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Characterization of racemization of chiral pesticides in organic solvents and water

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ABSTRACT

Eight chiral pesticides, which were selected to cover different pesticide species and origins of chirality, were investigated to explore their chiral stability in organic solvents and water. Profenophos, fenamiphos, quizalofop-ethyl, dichlorprop-methyl (DCPP-methyl) and acetochlor were showed stable under all test conditions. However, significant racemization was observed for malathion, phenthoate and fenpropathrin in methanol, ethanol and water, but not in *n*-hexane, isopropanol, acetone or methylene chloride. The kinetic parameters (rate constant k and half-life $T_{1/2}$) of the abiotic racemization were calculated through a mathematical model of the first-order reaction. Furthermore, the extent of racemization varied among the solvents and was also affected by temperature dependence. The racemization of malathion, phenthoate and fenpropathrin in water was documented to be pH-dependent and took place more rapidly at pH 7.0 than at pH 5.8. The observed racemization was deduced to occur via a proton exchange process at the chiral center, and the relationship between the abiotic racemization and pesticide structure was further explored. Findings from this study are useful for better understanding enantioselectivity of chiral pesticides in environment and also for proper analysis, formulating or handling of enantiopure products.

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1. Introduction

Chiral pesticides account for more than a quarter of currently used pesticides and this ratio is still increasing [1]. According to the number of chiral centers in the structure, a chiral pesticide may consist of two or multiple enantiomers or stereoisomers. Different enantio-/stereoisomers of a chiral pesticide often exhibit different biological property, toxicity and metabolism behavior in the environment, and the pesticidal activity of a chiral pesticide usually resides in one or several enantio-/stereoisomers [2]. To lower application rates and thus smaller amounts of chemicals released into the environment, efforts are being made to replace pesticide racemates (i.e., mixtures of enantio-/stereoisomers) by single biologically active enantio-/stereoisomer or enantio-/stereoisomerically enriched compounds [3,4]. The enantio-/stereoisomer-specific profiles of chiral pesticides have become important topics at the forefront of chemistry and toxicology research [5–7].

More recently, studies have shown that under certain conditions some chiral pesticides were configurationally unstable and could undergo significant isomer conversion. For instance, some pyrethroids, such as cypermethrin and cyfluthrin, were found to epimerize at the asymmetric carbon in the benzylic moiety (i.e., α-carbon chiral center) in short-chain alkyl alcohols (e.g., methanol and ethanol) or in water-alcohol mixtures [8–11]. It is obvious such conversion would reduce the efficacy of biologically active enantio-/stereoisomer due to the formation of nonactive enantio-/stereoisomer, and even make the use of enantio-/stereopure product pointless when conversion is fast enough. Moreover, as alcohols and water are often used in sample extraction, storage and analysis processes, isomer conversion may occur, causing analytical biases in chiral selective analysis. Potential isomer conversion must be considered significantly to ensure accurate and rigorous data from sample preparation and separation processes.

Researchers have observed interconversion between enantiomers in solvents for many chiral compounds with different stereolabile units [12–16]. The interconversion profiles can be determined by classical interconversion experiments of single enantiomers or by dynamic and stopped-flow chromatographic techniques. Assuming that the conversion between a pair of enantiomers was a process of equilibrium and the conversion in both directions obeyed first-order kinetics, the following equations can describe the dissipation of the starting enantiomer and the forma-

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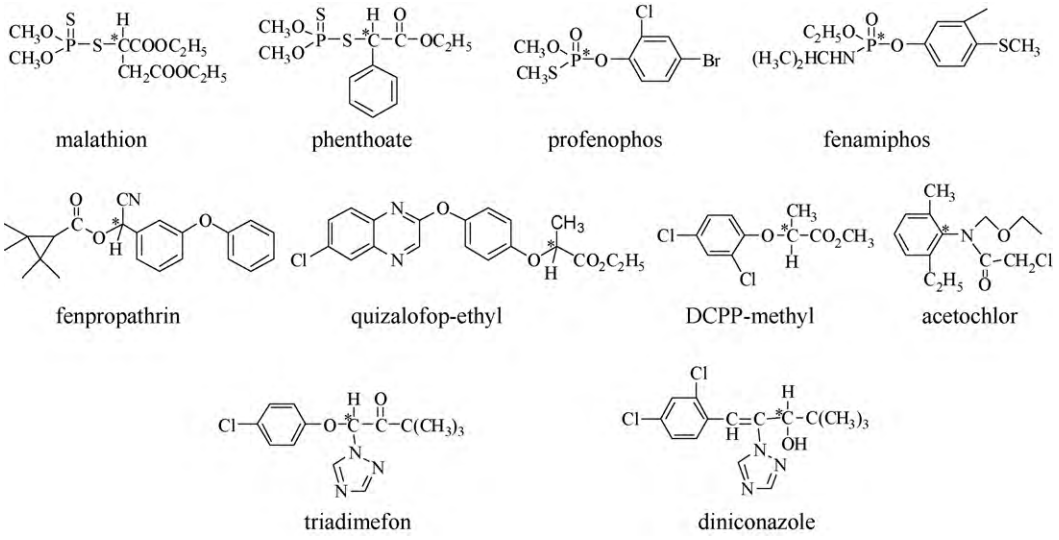

Fig. 1. Chemical structures of chiral pesticides (* indicates chiral position).

tion of the converted enantiomer [9,16,17]:

$$C_1 = 0.5C_0(1 + e^{-kt}) \quad (1)$$

$$C_2 = 0.5C_0(1 - e^{-kt}) \quad (2)$$

where C_1 is the concentration of the starting enantiomer at time t, C_0 is the initial concentration of the starting enantiomer, C_2 is the concentration of the resulted enantiomer at time t and k is the rate constant of conversion. The half-life of conversion ($T_{1/2}$) can be calculated via

$$T_{1/2} = \ln \frac{2}{k} \quad (3)$$

From the kinetic rate constants, the apparent free energy barriers $\Delta G^{\#}$ (T) can be calculated by the Eyring equation [15,16]:

$$\Delta G^{\#} = -RT \ln \left(\frac{k \cdot h}{k_b \cdot T} \right) \quad (4)$$

where k is kinetic rate constant, k_b is the Boltzmann constant, h Planck's constant, R the universal gas constant and T is the temperature in K.

In the case of chiral pesticides, however, up to now only several pyrethroids have received some considerations on their abiotic isomer conversion. Information related to the chiral stability of many other chiral pesticide species is still poorly learn [18,19]. In a recent study, we investigated the chiral stability of triazole pesticides, i.e., triadimefon and diniconazole, in various organic solvents and water [20]. The results revealed rapid racemization for triadimefon in methanol, ethanol and water, whereas diniconazole was chirally stable. In this study, eight chiral pesticides, which were selected to cover different pesticide species and origins of chirality, were investigated to explore their chiral stability in organic solvents and water. The pesticides included four organophosphorus insecticides (malathion, phenthoate, profenophos and fenamiphos), one pyrethroid insecticide (fenpropathrin), two phenoxyalkanoic ester herbicides (quizalofop-ethyl and dichlorprop-methyl or DCPP-methyl) and one acetamide fungicide (acetochlor). As seen in Fig. 1, each of the pesticides has one chiral center and thus consists of two enantiomers. Among them, profenophos and fenamiphos are P-chiral insecticides and acetochlor displays axial chirality. The other five pesticides are all C-chiral compounds. The relationship between the abiotic racemization and pesticide structure was further explored in this study.

The purpose of this study is not to add the fundamental knowledge of chiral pesticide chemistry, but rather to demonstrate that potential racemization of chiral pesticides due to solvents must be considered significantly during chiral selective analysis. Findings from this study are useful for better understanding enantioselectivity of chiral pesticides in environment and also for proper analysis, formulating or handling of enantiopure products.

2. Materials and methods

2.1. Chemicals and reagents

Analytical standards of phenthoate (98.0%) and DCPP-methyl (98.2%) were purchased from Dr. Ehrenstorfer (Germany). Standards of malathion (99.0%), profenophos (97.8%), fenpropathrin (99.5%) and quizalofop-ethyl (96.4%) were provided by National Pesticide Quality Inspection Center of China, and fenamiphos (98.5%) and acetochlor (93.7%) were from Shanghai Pesticide Research Institute. Stock solutions of the pesticides were made up at a concentration of 1 mg mL^{-1} in 100:10 hexane/isopropanol (v/v) and preserved at 4 °C. *n*-Hexane, methanol, ethanol, isopropanol, acetone and methylene chloride were all of analytical grade, redistilled and filtered through a 0.45-μm filter before use. Other solvents and chemicals were of analytical grade.

2.2. Enantioselective analysis and isolation of enantiomers of chiral pesticides

A Shimadzu LC-20AB high-performance liquid chromatography (HPLC) system (Shimadzu Corporation, Japan) consisted of a LC-20AB pump, a SPD-20A UV/VIS detector, a CTO-10AS column oven and a SIL-20A manual injector with a 20-μL sample loop. The signal was acquired and processed by a LC-20AB solution workstation. The HPLC columns used for enantioselective separation were a Chiralcel OD-H column (Daicel Chemical Industries Ltd. Japan, 250 mm × 4.6 mm i.d., 5-μm particle size) and a Chiralcel OJ-H column (Daicel Chemical Industries Ltd. Japan, 250 mm × 4.6 mm i.d., 5-μm particle size), each protected with a guard column of the same phase. The enantioselective separation was performed at 20 °C and the flow rate was set at 1.0 mL min^{-1}. The mobile phase was *n*-hexane with appropriate percentage of isopropanol modifier. Complete separation of the two enantiomers of each pesticide was accomplished after optimization of resolution conditions on the two chiral columns. The retention times of individual enantiomers are given in Table 1. For the purpose of station more clearly,

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