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Stereoselective quantitation of haloxyfop in environment samples and enantioselective degradation in soils

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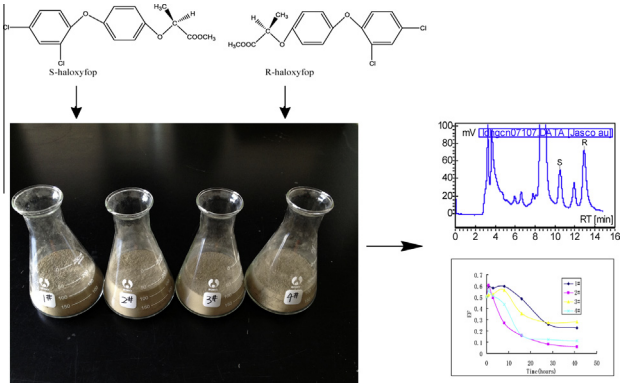
HIGHLIGHTS

- The enantiomers of haloxyfop was first separated on (R, R) Whelk-O 1 chiral column.
- The enantioselective residue analysis method of haloxyfop in environmental matrix was set up.
- Stereoselective dissipation of haloxyfop in four soils was investigated.
- The S-haloxyfop was preferentially degraded.

GRAPHICAL ABSTRACT



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ABSTRACT

The chiral separation of haloxyfop enantiomers was first performed on (R, R) Whelk-O1 chiral column (pirkle type) by high-performance liquid chromatography (HPLC). Chromatographic conditions such as mobile phase composition and column temperature were optimized, and the best resolution was obtained using hexane/n-propanol (98/2) with Rs value of 3.43. Chiral residue analysis methods for haloxyfop enantiomers in environmental matrices, such as soil and water, were developed with recoveries ranging from 85.95% to 104.25%. The results showed that these methods were effective enough for detecting the residual enantiomers environmental matrices. The behavior of haloxyfop in four soils was studied and the enantioselective degradation was found with enantiomer fraction values ranging from 0.058 to 0.61. The research work was extremely useful for investigating the fate of individual enantiomers in environment, the mechanism of the stereoselective behaviors, and the risk assessment of chiral pesticide.

1. Introduction

Pesticides provide numerous benefits, such as increasing food yield, decreasing damage to crops, and reducing disease vector populations. Nevertheless, as a major source of contamination and pollution in the environment, pesticide exposure can pose risks to human (Paraíba et al., 2003; Matamoros et al., 2009). So diverse mitigation strategies are implemented to make them safer, minimize their use, and reduce their unintended environment effects. Of the pesticides currently used, 28% are chiral, in which 20% of chiral pesticides are herbicides (Ulrich et al., 2012).

Aryloxyphenoxy-propionate (AOPP) herbicides are a class of fatty acid synthesis inhibitors, and they are regarded as selective and systematic herbicides, used in many crops like barley, wheat,

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wild oat, soybean, cotton, tomato and potato to control annual and perennial grasses (Bao et al., 2010; Bagheri et al., 2013). AOPPs are available as an ester and they can undergo decomposition to the bioactive acid in the environment (Roy and Singh, 2005; Lucini and Pietro Molinari, 2010). In addition, they are toxic to aquatic organisms, and also potentially teratogenic and carcinogenic to biological species (Dearfield et al., 1999).

AOPPs have an asymmetrical carbon atom in the propionate side chain and thus a pair of optical isomers. It had already been recognized that only the R-enantiomers of these compounds showed herbicidal activity in the 1950s (College et al., 1956). This different biological activity is not surprising as most biological reactions are enzymatically mediated. It has also been shown that the S-forms of AOPPs are more toxic and persistent in the environment than their antipodes. Consequently, enantiopure products (R-enantiomers) have been developed and replaced the racemic products in many countries (Müller and Buser, 1997). The use of active enantiomer not only reduced the amounts of pesticides released into the environment, but also avoided possible adverse effects of non-active isomers (Buerge et al., 2013a). Recent research found that the enantiomers of chiral compounds may also be converted to their antipodes (enantiomerization or racemization) (Zhang et al., 2010; Buerge et al., 2013b). This process may be problematic for pesticides, if it occurred under environmental conditions. When enantiopure products were used, it could decrease the amount of the active enantiomer and increase the side effects of the product (Buser and Müller, 1997). If enantiomerization is fast, it would even be pointless to use enantiopure products. For these reasons, a rapid, selective, and sensitive method is desirable for determining the two isomers of AOPPs directly from environment samples and investigating their behavior.

Haloxyfop is a foliar-applied AOPP herbicide for the selective control of annual and perennial grasses in broadleaf crops (Irzyk et al., 1990). It has demonstrated that haloxyfop is a potent inhibitor of acetyl-CoA carboxylase (E.C.6.4.1.2.), a key enzyme in fatty acid synthesis, which is obtained from non-tolerant species (Burton et al., 1987; Secor and Cséke, 1988). Haloxyfop has an asymmetrically substituted C-atom and thus consists of a pair of enantiomers. It has been reported that the R-haloxyfop has at least 1000-fold higher activity than the S-enantiomer when applied post-emergent (Gerwick et al., 1988), but comparatively little information is available on the resolution of haloxyfop enantiomers and their selective dissipation in environment samples.

In this study, an analytical method for the separation of haloxyfop enantiomers was first developed based on (R, R) Whelk-O 1 chiral stationary phase (CSP), and the enantiomers were identified by circular dichroism (CD) detector. The effects of modifier content in mobile phase and column temperature for the separation were investigated. More significantly, we also set up a valid method for enantioselective residue analysis in soil and water samples. Furthermore, the method was employed on the enantioselective degradation of haloxyfop in sterilized and nonsterilized soils. This may have some implications for better environmental and ecological assessment for chiral pesticides.

2. Materials and methods

2.1. Chemicals and Materials

Haloxyfop (98.5%) was obtained from Institute for Control of Agrichemicals Ministry of Agriculture. The solid phase extraction (SPE) column (AccuBond SPE ODS-C18 Cartridges, 500 mg, 6 mL) was supplied by Agilent Technologies. All solvents were of analytical grade, distilled, and filtered (0.45 μm) before used. Water was prepared by Millipore purification system.

2.2. Instrumentation and Chromatographic Conditions

Chromatography in this study was performed using an Agilent 1100 series HPLC equipped with a G1311A pump, G1322A degasser, G1328A injector, and G1315A DAD. JASCO 2000 HPLC (Jasco Co., Tokyo, Japan), equipped with pu-2089 plus pump, CD-2095 plus CD detector, and Chrompass workstation was used to determine the elution orders of the enantiomers.

Chromatographic separations were performed at room temperature by using the (R, R) Whelk-O 1 column (250 mm × 4.6 mm i.d.; 1-(3, 5-dinitrobenzamido)-1, 2, 3, 4- tetrahydrophenanthrene bonded CSP) purchased from Regis Technologies Inc., Morton Groove, IL (USA). Mobile phase was n-hexane with an appropriate percentage of ethanol, *n*-propanol, iso-propanol, *n*-butanol, iso-butanol or *n*-amylalcohol as a modifier. Flow rate was 1.0 mL/min, monitoring wavelength was 225 nm, and injection volume was 20 μL. Capacity factor (k), separation factor (α) and resolutions (Rs) were calculated from the formula $k = (t - t_0)/t_0$, $\alpha = k_2/k_1$, $Rs = 2(t_2 - t_1)/(W_1 + W_2)$, where t was the retention time and t_0 was the void time at given conditions, k was the capacity factor and W was the base line peak width. The influence of column temperature was also studied using n-hexane-IPA mobile phase.

2.3. Extraction of soil and water samples

The soil samples (25 g) were extracted by 50 mL of acetone in a 250 mL conical flask for 30 min on a mechanical shaker, filtered through a Buchner funnel, and extracted by 20 mL of acetone again. The combined acetone was extracted by 20 mL dichloromethane three times after adding 0.4 g sodium chloride. The combined dichloromethane organic extracts was dried by anhydrous sodium sulfate and evaporated to 1 mL by a vacuum rotary evaporator at 35 °C, and reconstituted in 1 mL isopropanol.

Water sample (100 mL) was extracted and cleaned using ODS-C18 SPE cartridges, which was preconditioned by 3 mL of methanol and 3 mL of Milli-Q water. Haloxyfop was eluted by 5 mL of methanol from SPE cartridge after sample loaded. The eluting solvent was collected and evaporated under nitrogen to dryness, diluted to 1 mL with isopropanol.

2.4. Treatment and incubation of Soils

Four test soils from different agriculture regions (0–10 cm) of China that had not been treated with haloxyfop in the last five years were used in this study. Their major properties are shown in Table 1.

Portions of 25 g of air-dried soils were placed into 250-mL flasks, adjusted to moisture content of 25% and maintained in the dark at room temperature for 7 d to activate the microorganisms in soils. After that, the soil samples were fortified by adding standard solution of rac-haloxyfop at spike level of 5 μg/g (dry soil). The soil samples were incubated with a water content of 25% at 25 °C in the dark for 60 d, covered with sterile cotton plugs. The moisture content in each flask was checked gravimetrically everyday, the loss of water by evaporation was compensated by adding distilled water. Each incubation was carried out in triplicate, and a blank sample was set.

To determine the microbial mediation roles in enantioselective dissipation, a set of soil samples were autoclaved twice at 120 °C for 2 h to eliminate microbial activity. Haloxyfop was added in sterilized samples, and then sealed with film to maintain sterile conditions. At appropriate time intervals, these samples were extracted and analyzed by HPLC.