing effect in total soluble sugars. However, fenitrothion treated fruits have significantly higher rate of sugar content than that of pirimiphos-methyl treated fruits. Pirimiphos-methyl residues significantly decreased the pH values, while fenitrothion has no effect on it. On the other hand, fenitrothion increased refractometric T.S.S, whereas pirimiphos-methyl decreased it. The mean values of % acidity were significantly increased in fruits treated with pirimiphos-methyl, while reduced it in fruits treated with fenitrothion.

Table (3): Effect of pirimiphos-methyl and fenitrothion residues on some fruit quality parameters of grape fruits.

Parameter	Treatments		
	Untreated	Pirimiphos-methyl	Fenitrothion
Total soluble sugars (mg glucose/100 mg)	119.50 [c] ± 2.12	126.50 [b] ± 1.94	135.40 [a] ± 2.91
pH value	3.60 [a] ± 0.21	3.50 [b] ± 0.06	3.60 [a] ± 0.23
% T.S.S.	14.90 [b] ± 1.36	14.70 [b] ± 1.60	15.70 [a] ± 1.10
% acidity	0.63 [b] ± 0.08	0.67 [a] ± 0.09	0.59 [c] ± 0.08

Each value is a mean of three replicates ± S.D of three recorded data (nine measurements). Means followed by the same letter. in each raw are not significantly different at $P \leq 0.05$.

It is well established that certain pesticides influence the chemical composition of the plant fruits to which they are applied. The insecticide, dimethoate did not influence T.S.S and sugars of peppers. (Shahin *et al.*, 1989). Profenofos residues increased T.S.S and acidity, but decreased the glucose, protein and ascorbic acid content of tomatoes (Ismail *et al.*, 1993). Also, Radwan *et al.*, (1995) reported that pirimiphos-methyl residues appeared to has significant effect on the total soluble sugars and ascorbic acid content of tomato fruits and broad bean seeds. Significant effect were also noticed on the total acid and pH values in bean seeds.

Data in Table (4) represent the effect of the tested insecticide residues on the percentage of fatty acids of grape fruits. The data revealed that the effect of both insecticide residues on the tested fatty acids was varied and exhibited apparent increase or decrease without significant differences between each insecticide treated and untreated fruits. Only fenitrothion significantly increased linoleic acid over the control samples. Also, no significant differences were noticed between treatments for the effect on the percentage of saturated and

Table (4): Effect of pirimiphos-methyl and fenitrothion residues on the percentage of tested fatty acids of grape fruits.

Acids		Untreated	Pirimiphos-methyl	Fenitrothion
Lauric	C12:0	1.26[a] ± 0.68	0.97[a] ± 0.51	2.02[a] ± 0.57
Myristic	C14:0	1.19[a] ± 0.31	2.35[a] ± 0.93	1.31[a] ± 0.53
Palmitic	C16:0	23.37[a] ± 8.06	28.20[a] ± 5.48	19.62[a] ± 5.93
Palmitolitic	C16:1	1.03[a] ± 0.53	0.94[a] ± 0.17	1.38[a] ± 0.62
Stearic	C18:0	9.34[a] ± 2.10	6.84[a] ± 0.83	5.77[a] ± 0.85
Oleic	C18:1	29.25[a] ± 9.25	29.07[a] ± 4.11	27.03[a] ± 7.46
Linoleic	C18:2	20.75[b] ± 4.28	19.82[b] ± 4.09	24.01[a] ± 7.03
Linolenic	C18:3	2.09[a] ± 0.96	1.58[a] ± 0.56	1.70[a] ± 0.32
Arachidic	C20:0	7.24[a] ± 0.98	3.74[a] ± 0.72	8.96[a] ± 1.87
Behenic	C22:0	1.38[a] ± 0.38	1.57[a] ± 0.33	3.65[a] ± 0.64
Erucic	C22:1	3.57[a] ± 1.05	5.06[a] ± 1.05	4.89[a] ± 1.83
Saturated %		43.77[a] ± 7.55	43.63[a] ± 2.50	41.03[a] ± 5.75
Unsaturated %		56.70[a] ± 7.46	56.35[a] ± 2.56	59.00[a] ± 8.65

Each value is a mean of three replicates ± S.D. Means followed with the same letter, in each raw are not significantly different at $p \leq 0.05$.

unsaturated fatty acids of grape fruits. These results are supported with those reported by Azhogina *et al.*, 1991 & 1996. They indicated that the organophosphorus insecticides; phosalone and metaphos changed the ratio of saturated and unsaturated fatty acids, decreased the level of palmitic and palmitoletic acids and increased the level of behenic and erucic acids when added to grape juice, malts, or wine.

In conclusion, all the formentioned results seem to indicate that we must avoid the consumption of pirimiphos-methyl or fenitrothion treated grapes before elapsing 21 days from application and pre-washing and/or processing of the fruits is advisable.

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الملخص العربى

متبقيات البيرموفوس و الفنتروثيون فى العنب وتأثير ذلك على بعض خصائص الجودة واختفائهم خلال طرق الإزالة والتصنيع

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تم دراسة ثبات إثنين من مبيدات الفوسفور العضوية (البريميفيوس-ميثايل و الفنيتروثيون) على أوراق وثمار العنب وكذلك تأثيرها على بعض صفات الجودة بالإضافة إزالة متبقيات كلا المبيدين من العنب خلال استخدام عمليات الغسيل المختلفة أو طرق التصنيع المنزلي.

وقد أوضحت الدراسة أن ٢١ يوم بعد الرش على العنب كافية لخفض متبقيات كلا المبيدين الى أقل من الحدود المسموح بها، كذلك وجد أن البريميفيوس-ميثايل أكثر بقاء (فترة نصف العمر ٤ر٥ ، ٤ر٤ يوم) بالمقارنة بالفنيتروثيون (فترة نصف العمر ٢ر٣ ، ٨ر٢ يوم) على الثمار والأوراق على التوالي.

كذلك أوضحت الدراسة أن الغسيل للثمار المعاملة بكلا المبيدين بمحاليل الغسيل المستخدمة قد أزال نسبة عالية من المتبقيات، كذلك قد أزالت عملية سلق أوراق العنب ١٩ر٧٧ % و ١٠٠ % تقريبا من الكميات المبدئية لكلا المبيدين ، كذلك عملية التصنيع المنزلي الثمار (زبيب وعصير) قد أزالت ١٠٠ % تقريبا من متبقيات كلا المبيدين.

وبدراسة تأثير كلا المبيدين على صفات الجودة فى ثمار العنب وجد انهما قد أحدثا زيادة معنوية فى السكريات الكلية والبريميفيوس-ميثايل أحدث زيادة معنوية فى النسبة المئوية للحموضة وخفض معنوي في قيمة الأس الهيدروجينى لعصير العنب ولم يحدث تأثير على النسبة المئوية للأحماض الدهنية ، وعلى الجانب الأخر فقد أحدث الفنيتروثيون خفض معنويا فى النسبة المئوية للحموضة ولم يحدث تأثير على نسبة الأحماض الدهنية فيما عدا أنه زود نسبة حمض اللينوليك .