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Review article

Deltamethrin: Properties, Mode of Action, and Safety Issues

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ABSTRACT:

The present paper explores the extensive use and impact of synthetic pyrethroids, focusing on deltamethrin as a representative compound. Pyrethroids, a class of insecticides derived from natural pyrethrins found in chrysanthemum plants, have gained popularity due to their effectiveness and environmental stability. Deltamethrin, a type II pyrethroid, is widely used in agriculture, public health initiatives, and residential settings. The paper delves into the mode of action of pyrethroids, specifically deltamethrin, elucidating their neurotoxic effects on insects. The study discusses exposure routes for the general population, emphasizing the potential risks associated with food residues. Metabolic pathways and environmental fate of deltamethrin are detailed, highlighting its stability, degradation, and limited mobility in the environment. This study addresses the broader issue of pesticide exposure, emphasizing the importance of establishing acceptable exposure limits. Occupational exposure is discussed, focusing on dermal absorption and associated symptoms. The literature reviews global usage patterns, emphasizing the prevalence of pyrethroids in insecticide formulations and their potential impact on non-target species. The study underscores the need for comprehensive risk assessments, considering both human and environmental aspects. It discusses the challenges posed by indiscriminate pesticide use, drawing attention to the bioaccumulation of DDT residues and the potential harm to non-target species. The paper concludes with a discussion on the histological changes observed in animal studies, emphasizing the importance of understanding the long-term effects of pyrethroid exposure on various organisms. Overall, the literature highlights the complex interactions between synthetic pyrethroids and the environment, emphasizing the importance of responsible pesticide management.

Keywords: Deltamethrin, properties, metabolism, fate, exposure limit.

1. INTRODUCTION

Man-made chemicals called pesticides are utilized to grow low-cost food. Every year, millions of tons of high-grade pesticides are employed in India to manage crop diseases and pests [1]. According to different classifications, pesticides are such as insecticides, fungicides, weedicides, herbicides, nematicides, and rodenticides, these pesticides make up 77% of all pesticides used in public health and various agricultural and animal husbandry techniques.

Following the elimination of organochlorine pesticides like DDT from the consumer market, a class of synthetic insecticides known as pyrethroids was developed in the 1970s. The natural pyrethroid, pyrethrin, which is present in the chrysanthemum, imparts biological activity (the capacity to kill insects) to the synthetic pyrethroids, but they also have enhanced environmental stability.

Pyrethroids are used extensively in public health initiatives, agriculture, forestry, and the textile sector [2]. Pyrethroid availability for consumer usage has grown since the late 1990s due to the gradual elimination of organophosphorus (OP) pesticide use in residential areas in the United States [3, 4].

From the beginning of human history, people have been trying to generate enough food. The destruction caused by crop disease and insect pests hindered his efforts. As agriculture expands quickly, many chemical pesticides are produced and applied globally to combat agricultural pests. A few of them are also employed for livestock captures and domestic uses. However, the indiscriminate application of pesticides contaminates the environment, impacting both people and animals. Ultimately harming non-target species, such as humans. Therefore, pesticide pollution of the environment harms both terrestrial and aquatic flora and fauna because it adds to the already significant difficulties in maintaining normal physiological processes in non-target organism, such as humans and domestic animals.

The group of insecticides that includes carbamate, organochlorine, and other chemicals is called pesticides. The pyrethroids that are currently commercially accessible are cypermethrin, deltamethrin, fenvalerate, and permethrin (mostly for agricultural insects), and allethrin, resmethrin, dphenothrin, and tetramethrin (for insects of public health relevance). Other pyrethroids are available as well, such as fenpropathrin, tralomethrin, cyhalothrin, lambdacyhalothrin, tefluthrin, cyfluthrin, flucythrinate, fluvalinate, International Journal of Pharma Research and Health Sciences, 2024; 12(1): 3696-701.

and biphenate (for agricultural insects), as well as furamethrin, kadethrin, and tellallethrin (often for home insects).

Because they rapidly convert to non-basic compounds through metabolism, the synthetic pyrethroid category of insecticides has minimal toxicity to mammals and an exceptionally fast knockdown effect on flying insects [5]. Esters of halo-substitutedchrysanthemic acid are known as synthetic pyrethroids. For some pyrethroid asymmetric center(s), 2-(4-chloophenyl)-3-methyl butyric acid and alcohol (such as allethrolene, 3-phenoxy benzyl alcohol) exist in the acid and/or alcohol moiety. Commercial products occasionally combine both optical (R/S and D/L) and geometric (cis / trans) isomers.

While pyrethroids include cypermethrin, deltamethrin, fenvalerate, and permethrin (primarily for agricultural insects) and allethrin, resmethrin, d-phenothrin, and teramethrin (for insects of public health importance), the majority of the insecticidal activity of such products may be found in just one or two isomers, such as d-phenothrin and deltamethrin.

2. TYPES OF PYRETHROID

Using diverse behavioral, neuropathological, toxicological, and metabolic characteristics, two different forms of synthetic pyrethroids have been found. For tremor, type I is also referred to as class 1 or T, and for choreoathetosissalivation, type II is also referred to as class 2 or cs [6, 7]. As per the authorities, pyrethroids that contain both a halogenated acid esterified with the -cyno-3phenoxybenzyl alcohol, like fenvalerate, deltamethrin, and cypermethrin, are responsible for type II poisoning syndrome. On the other hand, pyrethroids that lack one or both of these moieties, like permethrin, resemethrin, cismethrin, and tetramethrin, tend to cause type 1 syndrome in patients.

Sparring aggressive behavior, a sudden onset of tremors in the extremities, elevated body temperatures, and tremors throughout the body are the characteristics of type 1. The type I syndrome and the P.P.-DDT syndrome are extremely similar. Pawing and burrowing behavior, excessive salivation, a lowered body temperature (primarily because of saliva evaporation), tremors that lead to choreoathetosis (a sinous, writhing movement), muscle contractions and seizures, and death are the characteristics of type II. The molecules of type-I pyrethroids lack the -cyano group. The carbon component of type-II pyrethroid has an -cyano group present.

The natural substances known as pyrethrins, which have been isolated from plants in the Chrysanthemum genus, are the source of the pyrethroid class of insecticides [8]. While naturally occurring pyrethrins do possess insecticidal properties, they are also photosensitive by nature. To create more stable molecules that yet had the desired insecticidal and toxicologic qualities, the pyrethrin structure was changed [9]. The keto alcoholic esters of chrysanthemic and pyrethroic acids provide pyrethrins with their insecticidal characteristics. Strongly lipophilic, these acids quickly pierce the neural systems of several insects, paralyzing them [10]. Three characteristics are shared by all pyrethroids: an alcohol moiety, a core ester link, and an acid moiety.

Pyrethroids are usually found in stereoisomeric compounds due to the presence of two chiral carbons in their acid moiety. Additionally, some compounds include a chiral carbon on the alcohol moiety as well, allowing for a total of eight distinct stereo enantiomers and three chiral carbons. Stereospecific effects on Voltage-sensitive calcium channels (VSSCs) [11], acute mammalian neurotoxicity [12], and pyrethroid insecticidal action [13] all point to the existence of particular binding sites. There are multiple commercial products available for certain chemicals, with varying amounts of stereoisomer.

3. DELTAMETHRIN

Deltamethrin was referred to as decamethrin until 1980. Just two isomers, 1R,3R,S(benzyl) and lR,3S,S(benzyl), have insecticidal activity out of the eight potential stereoisomers with the general structure. Type II pyrethroid deltamethrin possesses a -cyanogroup on the 3-phenoxybenzyl alcohol.

In 1977, deltamethrin entered on market after being produced in 1974. In chemical terms, it is the alpha-cyano-3-phenoxybenzyl alcohol-containing [1R, cis; alphaS]isomer of eight stereoisomeric esters of the dibromo analog of chrysanthemic acid, 2,2-dimethyl-3-(2,2-dibromo vinyl) cyclopropane carboxylic acid (Br2CA).

Level of technical proficiency at 25 °C, deltamethrin has a specific gravity of 0.55g/cm³, making it a viscous yellow or brown liquid. Vapour pressure at 5 °C is 1.24x10-5 mPa, and it is comparatively non-volatile. At 25 degrees Celsius, it is almost completely insoluble in water (less than 0.2 mg/l), although it dissolves readily in organic solvents including kerosene, acetone, and xylene. Very stable when exposed to air. A cis-trans isomerization, ester bond splitting, and bromine loss take place under sunlight and UV radiation. DT50 is more stable in acidic medium than in alkaline ones. 2.5 d (pH)

Chemical Name

[1R-[1a(S*),3a]]-cyano(3-phenoxyphenyl) methyl 3-(2,2dibromoethenyl)-2,2-dimethylcyclopropanecarboxylate IUPAC NAME

Table 1: Some physical and chemical properties of deltamethrin			
dibromovinyl)-2,2-dimethylcyclopropanecarboxylate.			
(S)cyano-3-phenoxybenzyl	(1R)-cis-3-(2,2-		
dibromovinyl)-2,2-dimethylcycloprop	panecarboxylateRoth:		
(S)cyano-3-phenoxybenzyl	(1R,3R)-3-(2,2-		

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Some physical and chemical properties of deltamethrin			
01	Physical state	crystalline powder	

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02	Colour	colourless
03	Odour	odourless
04	Density (20 °C)	0.5 g/cm3
05	Relative molecular mass	505.24
06	Melting point (°C)	98-101
07	Boiling point	decomposes above 300 °C
08	Water solubility (20 °C)	< 0.002 mg/litre (practically insoluble)
09	Solubility in organic	Soluble solvents

3.1. MODE OF ACTION

Pesticides proceed through the liver before entering the bloodstream and starting their intrinsic effects, including choline esterase inhibition. Many pesticides cause harm by interfering with the mitochondria's ability to produce energy [14]. Pyrethroids act near or within the sodium channel in the nerve, causing significantly altered ionic currents and disrupted nerve function through membrane depolarization. Based on studies conducted on insects, crustaceans, frogs, and small mammals, it is generally agreed that the sodium channel in the nerve membrane is the major target site for all synthetic pyrethroid insecticides; that synthetic pyrethroids prolong the transient increase in sodium permeability of the nerve membrane during excitation, resulting in spontaneous depolarization and repetitive discharge that persistently causes muscle fasciculation, acetylcholine depletion, and muscular weakness; that effects are amplified at low temperatures and that -cyano (Type-II) pyrethroids are more potent neurotoxicants than non-cyano(Type II) pyrethroid.

Both type I and type II pyrethroids caused membrane depolarization, which resulted in several alterations in nervous system function. Depolarization in sensory neurons, which occurs locally from skin contact, sends large discharges to the central nervous system. Depolarization of presynaptic terminals causes hypersensitivity to external stimuli and paresthesia or tingling sensations, usually in the face skin. This increases transmitter release, disrupting synaptic transmission. Depolarization beyond a certain magnitude blocks nerve conduction and causes paralysis [15].

In general, animals may recover from these alterations in about a week. Pyrethroids hurt the neurological systems of many different species due to their molecular action on the sodium channel. When the complete material is removed, the pyrethroid interaction with the macromolecular target within the sodium channel will determine the level of toxicity. The elimination of pyrethroid from the nervous system varies with pyrethroid structure due to several parameters, including the rate of metabolism and the concentration in adipose tissues [16]. The general public is mostly exposed to deltamethrin through food residues, while it can also happen from its use in public health. When crops are treated using proper agricultural practices, residue levels are typically quite low—that is, excluding residues from post-harvest treatment. WHO and FAO have reviewed a large amount of data.

3.2. EXCRETION AND METABOLISM

Orally ingested deltamethrin is easily absorbed, but very less through the skin; the rate of absorption is highly dependent on the solvent or carrier. Deltamethrin that has been absorbed is easily digested and eliminated. The basic metabolic reactions include oxidation and/or hydrolysisinduced ester bond breaking, followed by oxidation of the freed acid and alcohol moieties. Urine is produced when the acid moiety (Br2CA) is converted into conjugates, primarily the glucuronide. One of the gem-methyl groups on it may also undergo hydroxylation, which is followed by conjugation and excretion. The aldehyde converts the unstable alcohol moiety into the acid, which is subsequently extensively eliminated in the urine, mostly as the 4'OH sulfate conjugate, after undergoing additional oxidation by hydroxylation on aromatic rings.

3.3. ENVIRONMENTAL EXPOSURE AND OUTCOME:

Total 70% of 14C-(acid, alcohol, or cyanolabeling)deltamethrin-[1R, cis; alphaS] was converted by cis/transisomerization to yield the [1R, trans; alpha S] and [1S, trans; alphaS] isomers, along with ester cleavage products, such as Br2CA and alpha-cyano-3-phenoxybenzyl alcohol, when it was exposed to sunlight as a thin film for 4–8 hours. Under glasshouse circumstances, deltamethrin was broken down in cotton plants, with a 90% loss taking place in 4.6 weeks after the initial half-life of 1.1 weeks. The principal byproducts of ester cleavage, oxidation, and conjugation were free and conjugated Br2CA, trans-hydroxymethyl-Br2CA, and 3-(4hydroxyphenyl) benzoic acid.

In an experimental setting, deltamethrin was incubated at 28°C in the sand and organic soil. Eight weeks after treatment, about 52% and 74%, respectively, of the administered deltamethrin was recovered from sand and organic soil. Because of its high adsorption on particles, insolubility in water, and extremely low application rates, deltamethrin is not mobile in the environment. Although there are no statistics on actual levels in the environment, environmental exposure is anticipated to be very minimal given current use patterns and typical usage circumstances—rapid degradation results in less harmful compounds.



Fig 1: Metabolic pathway of deltamethrin in mammals WHO 1990

3.4. POPULATION GENERAL AND OCCUPATIONAL EXPOSURE

The main food sources from which the general public is exposed to pyrethroids are fruits and vegetables. Pyrethroids are used in a lot of common domestic insect control items, like aerosol bombs, spray insecticides and pet shampoos. As a result, there is a chance of skin and respiratory exposure. Pyrethroids are rarely found at elevated quantities in drinking water or groundwater, except in shallow wells close to agricultural areas, due to their poor mobility in soil surfaces. In workplaces where pyrethroids are produced or used, workers may be exposed to these chemicals by inhalation and skin contact.



Fig 2: Degradation pathway of deltamethrin by UV light WHO 1990

In cases of occupational toxicity, dermal absorption of pesticides is particularly significant. The most commonly reported symptoms of occupational exposure in humans are skin paraesthesias, which are thought to be caused by sensory nerve endings firing repeatedly and should serve as a warning sign for overexposure. Poisonings caused by improper handling of pyrethroids mostly impact the central nervous system (CNS), presenting with symptoms such as headache, disorientation, convulsions, muscle fasciculation, and coma [17].

3.5 PESTICIDE EXPOSURE LIMITS

For the betterment of public health, it is essential to establish acceptable exposure limits for potentially harmful

compounds. The term "acceptable daily intake" (ADI) refers to the level of daily exposure to pesticide residue that, based on all available information at the moment, appears to pose a significant danger to human health throughout the life of an individual. The no observable effect level, or NOEL, is the amount of substance that, when given daily to a group of experimental animals, shows no effects at higher levels and no discernible difference between the test group and control group of animals [18]. The ADI is expressed in mg/kg/day. The general exposure of pyrethroids is assumed to be mostly caused by food residues. Crops that are grown using good agricultural practices typically have low residue levels. Although accurate data in the form of whole-diet studies are lacking, the general population exposure is likely to be minimal as a result [19]. Pesticides are applied indoors, there may be further exposure by ingesting or inhalation of contaminated household dust. Pyrethroids are either

undetectable or only present in extremely low amounts in indoor air, up to the lower nanogram level, due to their limited volatility. As a result, a household dust analysis is typically used to evaluate indoor exposure. Pesticides are extensively employed worldwide in public health to manage diseases spread by intermediate hosts or vectors, as well as in agriculture to safeguard crops. Organochlorines, like DDT, were widely utilized until the 1960s when their usage was banned in many developed nations in the 1970s as a result of the compound's buildup in the environment and humans. Subsequently, pyrethroids, carbamates, and organophosphates were created and widely employed.

The most popular pesticides are synthetic pyrethroid insecticides and organophosphorus insecticides. The majority of these pesticides are effective when administered according to manufacturer recommendations, handled carefully, and used for specified reasons. But as time has gone on, there has been increasing concern that the indiscriminate use of pesticides could result in their damaging effects. When a pesticide is applied properly, the chemical should land precisely on the target and entirely break down into harmless compounds. However, this doesn't happen, and only a portion of the pesticide kills the target pests while the remainder drifts into the surrounding area. It is one of the main concerns for environmental biologists. A two-year study of Delhi's Yamuna River revealed an extremely high level of DDT residue bioaccumulation in fish. According to Khan 2013, the pesticide chemical can also be extremely hazardous to non-target species, such as domestic animals, humans, wild animals, and beneficial species. In one study, organochlorine pesticide residues accounted for 99% of the residues in serum blood samples from Karachi residents, organophosphate pesticides for 25% of the residues, and pyrethroid pesticides for 28% of the residues [20].

Humans have been shown to absorb deltamethrin through the skin and gastrointestinal tract following acute poisonings brought on by overexposure to the chemical at work or by International Journal of Pharma Research and Health Sciences, 2024; 12(1): 3696-701.

ingesting goods containing it. The identification of a deltamethrin metabolite (3-(2,2-dibromovinyl)-2,2-dimethylcyclopropane carboxylic acid) in the urine of individuals experiencing acute deltamethrin intoxication validates the insecticidal absorption and metabolic breakdown in humans [21]. Deltamethrin-mediated harmful effects on organisms are most commonly manifested as oxidative stress [22].

Approximately one-fourth of the global insecticide market is made up of pyrethroid pesticides, which have been used in residential and agricultural formulations for more than 30 years [23]. Pyrethroids are frequently marketed and utilized in mixes that comprise two or more different substances [24]. Many human studies have revealed the effects of pyrethroid exposure, including children, pregnant women, and newborns [25]. While the acute toxicity of these substances to adults has been thoroughly documented, little is known about the potential pyrethroid's toxicity throughout development. Esterases quickly break down pyrethroids in humans, mostly in the liver. The metabolites that have been detoxified are removed by the kidneys; their elimination half-life (t.sub.1/2) is around six hours [26]. Sensitive enough for bio-monitoring, techniques for identifying pyrethroid metabolites in urine have been developed recently.

Pyrethroids can also have an indirect impact on birds since they pose a hazard to their food source. The most vulnerable birds are small insectivorous birds and waterfowl [27]. Applications of pyrethroids affect both beneficial insects and pests because they are harmful to all insects. Predator-prey relationships can be upset when predator insects are vulnerable to a lower dose than the pest. Numerous pieces of evidence indicate that the use of pesticides in poultry houses, storehouses, and crops, along with their careless application for animal spraying or dipping solutions to prevent ectoparasites, leaves behind residue that can have detrimental effects on human health [28].

More than 30% of all insecticides used worldwide are synthetic pyrethroids, the newest and largest class of broadspectrum pesticides utilized in veterinary, home, and agricultural settings [29]. Since 1973, more than a thousand pyrethroids have been created 24 [30]. In addition to carbon, they also contain compounds with nitrogen, sulfur, fluorine, chlorine, and bromine. Worldwide, pyrethroids are used extensively to combat pests, and there is a higher chance that the insecticide will contaminate food. Both people and domesticated animals may be harmed by this tainted food. It has the opposite effect on non-target organisms, such as vertebrates and invertebrates High levels of DDT and BHC, the two most common organochlorines, have been found in cereal grains, vegetables, milk, soil, air, fish, and even human tissues. Additionally, excessive concentrations of DDT and BHC-above the allowable limit-may contaminate breast milk. This suggests that increased pesticide use may cause cancer, teratogenic effects, or metagenic effects in humans. Following a single cutaneous application, methrin, deltamethrin, cypermethrin, and cyhalothrin were found in cows' milk.

4. CONCLUSION

In conclusion, the paper provides a comprehensive overview of deltamethrin, a widely used type II pyrethroid, with a focus on its properties, mode of action, and safety issues. The study highlights the extensive use of synthetic pyrethroids, emphasizing deltamethrin's popularity in agriculture, public health initiatives, and residential settings. It delves into the neurotoxic effects of pyrethroids, particularly deltamethrin, on insects, discussing exposure routes for the general population and underscoring potential risks associated with food residues.

The paper addresses the metabolic pathways and environmental fate of deltamethrin, emphasizing its stability, degradation, and limited mobility in the environment. It sheds light on the broader issue of pesticide exposure, emphasizing the importance of establishing acceptable exposure limits. Occupational exposure is discussed, focusing on dermal absorption and associated symptoms. Global usage patterns of pyrethroids and their potential impact on non-target species are reviewed.

The study emphasizes the need for comprehensive risk assessments considering both human and environmental aspects. It draws attention to the challenges posed by indiscriminate pesticide use, highlighting the bioaccumulation of DDT residues and potential harm to nontarget species. The paper concludes with a discussion on histological changes observed in animal studies, emphasizing the importance of understanding the long-term effects of pyrethroid exposure on various organisms. Overall, the literature underscores the complex interactions between synthetic pyrethroids and the environment, emphasizing the importance of responsible pesticide management.

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