Research Paper



Evaluation of the effect of polyesters containing a curcumin ring system on Bemisia tabaci

Journal of Chemical Research November-December I-6 © The Author(s) 2023 Article reuse guidelines: sagepub.com/journals-permissions DOI: 10.1177/17475198231221434 journals.sagepub.com/home/chl

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Abstract

The whitefly Bemisia tabaci is a destructive insect pest that infects many plants. Finding solutions to reduce the damage associated with whiteflies and their widespread use is of great interest. Therefore, the current research aims to synthesize four polyesters containing a curcumin ring system and investigate their effects against B. tabaci. The synthesized polyesters killed whitefly eggs and their nymphs. Polyester containing a methoxy group (P3) showed the best performance (80.3%) toward the mortality of insect eggs among all the tested polymers. Polyester containing a 4-hydroxybenzaldehyde moiety (P2) showed the lowest mortality efficiency (50.9%) against whitefly eggs after 72 h of treatment. The effect of polyester concentration on the mortality of insect nymphs varied during the treatment period. The mortality rate of nymphs after P3 treatment was the highest (78.0%), whereas that after P2 treatment was the lowest (46.9%). The polyester type, concentration, and treatment duration significantly affected the insect nymph mortality rate. Polyester containing a methoxy group for 72 h resulted in the highest mortality rate (90.0%) against whitefly nymphs.

Keywords

Bemisia tabaci, curcumin analogs, mortality rate, phenols, polyesters

Date received: I November 2023; accepted: 4 December 2023



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Figure 1. Structures of bis-phenols 1-4 and 2,6-pyridinedicarbonyl dichloride (5).

Introduction

The whitefly Bemisia tabaci (B. tabaci; Homoptera: Aleyrodidae) is a destructive insect pest that infects many plants such as eggplants, cucumbers, and cotton, for example.¹⁻⁴ Yellow spots on the leaves are formed due to nymphs and adults sucking the juice from the plants' vegetative parts. The developed sites can unify to produce irregular yellow areas due to chlorophyll deficiency.5-8 In addition, the insect saliva secreted during the feeding process causes the cessation of leaf growth. As a result, the leaves shrink in size, die, and eventually fall.9-12 The feeding process causes dust and fungi to accumulate on the respiratory stomata on the damaged surface of plant leaves, which negatively affects the photosynthesize and transpiration processes.¹¹ Whiteflies also facilitate the transition of plant viral diseases from infected plants to healthy ones and have caused a global decrease in the production of crops and vegetables in many parts of the world. Finding solutions to reduce the damage associated with whiteflies and their widespread use is of great interest; in particular, research has been directed toward finding an alternative to pesticides because of their ability to gain rapid resistance to them.13-16

Polyesters containing different functional groups and aromatic moieties have various applications.¹⁷ Efficient antioxidants can be derived from hydroxyl and carbonyl groups present in them. The aromatic moieties within polymeric chains increase their stability.¹⁸ In addition, the presence of heteroatoms (e.g. nitrogen and oxygen) containing asymmetric electron pairs can significantly increase their biological effectiveness. Polyesters resemble curcumins, which have lower toxicity than many pesticides.^{19–25} Therefore, this study aimed to evaluate the *in vitro* effect of polyesters containing curcumin moieties on whitefly eggs and nymphs.

Results and discussion

Synthesis of polyesters PI-P4

Bis-phenols 1–4 and 6-pyridinedicarbonyl dichloride (Figure 1) were used as precursors to produce polyesters



Figure 2. Structures of synthesized polyesters P1-P4.

P1–P4 (Figure 2). Bis-phenols 1–4 were prepared using a literature procedure.²⁶ Reaction of appropriate bis-phenols 1–4 and phenolphthalein in the presence of excess from 5 (two-mole equivalents) under a basic condition gave the corresponding polyesters P1–P4. It's worth mentioning that the proportion of bis-phenols 1–4 to phenolphthalein was equal (i.e. 1:1). Phenolphthalein and pyridine 2,6-dicarboxylic acid were selected to be included in the polymers to add extra functionality and improve the solubility of the prepared polymers. Phenolphthalein is a pH-sensitive dye that can be used to detect changes in the acidic environment around the whitefly. Pyridine 2,6-dicarboxylic acid is a chelating agent that can bind to metal ions and disrupt the whitefly's metabolism.

Polyester	Mortality rate (%) at different concentrations (%) of polyesters			Average mortality (%)
	5	10	15	
PI	59.2	61.8	64.9	61.9
P2	48.0	52.4	52.4	50.9
P3	67.4	83.5	90.0	80.3
P4	59.5	61.9	77.4	66.3
Average mortality (%)	58.5	64.9	71.2	

 Table I. Effect of polyesters PI-P4 on the mortality rate of whitefly eggs.

Effect of polyester, LSD (0.01) = 9.25. The effect of polyester

concentration, LSD (0.01) = 8.01. The interaction between the type of chemical compound and concentration, LSD (0.01) = 16.03. LSD: least significant difference.

The structures shown for polymers P1–P4 in Figure 2 are only representative, as a 1:1 mixture of appropriate bisphenol **1–4** and phenolphthalein was used. Therefore, it is not assumed that the incorporation of these compounds occurs alternately. The prepared polymers could contain one of the bis-phenols and the phenolphthalein in approximately equal proportion.

Effect of polyesters PI-P4 on whitefly eggs

The synthesized polyesters P1-P4 were evaluated to assess their mortality rates in whitefly eggs (Table 1). P3 had a significantly higher mortality rate against whitefly eggs than the others, with an average of 80.3%. The methoxy group in P3 may be responsible for its high efficiency. In contrast, P2, which contained 4-hydroxybenzaldehyde, showed the lowest (50.9%) mortality rate against whitefly eggs, even after a long duration of treatment (up to 72 h). Polyesters P1 and P4 led to similar mortality rates of 61.9% and 66.3%, respectively, owing to the similarity of their structures. The mortality rate of whitefly eggs increases as the polyester concentration increases. For example, the mortality rate of whitefly eggs was 90.0% when P3 was used at a concentration of 15%, compared with 83.5% at 10% and 67.4% at 5%. The whitefly egg mortality rate increased as the number of active ingredients within the polyesters increased. However, no significant difference was observed between the average mortality rates obtained at 10% and 15% concentrations.

Effect of polyesters PI-P4 on whitefly nymphs

Next, we investigated the impact of polyesters P1–P4 on the mortality rate of whitefly nymphs (Table 2). Using different polyesters resulted in a significant variation in the mortality rates of whitefly nymphs. P3 led to the highest mortality rate, with an average of 78.0%. In contrast, P2 had the lowest mortality rate, averaging 46.9%. The concentration of polyesters plays a vital role in determining the mortality rate. For example, the mortality rates of whitefly nymphs after P3 treatment were 80.4% and 83.0% at concentrations of 10% and 15%, respectively. However, there

Table 2.	Effect of	of polyesters	PI-P4	on the	mortality	rate of
whitefly n	ymphs.					

Polyester	Mortality rate (%) after different concentration (%) of polyesters			Average mortality (%)
	5	10	15	
PI	52.2	55.2	59.1	55.5
P2	47.1	46.6	47.0	46.9
P3	70.5	80.4	83.0	78.0
P4	47.7	52.8	61.0	53.8
Average mortality (%)	54.4	58.7	62.5	

The percentage was calculated according to equation (1). The effect of polyester concentration, LSD (0.01) = 5.05. The effect of polyester, LSD (0.01) = 5.83. The interaction between polyester and concentration, LSD (0.01) = 16.44. LSD: least significant difference.

 Table 3. Effect of duration of treatment on the mortality rate of whitefly nymphs using polyesters P1–P4.

Polyester	Mortalit differen	y rate (%) a t duration (lfter h)	Average mortality (%)	
	24	48	72		
PI	43.6	52.I	70.8	55.5	
P2	36.6	50.6	53.6	46.9	
P3	59.0	84.8	90.0	78.0	
P4	41.0	58.7	61.8	53.8	
Average mortality (%)	45.0	61.6	69.0		

The effect of polyester concentration, LSD (0.01) = 5.89. The effect of time, LSD (0.01) = 5.10. The interaction between polyester concentration and time, LSD (0.01) = 10.21. LSD: least significant difference.

was no significant difference in the average mortality rate of polyesters when 10% (58.7%) or 15% (62.5%) concentrations were used. The results presented in Table 2 are following those recorded in Table 1.

Effect of duration of treatment on whitefly nymphs using polyesters P1-P4

The time of treatment (24–72 h) of whitefly nymphs with polyesters P1–P4 was investigated (Table 3). The average mortality rate was 69.0% after 72 h of treatment, significantly higher than that obtained at 24 or 48 h. The concentration of polyesters and the duration of treatment affected the mortality rate of whitefly nymphs. P3 showed the highest mortality rate (90.0%) after 72 h of treatment, which was significantly higher than that observed in the presence of other polymers. P2 had the lowest mortality rate (36.6%) after 24 h of treatment.

Effect of the average concentration of polyesters PI-P4 and duration of treatment on whitefly nymphs

There was no significant difference in the mortality rate of whitefly nymphs (67.3%, 69.4%, and 70.4%, respectively)

of polyesters and time on the mortality rate	e of whitefly nymphs
I able 4. Effect of the interaction between	the concentration

Concentration (%)	Mortality rate (%) after different duration (h)			Average mortality (%)	
	24	48	72		
5	36.5	59.3	67.3	54.4	
10	45.6	61.1	69.4	58.7	
15	52.9	64.3	70.4	62.5	
Average mortality (%)	45.0	61.6	69.0		

The effect of polyester concentration, LSD (0.01) = 8.95. The interaction between polyester concentration and time, LSD (0.01) = 15.51. The effect of time, LSD (0.01) = 5.10. LSD: least significant difference.

Table 5. Effect of the interaction of polyester type,

 concentration, and treatment time on the mortality rate of

 whitefly nymphs.

Polyester	Concentration (%)	Mortal differe	Average mortality		
		24	48	72	(%)
PI	5	35.0	53.7	68.7	55.6
	10	45.0	49.9	70.5	
	15	50.8	52.8	73.8	
P2	5	33.2	53.5	54.6	46.9
	10	37.2	49.I	53.5	
	15	39.2	49.I	52.7	
P3	5	46.9	74.5	92.0	78.0
	10	61.2	90.0	90.0	
	15	68.9	90.0	90.0	
P4	5	31.0	55.4	56.5	53.8
	10	39.2	55.4	63.8	
	15	52.8	65.2	65.2	
Average mortality (%)		45.0	61.6	69.0	

The effect of concentration, LSD (0.01) = 5.10. The effect of time, LSD (0.01) = 5.1. The effect of the interaction of the three factors (type, concentration, and time), LSD (0.01) = 15.48. The effect of polyester, LSD (0.01) = 5.16. LSD: least significant difference.

at different concentrations (5%, 10%, and 15%, respectively) of polyesters P1–P4 used for 72 h (Table 4). After 24 h of treatment, using the 5% concentration led to the lowest mortality rate (36.5%).

Finally, the effects of each polyester's type, concentration, and treatment duration on the whitefly nymph mortality rate were investigated (Table 5). No significant difference was found in the mortality rate when different concentrations (5%, 10%, and 15%) of P3 were used. The highest mortality rate (92.0%) was achieved when P3 was used at a concentration of 5% after 72 h of treatment. P4 at concentrations of 5% and 10% after 24 h of treatment resulted in the lowest mortality rates, at 31.0% and 39.2%, respectively.

The current study is the first to investigate the effect of modified polyester on *B. tabaci*. Polyesters containing a curcumin ring system significantly affect the mortality rate of whitefly eggs and nymphs. The mortality rate of whitefly eggs and nymphs increased as the concentration of

polyesters increased. Among the tested polyesters, the polymer containing a methoxy group led to the highest mortality rate of whitefly nymphs. In addition, its effectiveness increased as the concentration and duration of treatment increased, owing to the presence of the methoxy group.²⁷ The interaction between polyester concentration and the treatment time also affected the mortality rate of whitefly nymphs. The highest mortality rate was observed at a concentration of 5% after 72 h of treatment.

Polyesters are environmentally friendly insecticides.^{28,29} They are biodegradable and do not leave any harmful residues. Polyesters can be combined with other insecticides to achieve a synergistic effect. Polyesters can be used as a foliar spray or applied to the soil. The mechanism of the mode of action of polyesters against whiteflies is not fully understood. However, polyesters may disrupt the feeding or reproductive behavior of whiteflies. However, more research is still needed to be able to confirm. In addition, the effectiveness of polyesters against whiteflies in different field conditions needs to be performed. Moreover, using polyesters combined with other insecticides to achieve a synergistic effect must be investigated.

Conclusions

Four polyesters were synthesized, and their effectiveness against *B. tabaci* was evaluated. The polyester containing a methoxy group was the most effective for killing whitefly eggs and nymphs. At a 10% or 15% concentration, such polyester caused a whitefly egg and nymph mortality rate of 90%. The methoxy group (electron donor) may explain the high efficiency of this polyester. Polyesters containing a curcumin ring system can be used as effective and environmentally friendly insecticides against whiteflies.

Materials and methods

General

Chemicals and reagents (analytical grade) were purchased from Merck (Gillingham, UK) and used without further purification. Infrared (IR) spectra were recorded on a Shimadzu FTIR-8400 Affinity spectrometer (Shimadzu, Kyoto, Japan). The experiments were conducted at the Department of Plant Protection, College of Agriculture, and the Department of Chemistry, College of Science, University of Basrah, from January to June 2022. Eggplant leaves infected with whiteflies were obtained from the greenhouses of the College of Agriculture. Phenols **1–4** were prepared based on a literature procedure, and their structures were as those reported previously.²⁶

Preparation of polyesters P1-P4

Triethylamine (1.1 mL, 8.0 mmol) was added to a stirred solution of phenols 1-4 (Figure 1; 2.0 mmol) in dichloromethane (DCM; 50 mL) containing phenolphthalein (0.636 g, 2.0 mmol) in a three-slot glass beaker at 20 °C. The inert atmosphere (dry nitrogen) was used while the mixture was stirred for 1.5 h at 10 °C to ensure complete

dissolution of the bis-phenol and phenolphthalein in the solvent. A solution of **5** (0.816 g, 4.0 mmol) in DCM (50 mL) was injected into the mixture in batches for 1 h while the temperature was maintained at 10 °C. The stirred mixture was left for 24 h at 10 °C and then poured into hexane (300 mL). The precipitated polymer was filtered, washed with hexane, and dried at 40 °C for 3 h in a vacuum oven to obtain viscous-like materials (Figure 2). P1—IR (KBr): 2924, 1755, 1647, 1359, 1508, 1435, 1277, and 1157 cm⁻¹. P2—IR (KBr): 2924, 1759, 1667, 1597, 1570, 1435, 1385, 1265, and 1165 cm⁻¹. P3—IR (KBr): 2929, 1758, 1603, 1512, 1465, and 1249 cm⁻¹. P4—IR (KBr): 2924, 1759, 1605, 1508, 1485, 1254, and 12,223 cm⁻¹.

Effect of polyesters on whitefly eggs

Sterile plastic Petri dishes (9 cm diameter) were used. A layer of sterile medical cotton moistened with water was added to each Petri dish and covered with an eggplant leaf (5 cm), which was washed with water to remove any impurities and traces of infection caused by whiteflies. Five pairs of whitefly adults (male and female) were transferred and left inside the cages for 24 h to lay eggs. The whitefly eggs (10 eggs) were left on each plate over eggplant leaves and sprayed with different concentrations (5%, 10%, and 15%) of polyesters (P1, P2, P3, and P4) at an average of 1 mL/dish using a sterile syringe. The control experiment involved dimethylformamide (1 mL per dish), and all experiments were performed in triplicate. The mortality rate of the whitefly eggs was calculated using the Orell and Schneider Equation (equation (1))

Treatment mortality rate –

Mortality rate (%) = $\frac{\text{Mortality rate in control}}{100 - \text{Mortality rate in control}} \times 100^{(1)}$

We studied the mortality rate of whitefly eggs and performed statistical analyses to assess the effect of polyesters on their mortality rate.

Effect of polyesters on whitefly nymphs

Five pairs of adults (male and female) were allowed to mate in cages. The eggs laid were left to let the nymphs come out. Ten nymphs were placed in sterilized Petri dishes and sprayed with different concentrations (5%, 10%, and 15%) of P1–P4 (1 mL/dish). Dimethylformamide (1 mL/dish) was used as the control. The experiments were performed in triplicate. The mortality rate of whitefly nymphs was evaluated after various treatment durations (24, 48, and 72 h) using equation (1). Statistical data were examined to assess how polyesters affect the mortality rate among the nymph population.

Statistical analysis

The GenStat Software Package was utilized for performing the statistical analyses.³⁰ To analyze the impact of polyesters on whitefly eggs, a two-factor analysis of variance (ANOVA) was conducted, which involved examining the type and concentration of the polyester. An analysis was conducted on the impact of polyester type, its concentration, and treatment duration on whitefly nymphs using a three-factor ANOVA. A significance level of 0.01 was utilized to assess any noteworthy differences between the treatments. To compare the mean differences between different treatments, the least significant difference (LSD) test was employed. This type of statistical analysis is typical in agricultural research.^{31,32}

Author contributions

Conceptualization: HMRM, HAA, BAA, and BAS; methodology: HMRM, HAA, BAA, and BAS; formal analysis: HMRM, HAA, BAA, BAS, NLH, and GAE-H; investigation: HMRM, HAA, BAA, and BAS; data curation: HMRM, HAA, BAA, BAS, NLH, and GAE-H; writing: HMRM, HAA, BAA, BAS, and GAE-H. All authors have read and agreed to the published version of the manuscript.

Declaration of conflicting interests

The author(s) declared no potential conflicts of interest with respect to the research, authorship, and/or publication of this article.

Funding

The author(s) disclosed receipt of the following financial support for the research, authorship, and/or publication of this article: We thank the University of Basrah for the technical support. GAE-H acknowledges the support from the Researchers Supporting Project (number RSP2023R404), King Saud University, Riyadh, Saudi Arabia.

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