

The effect of selected UV absorber on the photodegradation of deltamethrin and its insecticidal efficacy against 4th instars larvae of mosquito *Culex pipiens*

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Abstract: This research aims to investigate if by adding the UV absorber to deltamethrin, its efficacy vis-à-vis mosquito control could be improved and its residual toxicity could be extended after irradiated to simulating UV-sun radiation. Fabric cotton discs treated with deltamethrin admixed with the selecting UV absorber were exposed to simulating sunlight for different time. According to the results, the LT_{50} of deltamethrin extracted from the fabric cotton discs against 4th instars mosquito larvae were ranged from 73.65 to 551.1 min. Whereas, the LT_{50} of deltamethrin applied alone was 32.26 min. This data indicated that the UV absorbers improved the deltamethrin residual toxicity than deltamethrin alone. Regarding to the LC_{50} and the toxicity index values recorded of deltamethrin alone or in a mixture with the tested UV absorbers, the mixture of deltamethrin with menthyl anthranilate was the most toxic mixture followed by the mixture of deltamethrin with tannic acid then deltamethrin with scopoletin and gallic acid.

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1. Introduction

Pesticides are used extensively in agriculture, as their application is still the most effective means for controlling pest populations. However, overexposure to pesticides worldwide has been accompanied with problems related to toxic and genotoxic effects at sublethal concentrations to beneficial arthropods and non-target organisms, and health risks for humans (Dearfield *et al.*, 1999 and Bolognesi, 2003). Moreover, extensive and long-term use of pesticides may lead to insecticide resistance problems (Toshio and Scott, 2003 and Kakani, *et al.*, 2010). Deltamethrin; (S)- α -cyano-3-phenoxybenzyl-*cis*-(1R,3R)-2,2-dimethyl-3-(2,2-dibromovinyl)-2,2-dimethyl cyclopropanecarboxylate is a synthetic pyrethroid insecticide well known in the late 1970s and early 1980s as NRDC161 and decamethrin. The insecticide is active against a wide range of insects which attack crops, animals, and mankind. The greater stability of this compound than other earlier alternative pyrethroids has made it adequate for uses requiring longer residual activity (Bengston *et al.*, 1983). Currently deltamethrin is recommended by the World Health Organization Pesticide Evaluation Schemes (WHOPES) to defeat insect transmitted diseases such as malaria and yellow fever. Insecticide-treated nets impregnated with deltamethrin have become one of the most promising interventions to prevent malaria in highly endemic areas (Hougard, *et al.*, 2003 and Sarita, *et al.*, 2011).

In addition, deltamethrin is recommended in indoor residual spray programs. Applying insecticides that are lower in active ingredient content than declared could result in monetary loss and application of a sublethal dose of insecticide, leading to ineffective control and promotion of the development of resistance. Also, the most important factor affecting net effectiveness under field conditions is the residual concentration remaining on the net impregnated with deltamethrin that subjected to sunlight. Therefore, there are several attempting to improve the residual activity of deltamethrin insecticide and its stabilization against sun-radiation made by using photo stabilizer additive as adjuvant in the formulation such as benzophenone derivatives (Hussain *et al.*, 1990 and Hussain *et al.*, 1994). The objective of this research is to investigate if by adding the UV absorber to deltamethrin, its efficacy vis-à-vis mosquito control could be improved and its residual toxicity could be extended after irradiated to simulating UV-sun radiation.

2. Material and Methods

Determination of the effect of the organic compounds used as UV absorber on the stability of deltamethrin applied to cotton fabric screen.

Chemicals

All UV absorbers used during the course of studies are tabulated in Table (1).

Table 1. Chemical name of the organic compounds and green tea extracts used as UV absorber and its code number

Code no.	Name	Produced by
A ₃	Tannic Acid	BDH
A ₅	Catechin (3,5,7,3',4' pentahydroxy flavone)	Serva
A ₇	Chlorogenic acid	Serva
A ₉	Ferulic acid	Serva
A ₁₀	Scopoletin [7-hydrox-6-methoxy coumarin]	Serva
A ₁₃	Procatecuic acid (3,4-dihydroxy benzoic acid)	BDH
A ₁₄	Gallic acid	Merck
A ₁₇	Para amino benzoic acid	Merck
A ₁₈	Menthyl anthranilate	Aldrich
A ₂₅	2-hydroxy-4-methoxy benzophenon	Aldrich

Pesticide grade organic solvents; Acetone, dioxan, ethylene glycol and Methanol. Poly ethylene glycol (M_r 20000; Applied Science state College, PA). The active ingredient deltamethrin technical grade with purity of 97% was supplied by Agrochem Company, Alexandria, Egypt. White cotton (100%) fabrics were purchased from local market in Alexandria (Egypt).

Instrumentation

ELISA experiments were performed in 96-well microplates (Nunc, Roskilde, Denmark), and absorbance measurements were carried out using a Labsystems Multiskan EX microplate reader (BIO-TEC Instrument Inc., Winooski, VT) and M-1000 microplate shaker with incubator (MedTec Inc., Hillsborough, NC). Photodegradation experiments were carried out by use of a UV sun radiation lamp BHRF, 220 V, 300 W, Nippon, H.I.D. Self Ballasted mercury lamp, E40, 394992 (Tokyo, Japan). Controlled temperature water bath (KÖHERMANN, Germany). Incubator (Heraeus-Industrietechnik, Kleinostheim, Germany). Oven (Heraeus-Industrietechnik, Kleinostheim, Germany).

Screening of UV absorbers mixed with deltamethrin at ratio of 1:1 W/W on cotton discs under simulating UV sun radiation

Irradiation of deltamethrin impregnated cotton target with simulating UV sun radiation was carried out according to method described

by Hussain *et al.*, (1990) with slightly modification. Circle cotton targets 2 cm diameter were bunched out from white cotton (100%) fabrics and treated with aliquot of insecticide [50 μ L dioxan containing 100 μ g deltamethrin mixed with 100 μ g tested UV absorber]. Each treatment replicated three times. After the solvent had been evaporated, the cotton target were placed on aluminium spread sheet placed on stainless steel platform provided with cooling system for the control and maintenance of a constant temperature of 35 ± 1 °C. The platform was positioned under a UV sun radiation lamp (300 W, H. I. D. Nippon, mercury lamp). The lamp emitted radiation simulating the spectral distribution of natural sunlight. The lamp is designed to provide radiation intensity equivalent to mid-day natural sunlight ($1\text{ kW m}^{-2} = 1.42\text{ cal cm}^{-2}\text{ min}^{-1}$) at the irradiated surface when it is adjusted 50 cm above the surface. The lamp was positioned 12.5 cm above the samples and provided radiation intensity equivalent to approximately 16 times that mid-day natural sun light. The fabric cotton discs treated with deltamethrin and UV absorber were replicated three times and irradiated for a period 0.0, 45, 90, 180, and 360 min. to give simulation period approximately to 0.0, 12, 24, 48 and 96 hrs of the mid-day natural sunlight Fifteen cotton discs were irradiated as mentioned above each containing 100 μ g deltamethrin to calculate the half life (t_{50}) of insecticide as control samples. Three cotton discs each containing 100 μ g deltamethrin were kept in the dark at 35 ± 1 °C in the incubator as control sample to examine the effect of the temperature on the loss of insecticide.

Deltamethrin extraction and sample preparation

The deltamethrin remained as parent compound after had been irradiated on cotton targets and extracted twice with 2 ml acetone for each time by shaking 4min/each time. Acetone extracts were combined, and then two drops (15-25 μ L) of ethylene glycol as trap solvent was added to each vial. To avoid glass adsorption of deltamethrin; the vials were treated with 5% (w/v) poly (ethylene glycol) (PEG; molecular weight 20000), according to the method described by Helmuth *et al.* (1983). The remaining pesticide residues were dissolved by addition of 1ml methanol to each vial after the acetone had been stripped by stream of N₂ then vials were kept at 0.0 °C until the monitoring of deltamethrin concentration by enzymatic-linked immunosorbent assay

technique according to the method described by Soltan *et al.* (2009).

Bioassay test of deltamethrin against mosquito *Culex pipiens*

Insect tested

The mosquito culture was reared and collected from the culture of Pesticide Chemistry Department, Faculty of Agriculture, Alexandria University, Egypt, and was subsequently maintained under laboratory conditions.

Residual toxicity test for the effective UV absorbers mixed with deltamethrin

The fourth instar larvae of *Culex pipiens* were used to determine the insecticidal activity [residual toxicity] of acetone extracted of deltamethrin either applied to cotton discs individual or in mixture with the effective UV absorbers. The dipping method was used as a test technique to estimate the residual toxicity. This test was carried out according to the method described by Georghiou *et al.* (1966). Generally, each of the effective ten UV absorber compounds was combined with deltamethrin and applied to the cotton fabric disc at ratio [1:1 active ingredient w/w] as well as deltamethrin was applied alone to study the residual toxicity of deltamethrin against mosquito after irradiated to simulating UV-sun light at deferent irradiation time 0.0, 45, 90, 180 and 360 minutes. Determination was carried out by addition of 50 µl of the methanol extract from each cotton fabric disc to vessels containing 100 ml of distilled water containing ten fourth instars larvae of *Culex pipiens* in three replicates. The percent mortality resulting from each treatment was recorded after 24 hours and plotted against time of irradiation on logarithmic probit scale. The time of irradiation to deposit concentration of deltamethrin for the death of fifty percent of the larvae (LT_{50}) was determined directly from the time-mortality regression line in terms of min. as described by Finney (1971).

Toxicity index test

According to method recommended by WHO (1963), the fourth instar larvae of *Culex pipiens* were used to determine the insecticidal activity of deltamethrin alone and deltamethrin combined with any of ten UV absorber compounds. Percentage of mortality was

recorded after 24 hours, and then plotted versus the dosage on logarithmic probit scale paper and the data were subjected to probit analysis using the method of Finney (1971). The concentration required 50% death of the larvae (LC_{50}) was determined directly from the concentration mortality regression line in terms part per million (ppm). In all tests, percent mortality were corrected by abbot's formula (Abbott, 1925). The synergism or antagonism was calculated from toxicity index as described by El-Sebae *et al.* (1964) as follow:

$$\text{Tox. I.} = \frac{\text{Deltamethrin } LC_{50}}{\text{Deltamethrin : UV absorber [1:1 a.i W/W] } LC_{50}} \times 100$$

3. Results and Discussion

Persistence and stabilization of deltamethrin on cotton target fabric

Due to the high susceptibility of mosquito larvae to synthetic pyrethroid insecticides, bioassay technique using the 4th instars mosquito larvae, *Culex pipiens* was used in the present investigation. Bioassay test was carried out in order to determine which of the selecting UV absorbers according to their half life, has the longest residual activity and how the bioassay test was correlated with the ELISA technique.

Result illustrated in Table (2) summarized the residual effect of deltamethrin extracted from cotton target exposed to simulating sunlight for different time against 4th instars mosquito larvae. The LT_{50} of deltamethrin was 32.26 min. with confidence limit 42.59 - 24.34 min in comparison to half life value estimated by ELISA technique (36.1 min). Many study reported that the active deltamethrin-cis [1R, 3R; alpha S] when subjected to sunlight as thin film the *trans*-[1R, 3S; alpha S] and - [1S, 3R; alpha S] isomers were formed as well as (α -S, 1S *cis* isomer) and these isomers were less active than the parent deltamethrin to insect and mice (Ruzo *et al.*, 1977 and Maguire, 1990).

This result indicated that the ELISA technique was suitable to detect the effective isomer more than other inactive isomer and this result was supported by the earlier studies carried out by Lee *et al.*, (2002) which mentioned that the antibody binding is directed more toward the 1R-*cis* configuration which considered the active isomer.

Table 2. LT_{50} Values and half life values for certain UV absorbers mixed with deltamethrin at ratio [1:1 w/w] determined by the 4th Instars larvae of *Culex pipiens* and ELISA technique.

Tested mix.	LT_{50} min ^a	Confidence limits	Slope	Half life min. ^b
DM technical	32.26	24.340 - 42.589	-1.574455	36.1
DM + A ₃	243.9	186.91 - 319.04	-1.383609	178.30
DM + A ₅	208.9	155.86 - 280.88	-1.122354	256.2
DM + A ₇	139.4	118.18 - 164.34	-1.846212	177.70
DM + A ₉	300.7	198.2 - 459.8	-1.111986	319.14
DM + A ₁₀	551.1	379.8 - 690.5	-3.34820	501.09
DM + A ₁₃	73.65	60.300 - 89.9	-1.733612	259.40
DM + A ₁₄	497.8	354.38 - 701.29	-1.900104	383.76
DM + A ₁₇	364.6	290.83 - 457.75	-2.25123	377.66
DM + A ₁₈	364.6	290.83 - 457.74	-2.25123	260.574
DM + A ₂₅	80.34	64.052 - 100.64	-1.374436	172.24

a: deltamethrin half life (LT_{50}) detected by *Culex pipiens*

b: deltamethrin half life detected by enzyme linked immunosorbent assay

On the other hand, the LT_{50} of deltamethrin mixed with the selecting UV absorber ranged from 73.65 to 551.1min. This data indicated that the residual toxicity of deltamethrin was less than other mixtures containing any of the UV absorbers selected for this test.

Addition of UV-stabilizers A₅, A₇, A₁₃ and A₂₅ to deltamethrin gave superior improving of the deltamethrin persistence during the irradiation to simulating sunlight as measured by ELISA technique as half life ($t_{0.5}$) but these were not matched by those half life values obtained from insecticidal activity against mosquito expressed as LT_{50} . Other UV absorbers such as A₃, A₁₀ and A₁₄, had a greater LT_{50} than half life estimated by ELISA technique. These phenomena indicated that A₃, A₁₀ and A₁₄ might be having a synergistic effect on deltamethrin insecticidal activity and the other UV absorbers such as A₅, A₇, A₁₃ and A₂₅ having antagonistic effect on deltamethrin against mosquito larva.

Insecticidal activity of deltamethrin and its mixture with selected UV absorber against the 4th instars' larvae of mosquito

Regarding to the variation observed for the persistence studies between the ELISA technique and the bioassay technique using the fourth instars larvae of mosquito the acute toxicity of deltamethrin either applied individual or in a mixture with the selecting UV absorbers were evaluated against the 4th instar larvae of *C. pipiens*. Table (3) represents the LC_{50} as well as the toxicity index values of the tested chemicals. The mixture of deltamethrin with A₁₈ was the most toxic mixture followed by the mixture of deltamethrin with A₃ then deltamethrin with A₁₀ and A₁₄.

Table 3. LC_{50} Value and toxicity Index for certain UV absorber with deltamethrin at molecular ratio [1:1] against the 4th Instars larvae of *Culex pipiens*.

Tested mix. ^a	LC_{50} ppm	Slope	Confidence limits 95%	Tox. I. ^b
DM technical ^a	0.00033	0.78	0.00051 - 0.00022	100.0
DM + A ₃	0.00027	0.83	0.000475 - 0.000149	124.4
DM + A ₅	0.00067	0.97	0.001 - 0.00044	50.15
DM + A ₇	0.00034	0.789	0.00060 - 0.00019	96.8
DM + A ₉	0.00042	1.14	0.00061 - 0.00028	80.0
DM + A ₁₀	0.00030	0.796	0.00053 - 0.00016	111.6
DM + A ₁₃	0.00196	1.31	0.002647 - 0.00146	17.1
DM + A ₁₄	0.000304	0.912	0.000506 - 0.000181	110.5
DM + A ₁₇	0.00048	0.918	0.000765 - 0.000305	70.00
DM + A ₁₈	0.00026	0.805	0.000473 - 0.000143	129.2
DM + A ₂₅	0.00076	0.825	0.000185 - 0.000501	44.21

a: Mixture of deltamethrin and selected UV absorber

b: toxicity index = LC_{50} of deltamethrin / LC_{50} of deltamethrin + tested UV, absorber [1:1w/w]

However, the LC_{50} values and the toxicity index of deltamethrin mixed with the other UV absorbers against *C. pipiens* were decreased comparable to deltamethrin. The worst insecticidal activity was recorded for the mixture of deltamethrin + A₅ and deltamethrin + A₁₃. Both mixture decreased the toxicity of deltamethrin against fourth instars larvae

by two to five time, respectively, than the deltamethrin applied without UV absorber. This mean, that both UV absorbers might have antagonistic effect rather than other UV absorbers, although the addition of both UV absorbers resulted in an enhancement in the persistence of deltamethrin on the cotton fabric disc when exposed to simulating sunlight and measured by ELISA technique.

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