The influence of some pesticides on the bioactive plant components

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ABSTRACT

The effect of insecticides, methomyl and carbosulfan; fungicides, benomyl and thiophanate-methyl and herbicides, metribuzin and dinitramine with different concentrations, 0.5, 1 and 2 fold of the recommended rate on the level of the bioactive components; phenols, tannins and flavonoides was studied in squash and peasum. All the tested external defensive chemicals affected the formation of internal defensive chemicals. The tested insecticides and herbicides decreased phenols, tannins and flavonoides content, while the tested fungicides enhanced the formation of these chemicals.

Key words: Pesticides, bioactive plant components, phenols, tannins, flavonoides

INTRODUCTION

Plant secondary compounds (allelochemicals) are essential for the secondary metabolism and synthesized from lipid precursors and aromatic amino acids. Phenolic compounds probably constitute an important portion of the secondary compounds, which synthesized in the shikimate pathway. Phenols in plants have diverse functions such as stabilization of the structure, protection from herbivory and biocidal effects against pests (Friend, 1977; Sindhan and Jaglan, 1988 and Daniel et al., 1999).

The concentration of phenolic compounds in plant may be increased or decreased due to pesticide application. The alteration of the naturally occurring phenolic compounds by pesticides have been documented by several investigators. The synthesis of phenolic compounds in plants can be modulated by the application of herbicides and, to a lesser extent,

insecticides and fungicides (Daniel et al., 1999). In general, foliar spraying technique for either insecticides or herbicides had much inhibitory effect on the plant phenolic contents than the soil mixing technique for these pesticides (Sabra, 1993 and Salem, 1994).

The herbicides; linuron and oxyfluorfen increased phenolic contents in potato tubers (Marwaha, 1986), while linuron and terbutryn decreased the amount of total phenols in faba bean (El-Sherif, 1991). Also, the concentration of total phenolic compounds in carrot was reduced by aldicarb, carbofuran and fensulfothion (Aly and Doss, 1986 and Singh and Singh, 1988). The fungicide, propiconazole increased the concentration of free phenols in wheat (Abdel-Hak et al., 1987). In addition, oxycarboxine stimulated total phenolic contents in faba bean (El-Sherif, 1991).

The aim of the present study is to investigate the effect of the application of different rates of some pesticides on the content of phenolic compounds, as stress indicator, in squash and peasum plants.

MATERIALS AND METHODS

Pesticides:

Methomyl, S-methyl-N (methyl carbamoyl oxy) thio-Insecticides:

acetimidate. (Lannate 90 % SP, 300 g / fed., Du Pont Co.).

Carbosulfan, 2-3-dihydro-2,2-dimethyl-7-benzofuranyl (dibutylamino thio) N-methyl carbamate. (Marshal 25 % WP,

600 g / fed., FMC Agricultural Chemical Group).

carbamoyl)-2-benzimidazol 1-(butyl Methyl Benomyl, Fungicides: carbamate. (Benlate 50 % WP, 240 g / fed., Du Pont Co.).

Dimethyl[(1,2-phenylene)bis-(imino Thiophanate-methyl, carbonothioyl)] bis (carbamate). (Topsin-M 70 % WP, 400

g / fed., Nippon Soda).

Herbicides: Metribuzin, 4-amino-6-(1,1-dimethyl ethyl)-3-(methyl thio) 1,

2,4-triazin-5(4H) one. (Sencor 70 % WP, 300 g / fed., Bayer) N,N-diethyl-2,6-dinitro-4-trifluoromethyl-mphenylenediamine. (Cobex 24 % EC, 1 L / fed., Wacker-

Chemic)

Plants: Cucurbito pepo Var. Askondarancy (squash). Fam. Curbitaceae. Pisum sativum Var. Lancon (peasum). Fam. Leguminasae.

Soil: The soil samples were collected from the top (0-30 cm) layer of the untreated soil profiles and the soil properties are: pH 8.57, organic matter 1.34 %, calcium carbonate 12.24 %, sand 36.17 %, silt 22.24 %, clay 41.59 % and 13.70 meq / l. total soluble salts. Its texture class was clay loam soil. The soil was air dried and passed through a 2 mm sieve. The seeds of squash and peasum were cultivated in pots (14-cm diamter and 15-cm height). After emergence, the plants were thinned to 4 plants / pot. One plant from each pot was removed for assays at different time intervals 15, 30, 45 and 60 days.

Treatments: The plants were sprayed with insecticide or fungicide and incorporation with the soil in the case of herbicide, after 21 days from sowing. All pesticides were applied at three different rates 0.5, 1 (the recommended field rate) and 2 fold, with three replicates. The content of total phenols, tannins and flavonoides were determined after every 15 days following pesticides application. Also, the total phenols in untreated squash and peasum were monitored during the growing time.

Determination of total phenols and their major components: The total phenolic content, tannins and flavonoides were determined colourimetrically according to McGroth *et al.*, (1982); Swain and Hillis (1959) and Smith (1913), respectively.

Statistical analysis: The data were subjected to analysis of variance (ANOVA) (CoStat Statistical Software, 1990).

RESULTS AND DISCUSSION

Monitoring of total phenols in squash and peasum during the growing time: The amount of total phenols in both squash and peasum at different intervals, each 5 days up to 60 days of planting were determined as g / 100 g plant fresh weight. Fig. (1) showed that the growing time of squash can be divided into three periods, first period from planting time to 20 days, the second from 20 to 40 days and the third period from 40 to 60 days. The growing time of peasum had two intervals from planting to 35 days and

from 35 to 60 days. Generally, the highest amount of total phenols in both plants was presented at 45 days from planting.

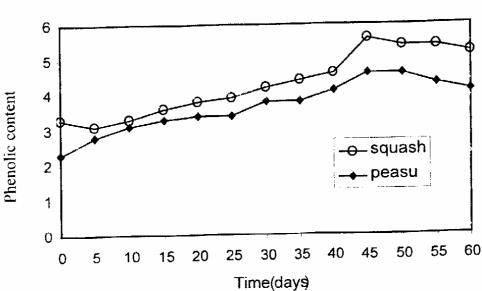


Fig. (1): The amount of total phenols in squash peasum during the growing time

Effect of the tested pesticides on total phenols and their major components in both squash and peasum: The data in Table (1) revealed that there were differences of phenol contents in squash and peasum at each level of the tested pesticides. Metribuzin and dinitramine reduced total phenolic content followed by methomyl and carbosulfan while, the fungicides benomyl and thiophanat-methyl stimulated total phenols in both plants compared to control. Squash was adversely affected than peasum in this consideration. These results are in harmony with those reported by El-Sherif (1991) who found that the herbicides; linuron and terbutryn decreased the amounts of total phenols, the insecticides; chlorpyrifos and

Table (1): Effect of the tested pesticides on total phenolic content in plants

Conc. (fold) Treatment)	Total pheonolic content							
		Squash			Peasum				
	0.5	11	2	0.5	1	2			
Methomyl	6.21 ^d	6.33 ^e	5.95 ^c	7.68ª	6.70 ^{cd}	6.48 ^{bc}			
Carbosulfan	5.88 ^e	6.49 ^d	5.56 ^d	6.54 ^c	6.50 ^d	6.19 ^c			
Benomyl	7.78 ^b	7.05 ^b	6.78ª	7.16 ^b	6.94 ^{bc}	6.81 ^{ab}			
Thiophanate-methyl	8.02ª	8.09 ^a	6.35 ^b	7.40 ^{ab}	7.62ª	6.88ª			
Metribuzin	4.88 ^g	5.16 ^f	4.67 ^e	6.31°	4.91 ^f	4.29 ^d			
Dinitramine	4.97 ^f	4.91 ^g	4.45 ^f	5.36 ^d	5.36 ^e	4.17 ^d			
Control	6.75°	6.75°	6.75 ^a	7.10 ^b	7.10 ^b	7.10a			
LSD _{0.05}	0.065	0.058	0.055	0.327	0.320	0.323			

The presented values are means of four measurements corresponding intervals; 15, 30, 45 and 60 days from treatment

Total phenolic content is expressed as g / 100g plant tissues

Values within the same column having the same letters are not statistically different from each other, p<0.05

chlorpyrifos-methyl caused a slight effect on this respect. However, the fungicides; oxycarboxine and fongarid increased phenolic contents in faba bean. Phenolic contents were stimulated in Vigna radiata by the application of thiophanate-methyl and phosphamidon (Siddiqui and Khan, 2001). Also, a substantial increase in total phenols was observed in susceptible and resistant varieties of wheat following treatment with benomyl or calixin (Siddiqui and Ahmed, 2002). The herbicide, metribuzin reduced the total phenolic contents in potato and the factor of reduction was found to be 1.1-3.3 when compared to control plants (Lydon and Duke, 1989 & 1993). The data presented in Table (2) indicated that the highest rate of the two tested insecticides decreased the total tannins in squash plant. No significant differences were observed in tannin contents in both plants due to either insecticide or fungicide treatment when compared with the control, especially with half and one fold of recommended field rates. The tested herbicides, metribuzin and dinitramine inhibited total tannins formation in squash plant at all tested concentrations and in peasum plant at two fold recommended rate.

Table (2): Effect of the tested pesticides on tannins content in plants

Conc. (fold) Treatment	Tannins content						
	0.5	Squash 1	2	0.5	Peasum 1	2	
Methomyl Carbosulfan Benomyl Thiophanate-methyl Metribuzin Dinitramine Control	0.25 ^{cd} 0.27 ^{bc} 0.30 ^{ab} 0.32 ^a 0.20 ^c 0.22 ^{de} 0.31 ^{ab}	0.28 ^b 0.27 ^b 0.32 ^a 0.29 ^{ab} 0.23 ^c 0.27 ^b 0.31 ^{ab}	0.25° 0.25° 0.30° 0.27° 0.27° 0.25° 0.31°	0.53 ^a 0.37 ^a 0.36 ^a 0.36 ^a 0.37 ^a 0.34 ^a 0.38 ^a	0.35 ^a 0.37 ^a 0.37 ^a 0.35 ^a 0.34 ^a 0.33 ^a 0.37 ^a	0.35 ^{ab} 0.35 ^{ab} 0.36 ^{ab} 0.36 ^{ab} 0.30 ^c 0.33 ^{bc} 0.38 ^a	
LSD 0.05	0.032	0.027	0.026	0.023	0.039	0.031	

The presented values are means of four measurements corresponding intervals; 15, 30, 45 and 60 days from treatment

Values within the same column having the same letters are not statistically different from each other, p<0.05

Table (3) indicated that all tested pesticides significantly decreased the concentrations of flavonoides in peasum plant at the three tested concentrations compared to control. The highest effect was recorded in the case of herbicides treatment. All tested pesticides at 0.5 fold of the recommended dose showed no significant differences of flavonoides in squash as compared to control. However, the rest rates inhibited flavonoides formation in squash plant.

Methomyl and carbosulfan decreased the total tannins but had no clear effect on flavonoides in squash and peasum, so that the effect of both insecticides on total phenols may be due to their effects on total tannins. Benomyl and thiophanate-methyl increased total phenol formation in both tested plants. This may be due to their stimulation in total tannins. On the other hand, the reducing effect of total phenols in both plants after treated with either metribuzin or dinitramine may be due to their reducing effect in

Total tannins is expressed as g / 100g plant tissues

both total tannins and flavonoides. The compounds which reduced the tannins content could be also decreased the strength of the plant because tannins considered the main substract for lignin formation. Moreover, the plant quality is decreased if the flavonoides were reduced. It had a major role on vitamins formation. In general, Pesticides altered phenolic contents and their constituents in the tested plants. These changes appeared to be specific for both the plant and the pesticide applied.

Table (3): Effect of the tested pesticides on the flavonoides content in plants

Conc. (fold)	Flavonoides content							
	Squash			Peasum				
Treatments	0.5	1	2	0.5	1	2		
Methomyl	7.99 ^a	7.96 ^c	7.75 ^e	6.06 ^b	5.65 ^e	5.37 ^d		
Carbosulfan	8.18 ^a	7.93°	7.81 ^d	5.92 ^d	5.71 ^d	5.59°		
Benomyl	8.22 ^a	8.10^{b}	7.91°	6.03 ^b	5.88 ^b	5.82 ^b		
Thiophanate-methyl	8.21 ^a	8.33ª	8.02 ^b	5.98°	5.80°	5.79 ^b		
Metribuzin	7.87 ^a	5.15°	5.74 ^f	5.65 ^e	4.67^{g}	4.51 ^f		
Dinitramine	7.03 ^b	6.51 ^d	4.84^{8}	5.56 ^f	5.36 ^f	4.94 ^e		
Control	8.17 ^a	8.17 ^b	8.17 ^a	6.26 ^a	6.26ª	6.26ª		
LSD _{0.05}	0.242	0.126	0.043	0.035	0.033	0.031		

The presented values are means of four measurements corresponding intervals; 15, 30, 45 and 60 days from treatment

Flavonoides content is expressed as g / 100g plant tissues

Values within the same column having the same letters are not statistically different from each other, p<0.05

It was noticed that the application of pesticides using lesser concentrations particularly fungicides induced the formation of phenolic contents and their major constituents; tannins and flavonoides. Whereas higher concentrations diminshed their contents. These results are in agreement with Garcia et al., (2001), Siddiqui and Khan (2001) and Siddiqui and Ahmed (2002).

In conclusion, the results in relation to control plants indicate that the application of the tested fungicides increased the total phenolic contents and their constituents. These results may imply an increased resistance of plants

to pathogen infection. On the other hand, it was found an inhibition of phenolic contents and their constituents by the application of herbicides. This observation suggest that the soil application of herbicides could be harmful for healthy plants and then reduce the capacity of these plants to combat the pest attack. Consequently, it may be suggested that synthesis of various metabolic products would be affected by the application of pesticides probably at higher concentrations. However, discriminate use of pesticides is, therefore, recommended.

REFERENCES

- Abdel-Hak, T.; A. A. Bassiouni; Y. Y. EL-Hyatemy and I. Shafik (1987). Evaluation of fungicides for the control of yellow stripe rust wheat. Egyptian J. Phytopathol., 19 (1-2): 85-96.
- Aly, M. I. and M. Doss (1986). Studies on aldicarb and carbofuran on imporving crop production. J. Agric. Mansuora Univ., 11 (4): 1570-1575.
- CoStat Statistical Software (1990). Microcomputer program analysis Version 4.20, CoHort Software, Berkeley, CA.
- Daniel, O.; M. S. Meier; j. Schlatter and P. Frischknecht (1999). Selected phenolic compounds in cultivated plants: Ecological functions, health implications, and modulation by pesticides. Archives of Environmental Health, 107: 109-114.
- EL-Sherif, M. G. (1991). The influence of some pesticides on some non-target processes occurred in soil. Ph. D. Thesis. Faculty of Agriculture, University of Alexandria.
- Friend, J. (1977). Phenolic substances and plant diseases. Recent Adv. Phytochem., 12: 557.
- Garcia, P. C.; R. M. Rivero; L. R. Lopez-Lefebre; E. Sanchez; J. M. Ruiz and L. Romero (2001). Direct action of the biocide carbendazim on phenolic metabolism in tobacco plants. J. Agric. Food Chem., 49 (1): 131-137.
- Lydon, J. and S. O. Duke (1989). Pesticide effects on secondary metabolism of higher plants. Pestic. Sci., 25: 361-374.

- Lydon, J. and S. O. Duke (1993). The role of pesticides on host allelopathy and their effects on allelopathic compounds. In: Pesticide Interactions in Crop Production. Beneficial and Deleterions Effects (Altman J. ed.). Boea Raton, FL: CRC Press, pp. 37-56.
- Marwaha, R. S. (1986). Biochemical changes in potato tubers with the application of some herbicides. Annals Biol., 2 (2): 117-124
- McGrath, R. M.; W. Z. Kaluzo; K. H. Daiber; B. William and C. W. Glennine (1982). Polyphenols of sorgham grain, their changes during malting and their inhibitory nature. J. Agric. Food Chem., 30: 450-456.
- Sabra, F. S. (1993). Studies on the efficiency of certain herbicides and their side effects on potato plants and soil. Ph. D. Thesis. Faculty of Agriculture, University of Alexandria.
- Salem, H. A. (1994). The effect of certain pesticides on some bioprocesses occurred in both soil and plant. Ph. D. Thesis. Faculty of Agriculture, University of Alexandria.
- Siddiqui, Z. S. and S. Ahmed (2002). Effects of systemic fungicides on protein, carbohydrate, amino acids and phenolic contents of susceptible (Mexipak) and resistant (Povan) varieties of *Triticum aestivum* L. Turk. J. Bot., 26: 127-130.
- Siddiqui, Z. S. and S. Khan (2001). Effect of systemic fungicides and insecticides on absorption spectra, chlorophyll and phenolic contents of *Vigna radiata* (L.) Wilczek. Pak. J. Biol. Sci., 4 (7): 812-814.
- Sindhan, G. S. and B. S. Jaglan (1988). Effect of fungicides on the biochemical response of ground nut plant against tikka leaf spot. Pl. Dis. Res., 3 (1): 57-59.
- Singh, S. P. and V. Singh (1988). Evaluation of olicakes and nematicides for the control of *Meloidogyne incognita* infecting eggplant. Indian J. Nematol., 18 (2): 366-368.
- Smith, R, B. (1913). Chemistry and Food Analysis. 3rd Edition. p. 291.

Swain, T. and W. E. Hillis (1959). The phenolic constituents of *Prunus domestica*. J. Sci. Food Agric., 10: 63-68.

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تأثير بعض المبيدات على مركبات نشطة حيويا في النبات

ماهر إبراهيم على فوقية عبد الفتاح مرسى أحمد عبد السلام خميس أحمد فرحات الأسود مسر قسم كيمياء المبيدات - كلية الزراعة - جامعة الإسكندرية - مصر

تمثل بعض المركبات الثانوية بالنبات اهمية كبيرة من حيث تحمل بل ومقاومة النبات للإصابة بالأفات لذا فقد تم دراسة تأثير مبيدين حشربين ميثوميل وكاربوسلفان ومبيدين فطربين بينوميل وثيوفينيت ميثايل ومبيدين للحشانش متروبيوزين وداي نيترامين وذلك بتركيزات نصف ومثل وضعف المعدل الحقل الموصى به وتأثيرها على بعض المركبات الكيماوية النشطة حيويا في النبات وهي القينولات والتانينات والفلافينات في كل من الكوسة والبسلة.

وقد أظهرت النتائج أن كل المبيدات المختبرة قد أثرت على تكوين المواد النشطة حيويا بالنبات، وكل من المبيدات الحشرية والحشائشية المختبرة قللت محتوى كل من الكوسة والبسلة للفينولات والتانينات والفلافينات وعلى العكس فإن المبيدات الفطرية قد حفزت تكوين هذه المركبات الحيوية داخل النبات.