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Synergistic activity of several acids in binary mixtures with synthetic insecticides on *Spodoptera littoralis* (Boisduval)

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The activity of binary mixtures of some inorganic acids (IAs) and organic acids (OAs) with certain recommended insecticides was evaluated against the 4th-instar larvae of *Spodoptera littoralis* in laboratory. Mixing organophosphate, pyrethroid and carbamate compounds with IAs and OAs have shown some useful synergistic effect. The joint effect of chlorpyrifos-methyl and esfenvalerate with IAs combinations showed a slight synergism by two IAs after 48h. However, the combination with methomyl resulted in highly synergistic activity after 48h, especially when methomyl was combined with phosphomolybdic acid. On the other hand, the combination of chlorpyrifos-methyl and esfenvalerate with ortho-phosphoric acid and phosphomolybdic acids resulted in antagonistic activity. Regarding the combinations of chlorpyrifos-methyl with OAs, data revealed that 9 of 16 showed synergism while the rest of cases showed antagonism after 48h. The combinations of esfenvalerate with OAs showed synergism in 13 of 16 binary mixtures, and antagonism in 3 cases after 48h. Combinations of methomyl and OAs, was found that both acetic and linolenic acids exhibited high synergistic activity followed by hexanoic and oleic acids. In adittion, antagonistic effect was noticed in binary mixtures of 4 OAs after 48h.

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INTRODUCTION

The cotton leafworm, *Spodoptera littoralis* (Boisduval) is a commonly found pest in different parts of the world. These caterpillars are very polyphagous, causing important economic losses in both greenhouses and open fields on a broad range of ornamental, industrial and vegetable crops. Besides, many populations have acquired resistance towards most insecticide groups (Alford 2000).

Pest control represents a critical factor and highly productive inputs for increasing crop yields and preventing crop losses before and after harvest. Till now chemical control has a main role in pest control programmes in both developing and undeveloping countries. The great majority of pesticides employed in Egypt are used to protect cotton which is still the cash crop for exportation. The often and indiscriminate use of pesticides has led to several adverse consequences and the environmental quality has been deteriorated to a great extent. However, health and environmental problems and increasing insect resistance to many of these synthetic pesticides, clearly indicate that basic research must be directed to search for new and more safer approaches or/and types of pest control agents. One of the most accepted approaches to improve the appliction of broad spectrum synthetic chemical pesticides is the inclusion of suitable additives or adjuvants in formulation (ALLER and DEWEY 1961).

The use of certain additives in pesticide formulations would improve their field performance and increase the bioactivity against insect pests with a consequent decrease in their rate of appliction or/and active ingredient used, which in turn reducing plant protection costs, thereby approaching close to the principle of integrated pest management (IPM) by reducing hazards to the environment. Screening plants for naturally occurring chemicals affecting insects may provide another new extra approach for insect control where many crude plant extracts and derivatives have been tested on notoriously devasting insect species (SALAMA *et al*. 1990 a,b; HEGAZY *et al*. 1992; CISNEROS *et al,* 2002; SABBOUR 2002)

With the recent extensive use of synthetic pesticides, several investigators have been searching for compounds that would increase the effectiveness of the synthetic insecticides against several insect species in addition to reducing the active ingredient of the synthetic insecticides used and consequently led to saving costs, minimizing environmental hazards and assist in resistance management strategies.

Reviewing the litteratures, acids of plant origin could be one of the candidate compounds in this respect, where tannins are present in over half of all plant species and have been considered part of the general group in plant antiherbivore chemistry (HASLAM, 1988). The trichome of chickpea plant secrete an acidic exudate (Khanna-CHOPRA and SINHA, 1987) that may contribute to insect resistance. The reduced pot damage may be correlated with the amount of acidic compounds in the exudate such as malic acid and oxalic acid (SRIVASTAVA and STIVASTAVA, 1989; REMBOLD *et al*. 1990 a,b; YOSHIDA *et al*. 1997). Also, tannins was identified as the major constituent in extracts of *Taxus* sp that caused larval mortality, when screening plants known to display insecticidal activity (GIBSON *et al*. 1995). Therefore the present investigation was carried out aiming to study the combined effect of using various inorganic and organic acids as additives on the toxicity of three synthetic insecticides representing different groups of chemicals against the 4th instar larvae of a lepidopterous polyphagous insect, *S. littoralis*, using leaf-dipping technique.

MATERIALS AND METHODS

MATERIALS

Insect

The larvae used in the present study were obtained from laboratory colony continuously reared away of insecticidial contamination in Sakha Agriculture Research Station, Egypt. Rearing of insects was conducted following the technique described by EL-DEFRAWI *et al*. (1964). Larvae were fed on fresh castor bean Ricinus communis L., leaves until pupation. Moths were fed on 10% sugar solution offered in a piece of cotton tissue soaked in this solution. Each jar was provided with branches of tafla, Nerium oleander, as an oviposition site. The rearing room was kept at constant temperature of 25+2 ºC and relative humidity of 65±5 %, a photoperiod of 16:8 (L:D) h.

Insecticides used

Commercial formulations of the following insecticides, representing different groups, were used in the bioassay experiments.

Organophosphate: Chlorpyrifos-methyl
(Reldan 50% E.C.).
Pyrethroid: Esfenvalerate
(Sumi–Alpha 5 % E.C.).
Carbamate: Methomyl
(Lannate 90% S.P.).

Chemical Additives

Inorganic acids

Hydrochloric HCL	(molecular weight= 36.46)	**Ortho-Phosphoric** H_3PO_4	(m.w.=98.00)
Hydrochloric HCL	(molecular weight= 36.46)	**Ortho-Phosphoric** H_3PO_4	(m.w.=98.00)
Molybdic Mo O_3	(m.w.=143.94)	**Phosphomolybdic** $H_3[P(Mo_3O_{10})_4].x\ H_2O$	(m.w.=1825.25)
Nitric HNO_3	(m.w.=63.01)	**Sulfuric** H_2SO_4	(m.w.=98.08)

Organic Acids

Acetic $C_2H_4O_2$	(m.w. 60.05)	**Maleic** $C_4H_4O_4$	(m.w. 116.07)
Benzoic $C_7H_6O_2$	(m.w. 122.12)	**Oleic** $C_{18}H_{34}O_2$	(m.w. 282.47)
Citric $C_6H_8O_7$	(m.w. 192.13)	**Oxalic** $C_4H_2O_5$	(m.w. 132.07)
D- Glutamic $C_5H_9NO_4$	(m.w. 147.13)	**Palmitic** $C_{16}H_{32}O_2$	(m.w. 256.43)
Gallic $C_7H_6O_5H_2O$	(m.w. 188.14)	**Pyrogallic** $C_6H_6O_3$	(m.w. 126.11)
Hexanoic $C_6H_{10}O_2$	(m.w. 116.16)	**Succinic** $C_4H_6O_4$	(m.w. 118.09)
Lactic $C_3H_6O_3$	(m.w. 90.08)	**Sulfanilic** $C_6H_7NO_3S$	(m.w. 173.19)
Linolenic $C_{13}H_{30}O_2$	(m.w. 278.44)	**Tannic** $C_{27}H_{24}O_{18}$	(m.w. 180.95)

Assessment of synergistic activity of several acids in binary mixtures with synthetic insecticides

This experiment was done to examine the synergistic activity of 22 acids in binary mixtures with certain conventional insecticides against newly moulted 4th instar larvae of *S. littoralis*, using the leaf dipping technique. Fresh castor bean leaves were dipped for 10 seconds in water dilutions of either insecticide only or insecticide–acid combination (100:1, a.i.). The treated leaves were left to dry before being offered to the larvae. The tested larvae were allowed to feed on treated leaves for 24 and 48h. At least five concentrations were prepared for each acid and four replicates with 25 larvae each were used for each concentration. Larvae fed on leaves dipped on water only served as control. Mortality counts were recorded after 24 and 48h and corrected using Abbott's formula (ABBOTT, 1925). The lc-p lines were drawn on log concentration-probit papers and statistically analyzed according to the method adopted by FINNEY (1971). Factor of synergism was calculated according to CHADWICK (1961) formula as follows:-

$$\text{Factor of synergism} = \frac{LC_{50} \text{ of the insecticide alone}}{LC_{50} \text{ of the insecticide in synergised form}}$$

RESULTS AND DISCUSSION

The joint effect of insecticide and inorganic acid (IAs) combinations

Combinations of chlorpyrifos-methyl and IAs

Data in Table 1 show the toxicity of the organophosphorous compound chlorpyrifos-methyl alone and compared with the combined effect when used in binary mixtures with IAs against *S. littoralis* 4th instar larvae at 48h posttreatment. The same performance was almost achieved with superiority of phosphomolybdic acid (1.62 fold) and molybdic acid (1.52 fold). Other tested IAs exhibited slight synergisitic activity (1.3-1.02 fold) except orthophosphoric which resulted in antagonism as manifested by factor of synergism of 0.9 fold.

Table 1. **The joint effect after 48h of combinations of chlorpyrifos-methyl and selected inorganic acids on 4th-instar *S. littoralis* larvae.**

Treatment (Insecticide + Inorganic acids)	**Slope ± S.E.**	**LC_{50} (95% C.L.) (ppm)**	**F.S***
Chlorpyrifos-methyl	2.01 ± 0.37	102.97 (79 – 128.9)	1
Chlo. meth. + Phosphomolybdic	1.58 ± 0.44	63.64 (32.4 – 86.4)	1.62
Chlo. meth. + Molybdic	1.51 ± 0.51	67.66 (1.52 – 277.7)	1.52
Chlo. meth. + Hydrochloric	3.15 ± 0.71	84.41 (44.5 – 121.2)	1.21
Chlo. meth. + Nitric	4.18 ± 0.68	94.99 (77.9 – 109.1)	1.08
Chlo. meth. + Sulfuric	3.05 ± 0.59	103.5 (79.9 – 122.7)	1.02
Chlo. meth. + Ortho-phosphoric	2.69 ± 0.57	105.67 (78.6 –127.5)	0.97

$$\text{* Factor of synergism} = \frac{LC_{50} \text{ of the insecticide alone}}{LC_{50} \text{ of the insecticide in synergised form}}$$

Chadwick (1961)

Combinations of esfenvalerate and IAs

Data in Table 2 show that all IAs exhibited remarkable synergism. Combination of esfenvalerate with phosphomolybdic acids resulted in a highly considerable synergism where F.S. reached 6.85 fold for the prementioned binary mixture. The other five IAs when combined with esfenvalerate resulted in moderate to slight synergism where the F.S. ranged between 1.79 to 1.33 fold.

Combinations of methomyl and IAs

Data in Table 3 show that 5 of the IAs tested in binary mixtures with methomyl resulted in moderate to slight synergism where F.S. reached 3.61, 2.9, 2.14, 1.83 and 1.15 fold for orthophosphoric, sulfuric, nitric, hydrochloric and molybdic acids, respectively. On the other hand phosphomolybdic acid exhibited antagonistic activity when tested in binary mixture with methomyl, recording F.S. of 0.91 fold.

The joint effect of insecticide and organic acid (OAs) combinations

Combinations of chlorpyrifos-methyl and OAs:

Regarding the toxicity of chlorpyrifos-methyl in binary mixtures with OAs at 48h

Table 2. **The joint effect after 48h of combinations of esfenvalerate and selected inorganic acids on 4th-instar *S. littoralis* larvae.**

Treatment (Insecticide + Inorganic acids)	**Slope ± S.E.**	**LC_{50} (95% C.L.) (ppm)**	**F.S***
Esfenvalerate	1.95 ± 0.45	12.37 (9.18 – 16.1)	1
Esfen. + Phosphomolybdic	1.39 ± 0.21	1.8 (1.21 – 2.52)	6.85
Esfen. + Hydrochloric	1.48 ± 0.34	6.88 (3.23 – 9.8)	1.79
Esfen. + Ortho-phosphoric	3.04 ± 0.5	7.78 (5.89 – 9.4)	1.59
Esfen. + Sulfuric	2.03 ± 0.45	8.32 (5.38 – 10.71)	1.48
Esfen. + Nitric	2.26 ± 0.46	8.99 (6.37 – 11.26)	1.37
Esfen. + Molybdic	1.48 ± 0.28	9.24 (6.59 – 12.62)	1.33

$$\text{* Factor of synergism} = \frac{LC_{50} \text{ of the insecticide alone}}{LC_{50} \text{ of the insecticide in synergised form}}$$

Chadwick (1961)

Table 3. **The joint effect after 48h of combinations of methomyl and selected inorganic acids on 4th-instar *S. littoralis* larvae.**

Treatment (Insecticide + Inorganic acids)	**Slope ± S.E.**	**LC_{50} (95% C.L.) (ppm)**	**F.S***
Methomyl	2.72 ± 0.63	156.92 (114.3 – 186.2)	1
Metho. + Ortho– phosphoric	2.17 ± 0.35	43.38 (29.91 – 55.5)	3.61
Metho. + Sulfuric	2.23 ± 0.35	53.96 (39.7 – 67.31)	2.9
Metho. + Nitric	2.01 ± 0.34	73.21 (55.5 – 91.78)	2.14
Metho. + Hydrochloric	3.57 ± 0.6	85.3 (69.2 – 99.07)	1.83
Metho. + Molybdic	5.92 ± 1.02	135.97 (123.5 – 146.8)	1.15
Metho. + Posphomolybdic	2.73 ± 0.76	171.22 (142.7 – 220.1)	0.91

$$\text{* Factor of synergism} = \frac{LC_{50} \text{ of the insecticide alone}}{LC_{50} \text{ of the insecticide in synergised form}}$$

Chadwick (1961)

Table 4. **The joint effect after 48h of organic acids and chlorpyrifos-methyl combinations on 4th-instar *S. littoralis* larvae.**

Treatment (Insecticide + Inorganic acids)	**Slope ± S.E.**	**LC_{50} (95% C.L.) (ppm)**	**F.S***
Chlorpyrifos-methyl	2.01 ± 0.37	102.97 (79 – 128.9)	1
Chlor. meth. + Palmitic	1.31 ± 0.29	52.52 (31.9 – 73.4)	1.96
Chlor. meth. + Pyrogallic	1.65 ± 0.45	62.81 (33.2 – 84.8)	1.63
Chlor. meth. + Tannic	2.08 ± 0.46	66.43 (44.2 – 84.6)	1.54
Chlor. meth. + Oxalic	3.04 ± 0.51	66.59 (51.7 – 79.6)	1.54
Chlor. meth. + Citric	2.1 ± 0.46	66.85 (44.8 – 84.9)	1.54
Chlor. meth. + Maleic	2.48 ± 0.4	76.25 (58.2 – 92.7)	1.35
Chlor. meth. + Gallic	2.08 ± 0.46	79.01 (56.08 – 99.8)	1.3
Chlor. meth. + Benzoic	2.2 ± 0.46	90.02 (68.8 – 122.9)	1.14
Chlor. meth. + Linolenic	2.44 ± 0.56	95.62 (64.1 – 118.5)	1.07
Chlor. meth. + Sulfanilic	2.18 ± 0.47	100.36 (78.4 – 127.9)	0.99
Chlor. meth. + Acetic	2.86 ± 0.58	105.55 (80.3 – 126.1)	0.97
Chlor. meth. + Oleic	3.61 ± 0.63	108.39 (89 – 125.4)	0.95
Chlor. meth. + Hexanoic	2.86 ± 0.46	116.25 (92.4 – 137.6)	0.88
Chlor. meth. + Succinic	1.62 ± 0.52	136.96 (63.3 – 198.9)	0.75
Chlor. meth. + Lactic	3.99 ± 0.61	165.14 (140.8 – 190.9)	0.62
Chlor. meth. + D-Gulatmic	1.59 ± 0.49	300.28 (209.7 – 442.3)	0.34

$$\text{* Factor of synergism} = \frac{LC_{50} \text{ of the insecticide alone}}{LC_{50} \text{ of the insecticide in synergised form}}$$

Chadwick (1961)

posttreatment (Table 4), it was obvious that only 9 out of 16 OAs resulted in synergism, ranging between high synergism (1.96 fold for palmitic acid) to slight synergism (1.07 fold for linolenic acid). In the same time the other 7 OAs exhibited antagonism in their binary mixtures with chlorpyrifos-methyl. However, the antagonistic activity in binary mixtures of the three OAs (lactic, succinic and d-glutamic) obtained at 48h posttreatment.

Table 5. **The joint effect after 48h of organic acids and esfenvalerate combinations on 4th-instar *S. littoralis* larvae.**

Treatment (Insecticide + Inorganic acids)	**Slope ± S.E.**	**LC_{50} (95% C.L.) (ppm)**	**F.S***
Esfenvalerate	1.95 ± 0.45	12.37 (9.18 – 16.1)	1
Esfen. + Tannic	1.27 ± 0.18	0.54 (0.33 – 0.79)	22.94
Esfen. + Gallic	1.37 ± 0.23	1.75 (0.94 – 2.85)	7.07
Esfen. + Pyrogallic	1.69 ± 0.29	3.66 (2.19 – 5.07)	3.37
Esfen. + Succinic	1.38 ± 0.27	4.14 (2.23 – 5.96)	2.98
Esfen. + Oleic	0.7 ± 0.27	5.49 (0.56 – 10.76)	2.25
Esfen. + Maleic	1.48± 0.27	6.53 (4.32 – 8.86)	1.89
Esfen. + Hexanoic	2.18 ± 0.46	7.67 (4.98 – 9.23)	1.61
Esfen. + Oxalic	1.05 ±0.26	8.99 (5.44 – 14.09)	1.37
Esfen. + Acetic	1.32 ± 0.43	9.3 (4.16 – 13.35)	1.32
Esfen. + Linolenic	1.44 ± 0.43	9.32 (4.77 – 12.98)	1.32
Esfen. + Sulfanilic	1.39 ± 0.27	11.35 (8.14 – 16.34)	1.08
Esfen. + D-Glutamic	1.34 ± 0.28	11.79 (8.38 – 17.44)	1.04
Esfen. + Lactic	1.07 ± 0.27	12.1 (7.93 – 20.07)	1.02
Esfen. + Palmitic	2.59± 0.55	13.79 (9.85 – 16.66)	0.89
Esfen. + Benzoic	1.21 ± 0.28	14.9 (10.42 – 25.79)	0.82
Esfen. + Citric	1.04 ± 0.27	17.63 (11.53 – 39.43)	0.7

$$\text{* Factor of synergism} = \frac{LC_{50} \text{ of the insecticide alone}}{LC_{50} \text{ of the insecticide in synergised form}}$$

Chadwick (1961)

Combinations of esfenvalerate and OAs

The combined effect of esfenavalerate in binary mixtures with OAs at 48h posttreatment against 4th instar larvae of *S. littoralis* are shown in Table 5. The data reveals the superiority of tannic acid in synergizing the synthetic pyrethroid esfenvalerate, recording F.S. of 22.94 fold. gallic acid induced high synergistic activity, recording a F.S. of 7.07 fold. On the other hand moderate synergism was achieved by pyrogallic (F.S. = 3.37 fold), succinic (F.S. = 2.98 fold) and oleic (F.S. = 2.25 fold), whereas 8 other acids (maleic, hexanoic, oxalic, acetic, linolenic, sulfanilic, d-glutamic and lactic) resulted in slight synergism where F.S. ranged between 1.89 to 1.02 fold. However, only three organic acids i.e., palmitic, benzoic and citric exhibited antagonistic activity, manifested by F.S. of 0.89, 0.82 and 0.7 fold, respectively.

Combinations of methomyl and OAs

Regarding 48h toxicity data (Table 6), both acetic and linolenic acids exhibited similar performance but of higher magnitude in synergism where the F.S. reached 18.88 and 6.55, respectively. Likewise, the antagonistic activity of gallic, palmitic, citric and pyrogallic acids were confirmed at 48h, recording F.S. of 0.97, 0.87, 0.83 and 0.79, respectively. The data also reveals moderate synergistic activity for hexanoic (F.S. = 3.17), oleic (F.S. = 2.65) and lactic (F.S. = 2.39) in their binary mixtures with methomyl where as the rest of the OAs tested exhibited slight synergistic activity (F.S. 1.78 –1.11).

Discussing the foregoing results, it could be seen that binary mixtures of chlorpyrifos-m, esfenvalerate and methomyl with the IAs induced varying degree of synergism and antagonism when applied against *S. littoralis* larvae.

Table 6. **The joint effect after 48h of organic acids and methomyl combinations on 4th-instar *S. littoralis* larvae.**

Treatment (Insecticide + Inorganic acids)	**Slope ± S.E.**	**LC_{50} (95% C.L.) (ppm)**	**F.S***
Methomyl	2.72 ± 0.63	156.92 (114.35 – 186.2)	1
Metho. + Acetic	1.12 ± 0.19	8.31 (3.84 – 13.31)	18.88
Metho. + Linolenic	1.67 ± 0.41	23.95 (4.34 – 45.66)	6.55
Metho. + Hexanoic	3.13 ± 0.41	49.44 (39.28 – 59.14)	3.17
Metho. + Oleic	2.68 ± 0.42	59.04 (46.42 – 71.71)	2.65
Metho. + Lactic	1.81 ± 0.56	65.52 (6.27 – 130.05)	2.39
Metho. + Sulfanilic	2.31 ± 0.54	87.97 (62.58 – 108.65)	1.78
Metho. + Maleic	2.75 ± 0.56	88.49 (67.64 – 106.09)	1.77
Metho. + Succinic	1.99 ± 0.54	113.22 (84.86 – 141.46)	1.38
Metho. + D-Glutamic	1.47 ± 0.43	126.94 (87.41 – 178.99)	1.23
Metho. + Oxalic	1.73 ± 0.44	129.89 (96.87 – 172.51)	1.2
Metho. + Benzoic	2.26 ± 0.56	133.31 (107.14 – 178.5)	1.17
Metho. + Tannic	3.88 ± 0.65	141.11 (120.7 – 159.02)	1.11
Metho. + Gallic	3.94 ± 0.55	160.59 (140.5 – 179.3)	0.97
Metho. + Palmitic	3.22 ± 0.51	179.67 (155.54 – 204.9)	0.87
Metho. + Citric	4.61 ± 0.89	188.11 (157 – 210.98)	0.83
Metho. + Pyrogallic	3.56 ± 0.65	197.79 (170.6 – 224.6)	0.79

$$\text{* Factor of synergism} = \frac{LC_{50}\text{ of the insecticide alone}}{LC_{50}\text{ of the insecticide in synergised form}}$$

Chadwick (1961)

The highest synergistic activity (> 5 fold), was recorded when esfenvalerate was mixed with phosphomolybdic acid (F.S = 6.85). However, moderate synergistic activity (2-4 fold) was achieved for methomyl in binary mixtures with orthophosphoric acid (F.S. = 3.61), sulfuric acid (F.S. = 2.9) and nitric acid (F.S. = 2.14). Additionally, slight synergism (< 2 fold), was recorded for chlorpyrifos-m in binary mixtures with phosphomolybdic acid (F.S. = 1.62), molybdic acid (F.S. = 1.52), hydrochloric acid (F.S. = 1.21), nitric acid (F.S. = 1.08) and sulfuric acid (F.S. = 1.02), in addition to esfenvalerate plus hydrochloric acid (F.S. = 1.79), ortho-phosphoric acid (F.S. = 1.59), sulfuric acid (F.S. = 1.02), nitric acid (F.S. = 1.08) and molybdic acid (F.S. = 1.52) and methomyl plus hydrochloric acid (F.S. = 1.83) and molybdic acid (F.S. = 1.15).

On the contrary, the reduction of activity or/and antagonism was remarkably recorded in binary mixtures of chlorpyrifos-m plus each of ortho-phosphoric acid (F.S. = 0.97), and also when methomyl was combined with phosphomolybdic acid (F.S. = 0.91).

Little attempts have been recorded in concern of studying the role of IAs and its salts as chemical additives in combinations with insecticides. SALAMA *et al*., (1990 a, b) found that inorganic salts increased the toxicity of *B. thuringiensis* subsp. *kurstaki* in *S. littoralis* and *Agrotis ipsilon* (Hufnagel) by factors ranging from 1.3 to 24.0. Also, DIMETRY and MATTER (1990) found that the inorganic gallic acid at lower and higher concentrations (0.001 – 0.01M), caused significant increase or decrease in the potency of *B. thuringiensis*. Furthermore, it was found that the inorganic boric acid and its salts at various concentrations produced considerable mortality of immature cat fleas (KLOTZ *et al*., 1994 and HINKLE *et al*. 1995), pharaon ants

(KLOTZ *et al*. 1996) and house flies (HOGSETTE and KOEHLER 1992, 1994). RECENTLY, MORRIS *et al*. (1995) found that 12 of the 13 inorganic salts tested in combinations with *B. thuringiensis* subsp., *kurstaki* significantly increased toxicity against bertha armyworm larvae.

Regarding the combined effect of OAs in binary mixtures with insecticides representing different groups, i.e. O.P. (chlorpyrifos-methyl), pyrethroid (esfenvalerate), and carbamate (methomyl), it was obvious that the highest synergistic activity (> 5 fold) was achieved when esfenvalerete was combined with tannic acid (F.S. = 22.94) and gallic acid (F.S. = 7.07), and methomyl was combined with either acetic acid (F.S. = 18.88), or linolenic acid (F.S. = 6.55). Moderate synergistic activity (2 – 4 fold), was recorded for binary mixtures of esfenvalerate and pyrogallic acid (F.S. = 3.37), succinic acid (F.S. = 2.98) and oleic acid (F.S. = 2.25), and methomyl when combined with either hexanoic acid (F.S. = 3.17), oleic acid (F.S. = 2.65) and lactic acid (F.S. = 2.39). However, slight synergistic activity was exhibited when chlorpyrifos-methyl was combined with either palmitic acid (F.S. = 1.96), or pyrogallic acid (F.S. = 1.63), and also when esfenvalerate was combined with maleic acid (F.S. = 1.89) or hexanoic acid (F.S. = 1.61), and too when methomyl was combined with sulfanilic acid (F.S. = 1.78) and maleic acid (F.S. = 1.77).

On the contrary the antagonistic activity was remarkably obvious when the chlorpyrifos-methyl was combined with d-glutamic acid recording F.S. of 0.34 fold. Remarkable antagonism was also recorded for both esfenvalerate and methomyl in their binary mixtures with palmitic acid (F.S. = 0.89 and 0.87) and citric acid (F.S. = 0.70 and 0.83), for both insecticides, respectively at 48h pottreatment.

The highly pronounced synergistic activity of tannic acid in combination with the synthetic pyrethroid esfenvalerate came in agreement with the enhancement of knockdown with pyrethroids in combination with *Taxus* media foliage and extracts that had been reported previously (SHANKS and CHAMBERLAIN, 1988). GIBSON *et al*. (1995) found that tannic acid exhibited activity similar to that of the *Taxus bacata* bark extract. Also, it was recorded that tannic acid inhibits the growth of lepidoptera larvae by depressing the midgut digestive emzymes (KLOCKE and CHAN 1980, KAROWE, 1989). Gut necrosis and major histopathological effect such as lessions and degerative epithelium has been resulted by tannic acid (BERNAYS and CHAMBERLAIN 1980; Steinly and BEREMBAUM, 1985). Furthermore, SALAMA and SHARABY (1985) indicated that tannic acid can act as general toxin that causes degradation of the peritrophic membrane and gut epithelium, the conditions resemble the effect *B. thuringiensis*. More recent work with insect herbivores support the concept that tannins act as toxin and feeding deterrent, particularly for polyphagous insects that do not typically feed on diet rich in tannins (RAUBENHEIMER and SIMPSON 1990, DE VEAU and SHULTZ, 1992).

As for the combined effect of oxalic acid, MITSURU *et al*. (1995) found that oxalic acid had significant growth inhibition on *H. armigera* larvae when included in a semi-artificial diet. The accumulation of oxalic acid is considered to be the mechanisms of *H. armigera* resistance in chickpea. Previous studies revealed that reduced pod damage in chickpea may be correlated with the amount of acidic compounds in exudate secreted by chickpea trichomes, which include malic acid and oxalic acid as major while fumaric acid and citric acid were detected as minor (SRIVASTAVA and STIVASTAVA, 1989 and REMBOLD *et al*. 1990 a,b). The slight synergistic activity of malic acid when combined with chlorpyrifos-methy and esfenvalerate came in agreement with the considerable increase (3.7 fold), in potency of the bioinsecticide Dipel against *A. ipsilon* when 0.5 % malic acid was used as chemical additive (SALAMA *et al*. 1989). A field trial performed with *Spodoptera frugiperda* (J. E. Smith) larvae held on plants within fine gauze bags indicated that application of maize flour granules containing virus + 1% boric acid caused a significant increase in virus-induced mortality compared to application of granules containing virus alone (CISNEROS *et al*. 2002). The oxalic and citric acids scored the highest enhancement in the efficiency of *Beauveria bassiana* and *Metarhizium anisopilae* against the first larval instar of *Phthorimaea operculella* Zeller, (SABBOUR 2002).

Finally, it could be seen that binary mixtures of chlorpyrifos-m, esfenvalerate and methomyl with the IAs and OAs induced varying degree of synergism and antagonism when applied against *S. littoralis* larvae.

RESUMEN

HATEM, A. E., H. B. HOMAM, R. A. AMER, S. S. M. ABDEL-SAMAD, H. A. SALEH, A. I. HUSSIEN. 2009. Actividad sinérgica de varios ácidos en mezclas binarias con insecticidas sintéticos contra *Spodoptera littoralis* (Boisduval). *Bol. San. Veg. Plagas*, **35**: 533-542.

La actividad de las mezclas binarias de algunos ácidos inorgánicos (ÁIs), y orgánicos (ÁOs) con ciertos insecticidas se probaron contra larvas de cuarto estadio de *Spodoptera littoralis* en laboratorio. La mezcla de organofosforados, piretroides y carbamatos con ÁIs y ÁOs resultó tener un efecto sinérgico. El efecto conjunto de clorpirifos-metil, esfenvalerato combinados con los ÁI, mostró una leve sinergia para los dos AI después de 48 horas. Sin embargo, la combinación con metomilo mostró una alta actividad sinérgica a las 48 horas, sobre todo cuando se combinó con ácido phosphomolybdico. Por otra parte, la combinación de metil-clorpirifos y esfenvalerato con ácido orto-fosfórico y ácidos phosphomolybdic resultaron antagónicos. Con referencia a las combinaciones de clorpirifos-metil con ÁOs, 9 de las 16 mezclas binarias resultaron sinérgicas y las 7 restantes antagónicas después de 48 horas. En las combinaciones de esfenvalerato y ÁOs, los datos muestran que en 13 de las 16 mezclas hubo sinergismo y sólo en 3 de ellas a las 48h. En cuanto a las combinaciones de metomilo con los ÁOs, fueron los ácidos acético y linolénico los que presentaron una mayor actividad sinérgica seguidos por los ácidos hexanoico y oleico. Por último, 4 de la mezclas de ÁOs mostraron un efecto antagónico después de 48h.

Palabras clave: Ácidos inorgánicos, ácidos orgánicos.

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