Degradation Path of Deltamethrin

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One of the most frequently and widely used pyrethroids is deltamethrin, often employed for the control of household insect pests. The presence of three chiral centers translates into eight possible different stereoisomers, with only one of them having insecticidal activity. Active deltamethrin (a-DLM) has an S configuration at the α−benzyl carbon and a 1-R-cis configuration at the cyclopropane ring.

Keywords: NMR spectroscopy ; analytics ; deltamethrin ; insecticidal paints

1. Overview

Pyrethroids are among the insecticidal compounds indicated by the World Health Organization for mitigation of vector-borne diseases. Active deltamethrin (with chiral configuration α-*S*,1-*R*-*cis*) is one of the most effective pyrethroids characterized by low toxicity to humans, and it is currently tested as active ingredient for insecticidal paints. Nevertheless, several degradation processes can occur and affect the insecticidal efficacy in the complex paint matrix. In the present study, a detailed NMR analysis of deltamethrin stability has been carried out under stress conditions, mimicking a water-based insecticidal paint environment. Two novel by-products, having a diastereomeric relationship, were identified and their structure was elucidated by combining NMR, HPLC, GC-MS, and ESI-MS analyses. These compounds are the result from a nucleophilic addition involving deltamethrin and one of its major degradation products, 3-phenoxybenzaldehyde. Given the known toxicity of the aldehyde, this reaction could represent a way to reduce its concentration into the matrix. On the other hand, the toxicology of these compounds towards humans should be addressed, as their presence may adversely affect the performance of deltamethrin-containing products.

2. Pyrethroids

Vector-borne diseases are among the main causes of illness and death; in the past 15 years, more than 600,000 cases of such diseases have been reported only in the US [1]. Mosquitoes are the most common vector together with ticks, related to the spread of malaria, Dengue fever, Zika virus, Chikungunya, and yellow fever. The most common solutions for preventing malaria involve the use of Long-Lasting Insecticide treated Nets (LLINs), where an insecticide is incorporated into the net fabric, or of the Indoor Residual Spraying (IRS) method, which consists in spraying residual insecticide on the interior walls of houses [2]. Both solutions have a limited effect though, and the need to find more effective vector control strategies is still compelling [3]; a recent approach promotes the use of Insecticide-Treated durable Wall Linings (ITWL) for protecting interior house walls [4].

The results achieved in paint technology in recent years are promoting this field as a new efficient vector control strategy. Recently, formulations commonly termed as insecticidal paints (IPs) have been developed; the active ingredient is added to the paint to provide a “ready-to-use” product in which the insecticide is released in a controlled way once the paint is dried [5][6][7].

Paints in general can be water-based (WB) or solvent-based (SB), the former being preferred for application in confined or poorly ventilated spaces, where solvent evaporation might be harmful or a nuisance. Water-based paints are generally preferred also because their use helps in reducing volatile organic compounds (VOCs) emissions, albeit temperature and humidity can constitute an issue for the stability of the formulation [8][9]. However, insecticides normally have low solubility in an aqueous environment, thus making it necessary to find an ingredient active at low concentrations (the insecticide content is usually kept between 0.1% and 4% wt for avoiding precipitation) [10].

Among WHO-recommended insecticides, pyrethroids are the most employed for insecticide-treated nets, thanks to their relatively low toxicity towards humans, their moderate cost, and the duration of their insecticidal activity [11]. Therefore, they represent good candidates as active ingredients in IPs [12][13].

Pyrethroids are synthetic insecticides known since 1970s [14], widely used in agriculture, industry, and for controlling insect pests spreading [15][16]. They are ester compounds whose basic structure consists in an aromatic alcohol and a cyclopropyl carboxylic acid (Figure 1). The stereochemistry around the aliphatic ring is usually expressed by clarifying the chiral configuration of carbon 1 and then referring to carbon 3 as *cis* or *trans* depending on the relative position of the substituents (1-*R*/1-*S*-*cis* if they are facing the same side, 1-*R*/1-*S*-*trans* in the opposite situation) [17].

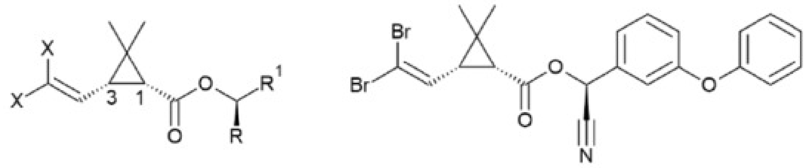

Figure 1. Chemical structure of (**left**) pyrethroids and (**right**) active (α-*S*,1-*R*-*cis*) deltamethrin (*a*-DLM).

One of the most frequently and widely used pyrethroids is deltamethrin, often employed for the control of household insect pests [18][19][20][21]. The presence of three chiral centers (Figure 1) translates into eight possible different stereoisomers, with only one of them having insecticidal activity. Active deltamethrin (*a*-DLM), depicted in Figure 1, has an *S* configuration at the α−benzyl carbon and a 1-*R*-*cis* configuration at the cyclopropane ring [22][23].

Degradation of deltamethrin can follow different paths, depending on the experimental conditions. UV-irradiation has been observed to cause ester cleavage, photooxidation, photoisomerization, decyanation, and dehalogenation [24][25]. In soil, degradation is mainly hydrolytic, photolytic, and microbial promoted [26]. Despite its low water solubility (<0.2 μg/L at 25 °C) [27], DLM degrades in an aquatic environment especially by oxidation and ester hydrolysis [28].

The insecticidal activity of DLM can be disrupted not only by chemical degradation but also by stereochemical modifications of its chiral centers (Figure 1). The most labile chiral center comprises the α−benzyl carbon atom which isomerizes relatively easily, giving rise to inactive deltamethrin (*i*-DLM), with chiral configuration α-*R*,1-*R*-*cis* [29].

Given the fact that DLM is a very effective insecticide with low toxicity for mammals, it constitutes a good candidate as an active ingredient for indoor applications, such as ITWL [4] and in insecticidal paints. A study published in 2004 investigated the efficiency of the insecticide embedded in a solvent-based paint (1% wt) [30], and a patent filed in the same period evaluated the synergistic effect of DLM and piperonyl butoxide, used to inhibit insect resistance [31].

Even if both SB and WB paints are indicated as suitable matrices, the most interesting formulation is the latter, since it allows overcoming the problems related to application in enclosed spaces, as previously pointed out. Nevertheless, some aspects must be considered during the design of a water-based paint formulation containing deltamethrin as an active ingredient: its low water solubility, sensitivity to alkaline environment (WB paints usually have a pH between 8 and 9) [10], and to other degradation paths possibly emerging from such complex matrixes.

Having precise information on the degradation products of deltamethrin in a WB paint-like matrix is then necessary for a clear understanding of the pathways that can take place and the related mechanisms. Ultimately, such understanding could contribute to more stable and environmentally friendly IP formulations, using lower concentrations of insecticide with the same or improved efficacy.

3. Conclusions

The aim of the present study was the elucidation of active deltamethrin degradation profile in an environment whose solvent composition mimics a water-based insecticidal paint. The thorough NMR analysis, performed on the insecticide over a four-week period, allowed the identification of a new pair of diastereomer by-products, which were characterized by combining NMR, HPLC, and MS analyses. Further studies focused on the elucidation of the chiral configuration are planned in the future.

The investigation carried out gives new insights into the insecticide degradation routes and might open the way to studies focused on determining the insecticidal and toxicological influence exerted by the by-products, leading ultimately to an optimization of the insecticidal formulation, and hence into a better product. It is important to underline that the reaction behind PBDM formation implicates the consumption of the 3-phenoxybenzaldehyde, known for its toxicity, even if at the expense of the insecticide.

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