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Chemical Stability Effect of Pyriproxyfen and Bifenthrin Insecticides and Their Toxicology Changes

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Abstract

In this study, we investigated the degradation of pyriproxyfen, bifenthrin and the performance of a mixture of pyriproxyfen and bifenthrin [formulas of missile 10% EC and zedorale 10% EC (pyriproxyfen), dioxin 20% EC (pyriproxyfen + bifenthrin), and (bifenthrin) flux 20% EC (Emulsion Concentration). Fourteen days were spent storing the tested insecticides at 54±2°C. During the storage period, samples were taken after 14 days to determine physical properties, such as emulsion concentration, as basic properties and to evaluate the chemical stability of the active ingredient using high-performance liquid chromatography and fingerprint analysis (GC-MS and IR). As well as the evaluation of their efficacy, toxicology studies show a very minute shift in LC_{50} for both *Spodoptera littoralis* and *Pseudococcus longispinus* recorded before and after storage of the insecticides tested. The obtained results showed that Pyriproxyfen's active ingredients were 9.95%, 9.86%, 9.83% and reached 9.81%, 9.72%, and 9.75% after 14 days of storage at 54±2°C for missile 10% EC, zedorale 10% EC, and dioxin 20% EC, respectively. While the active ingredients for bifenthrin in dioxin 20% EC and flux 20% EC were 9.93% and 19.692%, they reached 9.85% and 18.82% after 14 days of storage at 54±2°C, respectively. This result refers to the fact that missile 10% EC, zedorale 10% EC, and dioxin 20% EC are more stable than flux 20% EC. Stability at an elevated temperature was within the FAO limits for all sources before and after storage. Then the other tested GC/MS was used for the degradation of pyriproxyfen and bifenthrin insecticides; the major degradation product in pyriproxyfen was 1-(4-phenoxyphenoxy) propan-2-ol, and the major degradation product in bifenthrin was 2-methyl[1,1'-biphenyl]-3-carbaldehyde.

Keywords: insecticides, bifenthrin, pyriproxyfen, IR, GC/MS, physical properties, chemical stability, chemical composition, mealybug, cotton leaf worm, IR, and GC/MS.;

1. Introduction

An insect growth regulator (IGR) called pyriproxyfen and the synthetic pyrethroid bifenthrin are often used to get rid of different bug pests [1]. The synthetic pyrethroid bifenthrin [2-methylbipenyl-3-ylmethyl(z)-(1RS,3RS) 3,2-dimethylcyclopropane carboxylate] was developed in the 1980s. [2]. Bifenthrin is a pesticide that paralyses insects by effects on their nervous system. [3,4]. Moreover, it has been found to be extremely poisonous to fish and other aquatic species [4,5]. It is possible for residues to exceed permissible limits and pose a concern to consumer safety as a result of excessive use, premature harvesting, and insufficient time for pesticide breakdown prior to commercialization [6,7]. Due to the minute residues of contaminants, the use of bifenthrin in agriculture has become a major public concern concerns health, environmental contamination, and ecological circumstances. Broad-spectrum insect growth regulator pyriproxyfen is structurally similar to juvenile hormone. 4-Phenoxyphenyl (RS)2-(2-pyridyloxy) propyl ether [8] is its chemical name. Researchers have looked into the breakdown of pyriproxyfen and its enantiomers, as well as the chemical's persistence in soils, vegetables, plants, and fruits [8,9,10]. However, Paya et al. investigated the dissipation behaviour of

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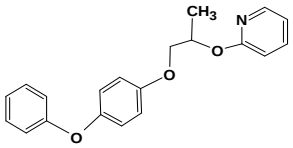
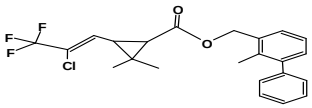
pyriproxyfen enantiomers in soil and sand under various conditions [11,12], Chang et al. investigated the impact of soil dissipation on the bacterial population [13], and Du et al. investigated button mushrooms [14]. During a heavy and uncontrolled infestation, the cotton leaf worm *Spodoptera littoralis* (Boisd) (Lepidoptera: Noctuidae) can inflict serious damage, reducing crop production by as much as 80%. *Delonix regia* is an ornamental plant with the common name Flambouyant [15] and may have pharmacological properties [16]. It is a tree used for street plantations in many countries and is sometimes rigorously infested with mealybugs at optimum temperatures of 54±2ºC [17]. The most devastating kind of pest to this type of tree in tropical settings is the long-tailed mealybug (*Pseudococcus longispinus*). On wide-host perennial plants, it can infest all plant parts, including the roots, which feed on sugary plant juices. Secreting honeydew encourages the growth of sooty moulds, as Aspergillus spp. make branches sticky and inject a toxin as they feed. Low population density induces slow plant growth and causes premature leaf or fruit drop and twig dieback. In heavy population density infestations, it can weaken photosynthesis in the leaves and cause the plant to completely die [18]. In this study, we investigated the degradation of pyriproxyfene and bifinithrin and their mixture under controlled conditions in line with their toxicological effects against cutworms, the cotton leaf worms, and soft insects, the long-tailed mealybug.

2. Experimental

2.1. The structure of tested the insecticides used.

Table (1). The structure of tested the insecticides used.

Trade name	Common name	Structure of Pyriproxyfen	Structure of Bifenthrin
Missile 10% EC	(Pyriproxyfen)	 *IUPIC*:4-phenoxyphenyl (RS)-2-(2-pyridyloxy) propyl ether[8].	 *IUPIC*: (2-methyl-3-phenyl phenyl) methyl (1R,3R)-3-[(Z)-2-chloro-3,3,3-trifluoroprop-1-enyl]-2,2-dimethylcyclopropane-1-carboxylate[19].
Zedorale 10% EC			
Flux 20% EC	Bifenthrin		
Dioxin 20% EC	(Pyriproxyfen + Bifenthrin)		

EC: Emulsion concentrate

2.2. Accelerated storage procedures.

Formulations of missile 10% EC and zedorale 10% EC (pyriproxyfen), dioxin 20% EC (pyriproxyfen + bifenthrin), and flux 20% EC (bifenthrin) were placed in bottles (approximately 50 ml). This bottle was exposed to storage at 54±2°C for 14 days. During the storage period, samples were taken at 0 and 14 days to determine the chemical and physical properties, as well as fingerprints by GC/MS and IR [20].

2.2.1. Standard preparation of the Pyriproxyfen and Bifenthrin.

10 mg of known purity pyriproxyfen and bifenthrin were weighed and completely dissolved in methanol in a 25 ml grade A flask.

2.2.2. Sample preparation for tested insecticides.

Accurately weighed sufficient samples of a formulation equal to 10 mg of standard, then gently mixed with methanol in a 25 ml volumetric flask dedicated to each sample.

2.2.3. Determination of the insecticides used by HPLC instrument.

The active ingredient percentages for missile 10% EC and zedorale 10% EC (pyriproxyfen), dioxin 20% EC (pyriproxyfen + bifenthrin), and flux 20% EC (bifenthrin) were determined before and after storage according to a modified method CIPAC [21]. Bifenthrin had a retention time (R.T.) was 3.450 minutes, and pyriproxyfen had a retention time (R.T.) of 4.337 minutes under these conditions. Some modifications (Agilent Technologies 1260 Infinity II) used an ultraviolet U.V detector, and the column Eslips Plus C18, di. 5 mm and len. 4.6 * 2.5 mm, was used. The mobile phase was methanol-acetonitrile (10:90) v/v, the temperature of the column was 40 degrees Celsius, and the wavelength was 210 nm.

2.2.4. Determination of the main physical properties as emulsion stability.

a. Preparation and determination of physical properties of standard water used:

All physical properties testing was conducted using non-CIPAC standard water, 18.3.1 WHO Standard Hard Water (342 ppm hardness), as specified by CIPAC MT 18.3 [22]. Distilled water was used to make up to 1000 ml of a solution containing 0.304 g of calcium chloride $CaCl_2$ and 0.139 g of magnesium chloride $MgCl_2.6H_2O$.

b. Emulsion stability evaluation for test formulation EC:

The test was carried out according to CIPAC [21]. 5 ml of the formulation was added to 95 ml of standard water (in a cylinder of 100 ml). The cylinder was immersed in water at 30±2°C for 30 minutes after being invested 30 times in one minute. After the emulsion had been motionless for 30 minutes, the amount of free oil cream that had separated at the top of the emulsion was observed.

c. Water Measurement:

The water percentages (%) of (pyriproxyfen) in missile 10% EC, zedorale 10% EC, and (pyriproxyfen + bifenthrin) in dioxin 20% EC formulations were measured using METTLER TOLEDO C_2O_5.

2.3. Toxicological studies:

2.3.1. Insect sources:

The first species tested were the cotton leaf worm was a susceptible laboratory reared strain under controlled conditions at 25 ± 2ºC and 16:8 h light: dark feeds on Castor bean plant leaves *Risinus* comunus. The second insect attained from *Delonix regia* trees seriously infested with the long tailed mealy bug *Pseudococcus longispinus*. The tree branches were catted to pieces that full of with developmental stages, transferred to the laboratory and picked up by Fine Bruch immediately for bioassay evaluation carried out. Information about insecticides used in this study found in table (1).

2.3.2. Cotton leaf worm bioassays

Bioassays were performed on all strains using the leaf dip method, according to Paramasivam [23]. Uninfected cotton Leaves were dipped individually in serially diluted formulations in water for 5 seconds of the tested insecticide concentration and left to dry, while controls were dipped in water only. Afterward, treated leaves were placed individually in a 9-diameter petri dish filled with 10 individuals of one-day-old, 4th instar larvae, and three replicates were prepared for each concentration. The dishes were kept in good condition under carefully monitored circumstances at 54±2°C, 16:8 hours of light to dark, and 75% humidity. Mortality was recorded 24 hours after treatment. For $LC_{50,\ 90}$ estimates in accordance with Finney [24], recorded leaf-dip bioassay data were submitted to the Polo Computer Software programmed [25], where corrections for mortality were included.

2.4. Mealy bug insecticide bioassay:

The slide-dip technique tests for mealybug contact activity evaluation according to Mollet and Dennehy [26,27] were completed. About ten fourth-instar nymphs of the long-tailed mealybug individuals were pushed separately under binoculars by a fine brush to stick on the double-faced adhesive band prepared previously and stacked on the glass slides. Seven serially diluted concentrations on water of insecticide formulations stored and un-stored under 54±2°C conditions were prepared; the slides were immersed for 5 seconds and stacked on plates, left to dry; the controls were immersed in water only; and three replicates were performed. Slides maintained under laboratory conditions were 12:12 h day light: dark, 75% humidity, and 54±2°C temperature. Mortality was counted after 2 hours for every slide using binoculars, and individuals that did not respond to brush touch were considered dead.

2.5. Gas-Chromatography-Mass spectrometry analysis of (Pyriproxyfen) missile 10%EC and zedorale 10%EC, (Bifenthrin and Pyriproxyfen) dioxin 20%EC and (Bifenthrin) flux 20%EC.

Agilent 7890 B and 5977 A MSD gas chromatography instruments used a fused silica capillary column (30 m, 0.025 mm, HP-5-0.25 micron, -60 to 325/325ºC), a direct capillary interface, and a mass spectrometer detector from Agilent. For the purpose of injecting samples, the following conditions were utilised: The split ratio was 10 to 1, and the split flow rate was 10 millilitres

per minute. As the carrier gas, helium was utilised at a flow rate of approximately 1 millilitre per minute while operating in pulsed split mode. The volume of the injection was 1 µL, and the delay caused by the solvent was 4 minutes. The injection volume was 1 µL, and the solvent delay was 4 minutes. The injector temperature was maintained at 280 degrees Celsius for the whole 34-minute bake cycle, which began at 50 degrees Celsius and ramped up to 190 degrees Celsius over the course of 0.5 minutes, 210 degrees Celsius over the course of 1 minute, and 300 degrees Celsius over the course of 2 minutes. The mass spectral database W9N11 was used to determine which peaks had been isolated.

2.6. The absorbance of (Pyriproxyfen) missile 10%EC and zedorale 10%EC, (Bifenthrin and Pyriproxyfen) dioxin 20%EC and (Bifenthrin) flux 20%EC in infrared (IR spectra).

We used a modified Fourier transform infrared spectrometer (Avtra 330 Thermo Nicolet) to examine the effect of storage on the absorption of feature groups and the fingerprint of pyriproxyfen and bifenthrin formulations. We combined 0.01 g of the sample with 0.1 g of dry potassium bromide (KBr) in an agate mortar and pestle before transferring 0.03 g of the resulting combination to a clean stainless steel slide with the help of forceps. The sample was put onto a slide and pushed through a piston to create a transparent, thin layer.

3. Results and Discussion

3.1. Effect of storage on the stability of Pyriproxyfen and Bifenthrin:

Table 2 shows the effect of storage at 54±2°C for 14 days on the stability of the commercial (Pyriproxyfen) missile (10% EC) and zedorale (10% EC), (Bifenthrin and Pyriproxyfen) dioxin (20% EC), and (Bifenthrin) flux (20% EC). Pyriproxyfen's active ingredients were 9.95%, 9.86%, and 9.83% and reached 9.81%, 9.72%, and 9.75% after 14 days of storage at 54±2°C for missile 10% EC, zedorale 10% EC, and dioxin 20% EC, respectively. Also, percentage losses reached 1.41, 1.42, and 0.81 after 14 days of storage for missile 10% C, zedorale 10% EC, and dioxin 20% EC, respectively. While the active ingredients for bifenthrin in dioxin 20% EC and flux 20% EC were 9.93% and 19.692%, they reached 9.85% and 18.82% after 14 days of storage at 54±2°C, respectively.

Table (2): Effect of storage on the stability of Pyriproxyfen, Bifenthrin, and (mixture of Pyriproxyfen+ Bifenthrin).

Storage Periods (Days)	Missile 10%a.i Pyriproxyfen		Zedorale 10% a.i Pyriproxyfen		Dioxin 20% a.i Pyriproxyfen10%+ a.i Bifenthrin10%				Flux 20% a.i Bifenthrin	
	Pyriproxyfen	% loss	Pyriproxyfen	% loss	Pyriproxyfen	% loss	Bifenthrin	% loss	Bifenthrin	% loss
0	9.95	0.00	9.86	0.00	9.83	0.00	9.93	0.00	19.69	0.00
14	9.81	1.41	9.72	1.42	9.75	0.814	9.85	0.806	18.82	4.4

(a.i) active ingredient; (0) before one-hour storage

Also, the percentage loss reached was 0.80% and 4.4% after 14 days of storage for bifenthrin for dioxin (20% EC) and flux (20% EC), respectively. This result refers to the fact that missile 10% EC, zedorale 10% EC, and dioxin 20% EC are more stable than flux 20% EC. Stability at an elevated temperature: the determined average active component content of pyriproxyfen after 14 days of storage at 54±2°C shall not be less than 95% of the determined average content found before storage [28]. On the other hand, for stability at an elevated temperature after storage at 54±2°C for 14 days for bifenthrin, no less than 95% of the original average level of active ingredients must be present after storage [29].

3.2. The effect of storage on the emulsion stability:

According to the results, emulsion stability was measured for brand-name commercial formulations of dioxin (20% EC), missile (10% EC), zedorale (10% EC), and flux (20% EC) before and after 14 days of storage at 54±2°C. Results indicated that missile, zedorale, and flux formulations passed

successfully through the emulsion before and after 14 days of storage. Except for dioxin formulation, after 30 minutes, the cream and precipitate layers are discovered to be higher than 2 ml in the bottom cylinder, and the maximum level is found to be around 2 ml, according to the JMPS [30].

3.3. Coulometric KF Titrator:

Water content was undetectable for missile 10% EC and zedorale 10% EC, while dioxin 20% EC was 0.315% before storage and decreased to 0.2921% after 14 days of storage at 54±2°C. According to FAO [31], it was found that the water content in pyriproxyfen in dioxin formulation 20% EC is lower than 0.3% after storage. But Flux 20% EC (a.i., bifenthrin) was not found to have water content according to FAO specifications. The presence of water in the formulation changes the surfactant during the storage period, where part of the surfactant distributes from interference to the aqueous phase, leading to a decrease in the correlation of the essential oil. Surfactants and solvents cause an increase in the partical [32].

3.4. Toxicological studies:

Tables (3) and (4) found cotton leafworm *S. littoralis* toxicity response data and the long-tailed mealybug *P. longispinus* exposed to the insecticides tested before and after storage for 14 days under 54±2°C oven heat conditions. Results (Slop, LC_{50} and LC_{90}) were found in tables 2 and 3. Data showed that the LC_{50} of before storage was considerably less than the LC_{50} of after storage bioassay, which means that storage under this definite temperature degree for 14 days affects the toxicity response of those pests, and the LC_{50} showed only a minute shift occur from 0.09, 0.065, 0.087, and 0.055 ppm to 0.21, 0.22, 0.2, and 0.2 ppm after storage for *S. littoralis* for missile Pyriproxyfen 10%, zidorale pyriproxyfen 10%, bifenthrin 20% alone (Flux), and bifenthrin mixture with pyriproxyfen (Dioxin) 10 and 10%, respectively. And considerable shifts of *P. longispinus* toxicity values occur from 0.07, 0.048, 0.046, and 0.04 to 0.08, 0.16, 0.15, and 0.05 ppm respectively, of the same arrangement of the insecticides. But dioxin (mixture product) showed much efficiency more than toxicity of each insecticide alone, where LC_{50}s were different and looked smaller values, where substantial potentiation found between both compounds. The data before and after storage were significantly different by ANOVA statistical options between and within the two groups of toxicity ($F = 9.34$, df = 1, 6, and $p = 0.023$). The toxicity variations between pyriproxyfen and bifenthrin are due to the mode of action of both compounds and the nature of the tested insects, the cotton leafworm (caterpillar) and the mealybug (soft body), in this study. This mealybug individual has a considerable amount of wax present on their bodies, and the first instar is the most susceptible to pesticides, more so than the cotton leafworm. From the review of the literature, pyriproxyfen's effectiveness in reducing the cotton mealybug *Phenacoccus solenopsis* incidence in laboratory and field conditions was high and easy to control [33,34]. They tested thiamethoxam, which caused complete mortality of *P. solenopsis* and its predator when applied at the highest field rates. At the highest field rates examined, thiamethoxam was lethal to both P. solenopsis and its predator. However, lufenuron, pymetrozine, and pyriproxyfen resulted in modest mealybug mortality while being quite nontoxic to their predators according to El-Zahi [35], the most common insecticides used to control this pest are imidacloprid, thiamethoxam, flonicamid, emamectin-benzoate, chlorpyrifos, methomyl, deltamethrin, and KZ-oil. The development of resistance occurs with pyriproxyfen or bifenthrin, and control failure occurs [36]. They discovered that 14 generations of laboratory selection with bifenthrin led to 178-fold resistance in a *P. solenopsis* population originally obtained from the wild.

Table 3: Toxicity responses of the cotton leafworm S. littoralis and the long tailed mealybug P. longispinus exposed to some insecticides alone and their mixtures before storage.

	S.littoralis response				*P. longispinus* response			
Insecticide	Slope ±SE	LC_{50} (95% CI)	LC_{90} (95% CI)	$\chi 2$	Slope ±SE	LC_{50} (95% CI)	LC_{90} (95% CI)	$\chi 2$
Missile	0.97±0.20	0.09(0.03-0.22)	1.9(0.79-4.9)	0.84	1.54±0.15	0.07(0.028-0.15)	0.53(0.26-0.1)	0.95
Zedorale	1.06±0.20	0.065(0.026-0.16)	1.0(0.42-2.6)	0.92	0.77±0.26	0.048(0.015-0.16)	2.2(0.68-7.1)	0.76
Flux	1.58±0.147	0.087(0.043-0.16)	0.56(0.29-1.1)	0.81	1.3±0.188	0.046(0.02-0.1)	0.45(0.19-1.0)	0.95
Dioxin	1.4±0.17	0.055(0.025-0.1)	0.46(0.2-1.0)	0.97	1.1±0.20	0.04(0.01-0.01)	0.58(0.23-1.5)	0.98

Table 4: Toxicity responses of the cotton leafworm S. littoralis and the long tailed mealybug P. longispinus exposed to some insecticides alone and their mixtures after storage.

	S.littoralis response				*P. longispinus* response			
Insecticide	Slope ±SE	LC_{50} (95% CI) ppm	LC_{90} (95% CI)	χ2	Slope ±SE	LC_{50} (95% CI)	LC_{90} (95% CI)	χ2
Missile	2.15±0.108	0.21(0.13-0.35)	0.86(0.53-1.4)	0.91	1.4±0.17	0.08(0.037-0.17)	0.76(0.35-1.6)	0.96
Zedorale	2.38±0.10	0.22(0.14-0.36)	0.79(5-1.2)	0.98	1.26±0.17	0.16(0.07-0.3)	1.7(0.79-3.7)	0.88
Flux	1.73±0.13	0.20(0.10-0.36)	1.0(0.6-2.0)	0.95	1.03±0.19	0.15(0.06-0.37)	2.6(1.0-0.52	0.82
Dioxin	1.4±0.15	0.2(0.1-0.4)	1.6(0.83-3.2)	0.94	1.36±0.18	0.05(0.02-0.1)	0.43(0.2-0.98)	0.99

3.5. Identification of (Pyriproxyfen) missile 10%EC and zedorale 10%EC, (Bifenthrin and Pyriproxyfen) dioxin 20%EC and (Bifenthrin) flux 20%EC in infrared:

The data in Figs. (1) and (2) were found to reveal all possible conformations of (Pyriproxyfen) missile 10%EC and zedorale 10%EC, (Bifenthrin and Pyriproxyfen) dioxin 20%EC, and Bifenthrin (flux 20%EC) before and after storage.

Fig. 1 shows that the peaks of pyriproxyfen based on the amide band (-N=) are generally from 1596.09–1595.27 cm^{-1}. Also, aryl ether gives two bands: an asymmetric (C-O-C) stretch from 1272.70 to 1222.74 and from 1047.64 to 1039.52 cm^{-1}. The characteristic peaks of (C-H) stretching vibrations and skeleton vibrations of the benzene ring from 3022.06–3019.86, 1537.73–1504.26, 1432.60–1382.87, and 844.30–844.21 cm^{-1} were, respectively. Methyl's symmetric stretching vibrations of (C-H) are responsible for the peak between 2924.38 and 2922.05 cm^{-1}. This is due to the presence of pyriproxyfen Because of this tight relationship, the IR spectra of biomacromolecules may be employed for assaying their second structure using amide bands [37].

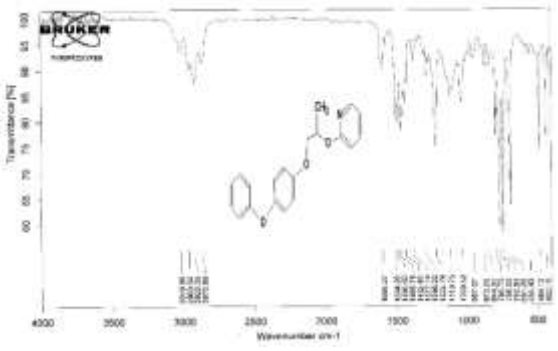


Fig. (1). Infrared spectrum of Pyriproxyfen.

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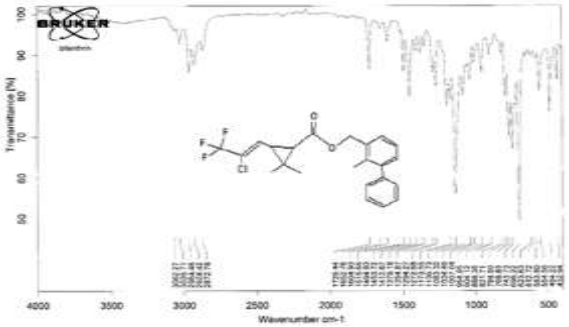


Fig. (2). Infrared spectrum of Bifenthrin

On the other hand, Fig. (2) shows that the characteristic peaks of bifenthrin at 3062.27, 1515.65, 1494.93, and 821.71 cm^{-1} were respectively assigned to (C-H) stretching vibrations and skeleton vibrations of the benzene ring. The peaks at 2928.42 and 1726.44 cm^{-1} were respectively attributed to symmetric stretching vibrations of (C-H) for methyl and (-C=O) for ester groups. The stretching frequencies of (C-F) and (C-Cl) occur in the bifenthrin at regions 1083.32 cm^{-1} and 794.50 cm^{-1} respectively.

The (C-H) stretching band in bifenthrin is observed to be at 2700-3200 cm^{-1} while the (B-F) stretching band is observed to be at 950-1152 cm^{-1}. The existence and reintegration information of H-bonding in PILs (polymeric ionic liquids) were deduced before and after extraction based on changes in the aforementioned stretching bands [38].

Finally, we note that there is no difference in pyriproxyfen and bifenthrin concentrations measured by IR before and after storage.

3.6. Identification of (Pyriproxyfen) missile 10%EC and zedorale 10%EC, (Bifenthrin and Pyriproxyfen) dioxin 20%EC and (Bifenthrin) flux 20%EC by chemical ionization GC/MS spectroscopy:

The GC -MS study's results for classifying pyriproxyfen breakdown products before and after the effect of storage are displayed in Table (5) and Figs. (3, 4). We found the following breakdown products, i.e., pyriproxyfen (m/z = 321.4), which were identified as the pathways for the degradation of pyriproxyfen (I) phenyl ring and ether cleavage to generate 4-{2-[(pyridin-2-yl) oxy] propoxy} phenol (II). Formation of the corresponding 1-(4-phenoxyphenoxy) propan-2-ol (III) by cleavage of the pyridine. Substitution of the phenol group by hydrogen atoms leads to the formation of 2-[(pyridin-2-yl) oxy] propan-1-ol (IV). Then (IV) is divided by (-OH) to form 2-[(prop-1-en-2-yl) oxy] pyridine (V). On the other hand, 1-(4-phenoxyphenoxy) propan-2-ol (III) cleaves into 4-phenoxyphenol (VII) and 4-(2-hydroxypropoxy) phenol (VII). The pyriproxyfen molecule contains an asymmetric carbon atom and can therefore exist as both (R)- and (S)-isomers.

The main identified residue in pyriproxyfen was 4′-OH-Pyr [4-(4’-hydroxyphenoxy phenyl) (RS)-2-(2-pyridyloxy) propyl ether] and the minor products were PYPAC [(RS)-2-(2-pyridyloxy) propionic acid], DPH-Pyr [4-hydroxyphenyl (RS)-2-(2-pyridyloxy) propyl ether] and 4-(4-hydroxyphenoxy) phenyl (RS)-2-hydroxypropyl ether, according to James [39].

According to Fukushima [40], pyriproxyfen primarily undergoes hydroxylation at the 4´-position of the terminal phenoxyphenyl ring to create 4′-OH-Pyr, cleavage of the propylpyridyl ether to create POPA ((RS)-2-hydroxypropylphenoxyphenyl ether), cleavage at the propyl phenyl ether to create PYPA ((RS)-2-(2-pyridyloxy) propyl alcohol), POP (4-phenoxyphenol), and desphenylation following the conjugation of these metabolites.

Data reported in Table (5) demonstrate that the R.t. of a breakdown product of pyriproxyfen was before storage at 23.78 minutes and after 14 days of storage at 23.89 minutes and was easily degraded into pyridin - 2 -ol. The R.T. was before storage at 4.33 minutes and after 14 days of storage at 5.89 minutes.

Table (6) and Figs. (4,5) classify the degradation products of bifenthrin before and after the effect of storage. The following degradation of bifenthrin proceeds by hydrolysis, i.e., bifenthrin m/z = (422.9). found were identified as the pathways for the degradation of bifenthrin (1): 2,3-dimethyl-1,1'-biphenyl cleavage to generate 3-[(1Z)-2-chloro-3,3,3-trifluoroprop-1-en-1-yl]-2,2-dimethylcyclopropane-1-carboxylic acid (2) Formation of 3-[(1Z)-2-chloro-3,3,3-trifluoroprop-1-en-1-yl]-2,2-dimethylcyclopropane-1-carbaldehyde (3) by cleavage of the 3-[(1Z)-2-chloro-3,3,3-trifluoroprop-1-en-1-yl]-2,2-dimethylcyclopropane-1-carboxylic acid (2).

Data also in Table (6) show that R.t. of a breakdown product of bifenthrin was before storage at 23.22 minutes and after 14 days of storage at 23.56 minutes, easily degrading into 2,3-dimethyl-1,1'-biphenyl, R.t. was before storage at 4.16 minutes and after 14 days of storage at 4.55 minutes.

Bifenthrin may be broken down by microorganisms in three different ways: by ester cleavage, hydroxylation, and oxidation. These processes ultimately lead to the formation of benylphenoxy acid, BP alcohol, and BP aldehyde. There is a lot of evidence that bifenthrin is adsorbed onto soil and aquatic suspended particles [41]. In addition, 4′-hydroxy bifenthrin can be synthesised by hydrolysis. The synthesis of 4′-hydroxy bifenthrin is the primary breakdown pathway in soils, while BP (benylphenoxy) acid and BP alcohol are generated via photolysis and ester cleavage, respectively.

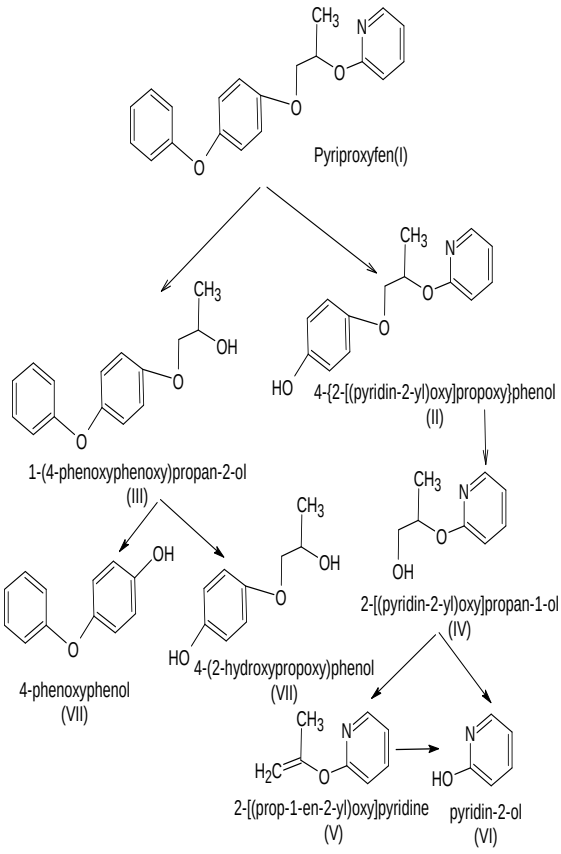


Fig. (3). Degradation pathway of Pyriproxyfen

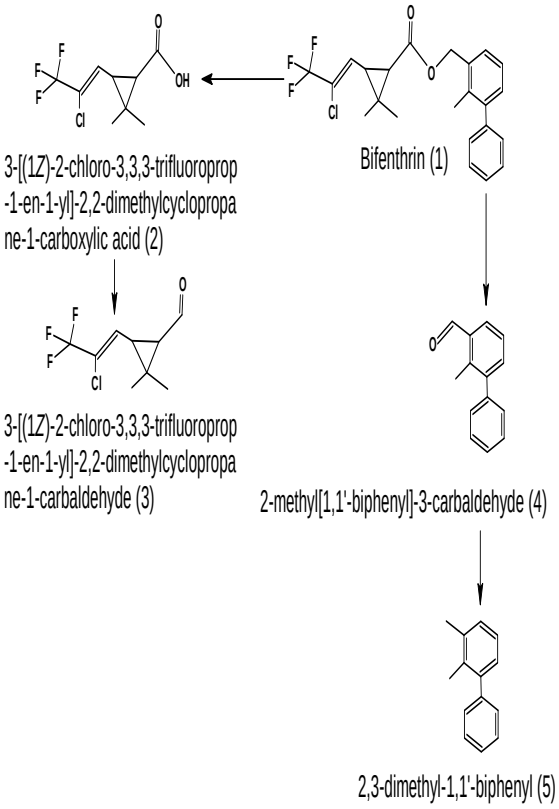


Fig. (5). Degradation pathway of Bifenthrin

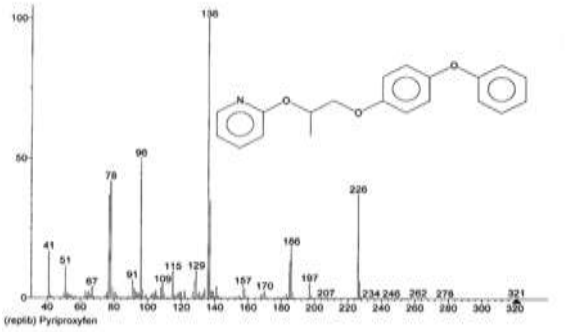


Fig. (4). GC/MS Chromatogram for Pyriproxyfen

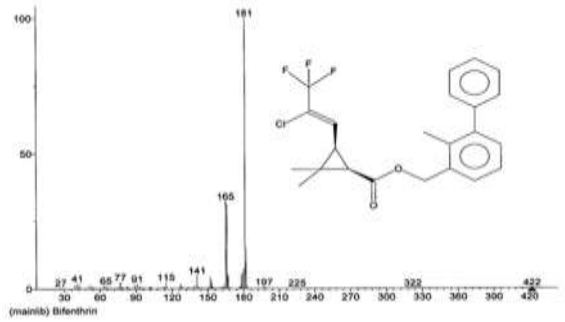
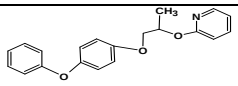
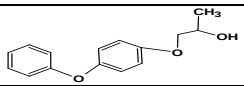
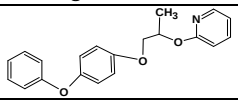
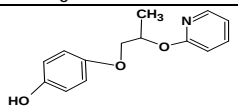
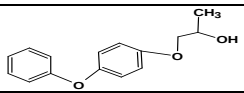
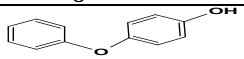
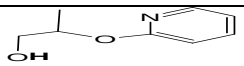
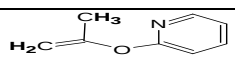
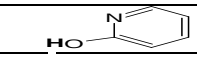


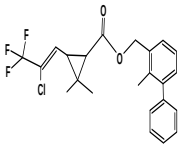
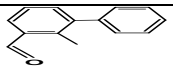
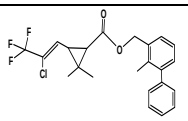
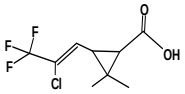
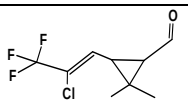
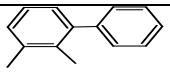
Fig. (6). GC/MS Chromatogram for Bifenthrin

Table (5): Identification of the degradation products of Pyriproxyfen by GC-MS

Storages periods	Chemical Name	Chemical structure	Molecular formula	Molecular weight	Retention time
Before Storage	4-phenoxyphenyl (RS)-2-(2-pyridyloxy) propyl ether		$C_{20}H_{19}NO_3$	321.3	23.78
	1-(4-phenoxyphenoxy) propan-2-ol		$C_{15}H_{16}O_3$	244.2	4.33
After Storage	4-phenoxyphenyl (RS)-2-(2-pyridyloxy) propyl ether		$C_{20}H_{19}NO_3$	321.3	23.89
	4-{2-[(pyridin-2-yl)oxy]propoxy}phenol		$C_{14}H_{15}NO_3$	245.2	4.97
	1-(4-phenoxyphenoxy) propan-2-ol		$C_{15}H_{16}O_3$	244.2	5.96
	4-phenoxyphenol		$C_{12}H_{10}O_2$	186.2	4.55
	2-[(pyridin-2-yl)oxy]propan-1-ol		$C_8H_{11}NO_2$	153.2	8.60
	2-[(prop-1-en-2-yl)oxy]pyridine		C8H9NO	135.2	5.96
	pyridin-2-ol		C_5H_5NO	95.1	5.89

Initial: One hour before storage; Retention time (min); Molecular weight (g/mol)

Table (6): Identification of the degradation products of Bifenthrin by GC-MS

Storages periods	Chemical Name	Chemical structure	Molecular formula	Molecular weight	Retention time
Before Storage	(2-methyl-3-phenyl phenyl) methyl (1R,3R)-3-[(Z)-2-chloro-3,3,3-trifluoroprop-1-enyl]-2,2-dimethylcyclopropane-1-carboxylate		$C_{23}H_{22}ClF_3O_2$	242.6	23.22
	2-methyl[1,1'-biphenyl]-3-carbaldehyde (4)		$C_{14}H_{12}O$	196.3	4.16
After Storage	(2-methyl-3-phenyl phenyl) methyl (1R,3R)-3-[(Z)-2-chloro-3,3,3-trifluoroprop-1-enyl]-2,2-dimethylcyclopropane-1-carboxylate		$C_{23}H_{22}ClF_3O_2$	242.6	23.56
	3-[(1Z)-2-chloro-3,3,3-trifluoroprop-1-en-1-yl]-2,2-dimethylcyclopropane-1-carboxylic acid (2)		$C_9H_{10}ClF_3O_2$	242.6	17.70
	3-[(1Z)-2-chloro-3,3,3-trifluoroprop-1-en-1-yl]-2,2-dimethylcyclopropane-1-carbaldehyde (3)		$C_9H_{10}ClF_3O$	226.6	15.87
	2-methyl[1,1'-biphenyl]-3-carbaldehyde (4)		$C_{14}H_{12}O$	196.3	4.55
	2,3-dimethyl-1,1'-biphenyl (5)		$C_{14}H_{14}$	182.3	5.96

Initial: One hour before storage; Retention time (min); Molecular weight (g/mol)

4. Conclusions

Generally, we evaluated the effect of storage at 54±2°C for 14 days on insecticides (Pyriproxyfen): missil 10% EC and zedoral 10% EC, (Bifenthrin and Pyriproxyfen): dioxin 20% EC, and (Bifenthrin): flux 20% EC, and determined physical properties such as emulsion stability, the active ingredient for Pyriproxyfen, and Bifenthrin by HPLC and fingerprint (GC/MS and IR spectra). Also, the evaluation of their efficacy by toxicology studies shows a very minute shift in LC_{50} for both *Spodoptera littoralis* and *Pseudococcus longispinus* recorded before and after the storage of insecticides tested. Where dissimilar LC50 values detected for each insecticide alone and their mixture product. While GC/MS was used for the degradation of Pyriproxyfen and Bifenthrin insecticides, the major degradation product in Pyriproxyfen was 1-(4-phenoxyphenoxy) propan-2-ol, and the major degradation product in Bifenthrin was 2-methyl[1,1'-biphenyl]-3-carbaldehyde.

Conflict of interest

The author declares there is no conflict of interest.

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