Photodegradation of Deltamethrin and Fenvalerate under Simulated Solar Light Irradiation and Identification of Photoproducts

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Deltamethrin and Fenvalerate are synthetic pyrethroids insecticides. There are many applications for pyrethroids, increasingly ranging from agricultural uses to home pest control, with a probability to contaminate aquatic environments. During exposure to solar natural light, pyrethroids are broken down and produced photoproducts in environment. In this work the photodegradation and environmental fate of these pyrethroids under simulated natural conditions were investigated. The major photoproducts and degradation intermediates were identified by gas chromatography-mass spectrometry analysis. On the basis of the structurally identified photoproducts a possible degradation pathway is proposed for the photolysis of pyrethroids in natural water.

Keywords: Pyrethroids, Deltamethrin, Fenvalerate, Photodegradation, Simulated solar light irradiation

In recent years, synthetic pyrethroid pesticides have been widely used in agriculture and home pest control due to their high insecticidal activity, long-term stability, and good compatibility [1]. For example, Deltamethrin (DLT) and Fenvalerate (FEN) are often used to kill fruit orchard pests, and they are widely used in domestic pesticides such as mosquito-repellent incense (fig. 1); like all pyrethroids, prevents the sodium channels from functioning, so that no transmission of nerve impulses can take place and mode of action is non-systemic insecticide with contact and stomach action [2]. Inevitably, these pesticides will then enter the environment, which results in environmental pollution, ecological destruction, and human health risks. In the natural environment, pyrethroids can be degraded through several possible processes, including photodegradation, biodegradation, and hydrolysis. Photodegradation is the most common degradation processes in the environment and has the advantage of having a higher degradation rate and being faster than biodegradation and hydrolysis. It is of great research significance and highlights the importance of understanding the processes, mechanisms, intermediates, and final products of the photodegradation of pyrethroids within the natural environment [3-5]. Since the formation of highly toxic reaction intermediates is possible, identification of the degradation products is essential. The purpose of this study was to analyze and identify the photodegradation products of DLT and FEN using gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS). Based on the identified intermediates, a plausible degradation pathway for DLT and FEN is proposed.

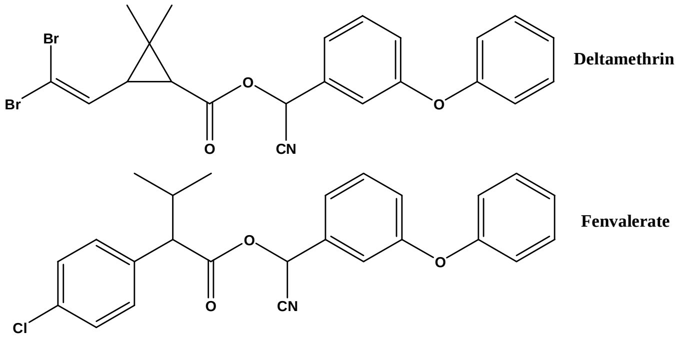

Fig. 1. Structure formula of Deltamethrin (DLT) and Fenvalerate (FEN)

Experimental part

Materials and methods

Chemicals and Reagents

Deltamethrin (DLT) and Fenvalerate (FEN) technical grade (98.0%) were a gift from Iran Chemical Complex. Analytical grade standards of high purity were obtained from Fluka and were used without further purification and all the chemicals and solvents were obtained from E-Merck (Darmstadt, Germany).

Water sampling

Natural waters used in the experiments were collected from the Mazandaran province in North Iran and was natural water of Babolrood River. The natural water sample was collected from the top meter of water body in 2.5-L pre-cleaned amber glass bottle and stored at 4°C prior to use. Water sample was used without previous treatment and

Table 1
PHYSICO-CHEMICAL PROPERTIES OF THE BABOLROOD RIVER

pH	Conductivity (μS/cm)	TDS[1] (mg/L)	TOC[2] (mg/L)	Salinity ($^{o}/_{oo}$)	NO_3^- (mg/L)
7.52	401	221	2.85	0.41	3.43

[1]TDS: Total Dissolved Solids, [2]TOC: Total Organic Carbon

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filtration. Physico-chemical characteristics of sample of Babolrood River natural water are given in table 1.

Methods of photodegradation

The photochemical stability of DLT and FEN were tested using a Sunset CPS+ photo simulator from Heraeus (Hanau, Germany), for the photodegradation the pyrethroids equipped with a Xenon arc with a 300-W mercury lamp and a 1000-W xenon lamp and special glass filters restricting the transmission of wavelength below 290 nm. The light source was on the top of the reactor and average irradiation intensity of 750 W/m^2 was maintained throughout the experiments measured by an internal radiometer. Chamber and black panel temperatures were regulated by pressurized air-cooling circuit and monitored using thermocouples supplied by the manufacturer. The temperature of samples did not exceed 20°C using tap water cooling circuits for the UV-reactor. The distance between the irradiated solutions and the lamps was 15 cm. Irradiation experiments were carried out by exposing 200 mL of aqueous solution of DLT and FEN (20 mg/L) containing 0.2% sodium azide (for biological degradation resistance) under artificial solar irradiation. During irradiation, the samples were magnetically stirred. All experiments were carried out at room temperature and *p*H 6. A dark control experiment was also conducted in this experiment. The treated water samples were processed for DLT and FEN photodegradation on 28 h after treatment that almost is equal with sunlight natural irradiation at 7 sunny days.

Extraction procedure

Treated water samples (200 mL) were taken in a separator funnel and 10 g sodium chloride was added. Photoreactions of DLT and FEN photodegradation in different solvents (such as n-hexane, methanol/water) were also studied. The photoproducts in the methanol/water solution were twice extracted by n-hexane. The n-hexane layers were then combined into a centrifuge tube. The extracted liquid was then evaporated to 1 mL under a stream of nitrogen for GC analysis. The final samples were stored in the dark place while awaiting analysis.

Analysis

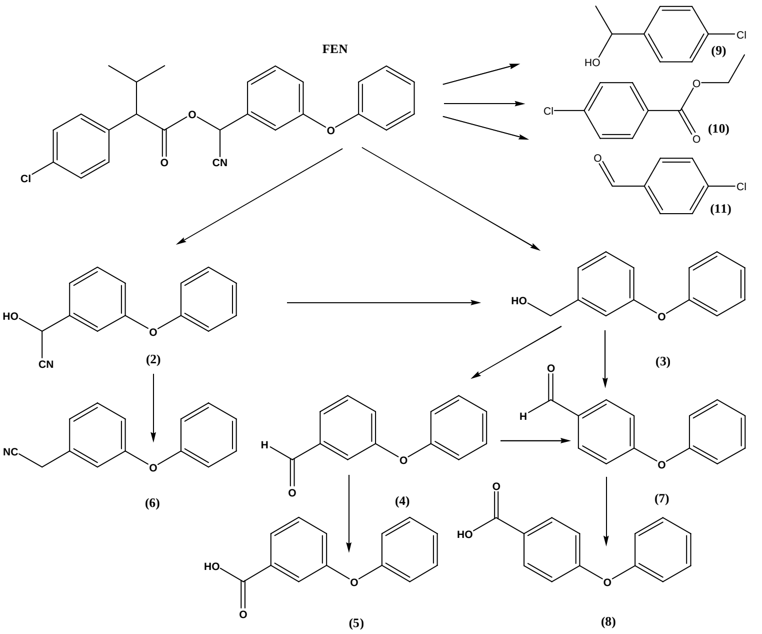
A Hewlett-Packard system consisting of a 5890 GC system equipped with a micro-electron capture detector (μECD) and capillary column HP-5MS (30 m . 0.32 mm, 0.25 μm) and an Agilent 5975C mass spectrometer coupled to GC was used to analyze the photoproducts. Chromatographic data were monitored by Xcalibur® 1.4 software. For GC method, the GC oven temperature program was as follows: 150°C, hold for 1 min, 15°C/min to a final temperature of 290°C, hold for 10 min. The temperature of the injector and detector were set at 220 and 300°C, respectively. The 1 μL sample was injected into GC with splitless mode. Nitrogen was used as the carrier gas at a constant f of 1 mL/min. For GC-MS method, the GC oven temperature program was as follows: 50°C, hold for 1 min, 25°C/min to 180°C, hold for 1 min, 10°C/min to a final temperature of 290°C, hold for 8 min. Helium was used as the carrier gas at the rate of 1.0 mL/min. The MS was operated in electron ionization mode with a potential of 70 eV. The spectra were obtained in full scan mode [6].

Results and discussions

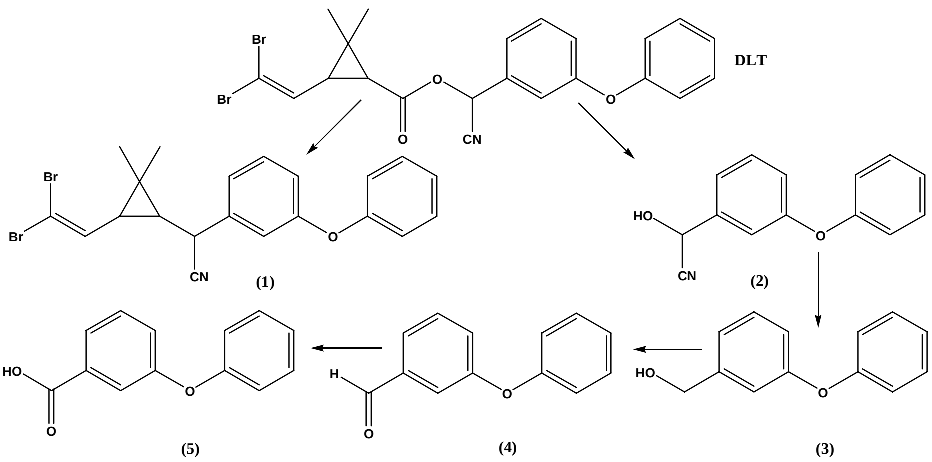
The intermediate products formed in photodegradation of DLT and FEN in the aqueous solution after 28 h were investigated by GC/MS analysis. UV irradiation was simulated with a mercury lamp and sunlight was simulated with a xenon lamp. As a result, the degradation rates of the two pyrethroids were faster under mercury lamp irradiation than xenon lamp irradiation [4,6]. The structures of photoproducts are represented in scheme 1 and 2, together with the parent compound. Photodegradation pathways for the two pyrethroids were proposed on the basis of the photoproducts identified.

Photodegradation mechanism of DLT and FEN

The photodegradation of two pyrethroids included four main reactions that are, ester cleavage, photooxidation, photoisomerization, and decyanation. Photoproducts were identified by the molecular ion and mass fragment ions (table 2). Reactive oxygen species (ROS) can be produced by sunlight in a water environment and may participate in the indirect photolysis of a trace pyrethroid [7]. Pyrethroid molecules contain double bonds that are



Scheme 1. Scheme of the proposed photodegration pathway for FEN



Scheme 2. Scheme of the proposed photodegration pathway for DLT

Table 2
IDENTIFIED PRODUCTS BY GC/MS IN THE PHOTODEGRATION OF DLT AND FEN

Pyrethroid	**No.**	**Name of product**	**RT (min)**	***m/z*, Characteristic ions (%)**
Deltamethrin	DLT	Deltamethrin	21.89	172 (28), 181 (100), 253 (64)
	5	3-Phenoxybenzoic acid	14.526	115 (21), 141 (33), 197 (79), 228 (100)
	4	3-Phenoxybenzaldehyde	10.177	77 (27), 141 (33), 169 (34), 198 (100)
Fenvalerate	FEN	Fenvalerate	21.034	125 (100), 167 (78), 181 (49), 225 (68)
	6	3-Phenoxyphenyl acetonitrile	19.255	51 (20), 77 (40), 141 (35), 209 (100)
	8	*p*-Phenoxybenzoic acid	14.691	115 (8.3), 141 (12.5), 197 (100), 228 (85)
	5	3-Phenoxybenzoic acid	14.526	115 (21), 141 (33), 197 (79), 228 (100)
	4	3-Phenoxy benzaldehyde	10.177	77 (27), 141 (33), 169 (34), 198 (100)
	9	1-(4-Chlorophenyl) ethanol	7.802	77 (70), 113 (26), 141 (100), 156 (29)
	10	4-Chlorobenzoicacid ethyl ester	7.516	50 (8), 75 (15), 111 (38), 139 (100)
	11	*p*-Chlorobenzaldehyde	6.005	50 (21), 75 (30), 111 (57), 139 (100)

unstable to light, so photooxidation degradation is the major reaction in the pyrethroid photodegradation process.

In the photodegradation of DLT, debromination, photoisomerization, and ester bond cleavage were observed in previous studies [4,5]. In this experiment, photoproducts 3-phenoxy benzaldehyde (**4**) and 3-phenoxybenzoic acid (**5**) were observed. Photoproduct (**4**) was formed from the dehydrocyanic acid of compound hydroxyl 3-phenoxyphenyl acetonitrile (**2**). Compound (**2**) could be the result of the ester cleavage of deltamethrin. Photoproduct (**4**) was most likely derived from the photooxidation of 3-phenoxy benzalcohol (**3**). Compound (**3**) could be a result of the ester cleavage and subsequent decyanation of deltamethrin. Photoproduct (**5**) may be generated from the photooxidation of photoproduct (**4**). Compound (**2**) was not detected, it might be because the concentration of these compounds was too low to be detected, or that the compound degraded quickly into other products. A plausible pathway for the photodegradation of fenvalerate is shown in scheme 1. Photoproducts (**4**), (**5**), (**8**), (**6**), (**9**), (**10**), and (**11**) were observed in this study. The product *p*-phenoxybenzaldehyde (**7**) was derived from the photochemical isomerization of (**4**). The 3-phenoxybenzoic acid (**5**) and *p*-phenoxybenzoic acid (**8**) may be from the oxidation of photochemical products (**4**) and (**7**), correspondingly. The 1-(4-chlorophenyl) ethanol (**9**) was most likely formed from the ester cleavage of fenvalerate. The new compound (**6**) may be 4-chlorobenzoic acid ethyl ester, the result of the chemical bond cleavage and subsequent decyanation of fenvalerate [6].

Conclusions

Information on degradation products is necessary to understand the environmental fate of pesticides and to establish important degradation pathway, which will allow us to get a better knowledge of the transformation of target compounds in the environment. Moreover, the study of contaminant photochemical behaviour is a key issue in terms of the formation of toxic transformation products. The photodegradation of Deltamethrin and Fenvalerate under simulated solar light irradiation conditions on natural water of a river in North of Iran has been observed to proceed essentially through four main reactions that are, ester cleavage, photooxidation, photoisomerization, and decyanation. The results reported here show that the combination of gas chromatography-mass spectrometry analysis, positive and negative ions and exact mass measurements represent a powerful analytical approach for the confirmation of the molecular structure of photodegradation intermediates. More detailed research on the degradation mechanism of pyrethroids, however, should be further explored.

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