



Enantioseparation and determination of the chiral phenylpyrazole insecticide ethiprole in agricultural and environmental samples and its enantioselective degradation in soil



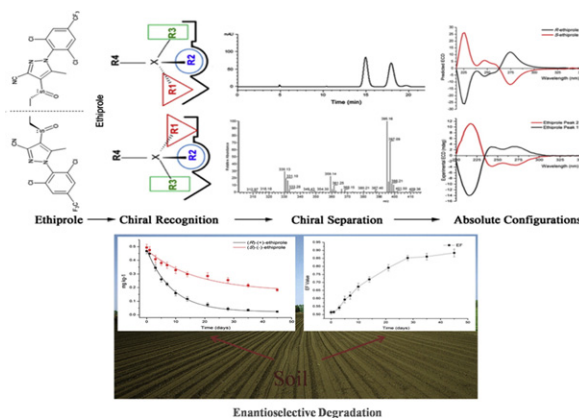
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HIGHLIGHTS

- The ethiprole enantiomers were completely separated.
- A novel method for enantioselective determination of ethiprole was developed.
- The absolute configurations of ethiprole enantiomers were firstly determined.
- The (R)-(+)-ethiprole was preferentially degraded in soil.

GRAPHICAL ABSTRACT



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ABSTRACT

An effective method for the enantioselective determination of ethiprole enantiomers in agricultural and environmental samples was developed. The effects of solvent extraction, mobile phase and thermodynamic parameters for chiral recognition were fully investigated. Complete enantioseparation of the ethiprole enantiomers was achieved on a Lux Cellulose-2 column. The stereochemical structures of ethiprole enantiomers were also determined, and (R)-(+)-ethiprole was first eluted. The average recoveries were 82.7–104.9% with intra-day RSD of 1.7–8.2% in soil, cucumber, spinach, tomato, apple and peach under optimal conditions. Good linearity ($R^2 \geq 0.9991$) was obtained for all the matrix calibration curves within a range of 0.1 to 10 mg L⁻¹. The limits of detection for both enantiomers were estimated to be 0.008 mg kg⁻¹ in soil, cucumber, spinach and tomato and 0.012 mg kg⁻¹ in apple and peach, which were lower than the maximum residue levels established in Japan. The results indicate that the proposed method is convenient and reliable for the enantioselective detection of ethiprole in agricultural and environmental samples. The behavior of ethiprole in soil was studied under field conditions and the enantioselective degradation was observed with enantiomer fraction values varying from 0.494 to 0.884 during the experiment. The (R)-(+)-ethiprole ($t_{1/2} = 11.6$ d) degraded faster than (S)-(–)-ethiprole ($t_{1/2} = 34.7$ d). This report is the first describe a chiral analytical method and enantioselective behavior

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of ethiprole, and these results should be extremely useful for the risk evaluation of ethiprole in food and environmental safety.

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1. Introduction

Chiral insecticides, which are the mainstay of modern insecticides, are used to increase crop production and reduce insect-borne disease. Phenylpyrazole insecticides are widely used in crop protection and public hygiene in Asian due to their effectiveness against a wide range of insects (Raveton et al., 2006; Tingle et al., 2003). Phenylpyrazole insecticides exhibit good insecticidal activity that disrupts the insect central nervous system by blocking the passage of chloride ions through the GABA receptor (Moffat, 1993). In recent years, because many insects have developed resistance to various types of insecticides, the phenylpyrazole insecticide has been extensively used around the world for pest control applications (Tang et al., 2010). The phenylpyrazole insecticide has an asymmetric sulfur atom as a chiral center, which is different from pyrethroids and organophosphates. Enantiomers have identical physico-chemical properties, and their interactions with biological macromolecules are chiral selective, leading to enantiomer selectivity in biodegradation, ecotoxicity and human health effects (Tan et al., 2008). The potential for adverse effects is most likely greater than expected from data for the achiral results due to a wide range of chiral pesticides that were not included in the assessment. Therefore, the enantioselective separation of phenylpyrazole insecticides have attracted considerable attention in recent years.

Ethiprole (Fig. 1) (5-amino-3-cyano-1-(2,6-dichloro-4-trifluoromethylphenyl)-4-ethylsulfanylpyrazole) is a broad spectrum chiral phenylpyrazole insecticide used to control chewing and

sucking insects. Ethiprole is one of the best-selling insecticides which is used on a wide range of crops, such as rice, vegetable, cotton, corn, alfalfa, peanuts, and fruits (Caboni et al., 2003). Similar to most chiral pesticides, ethiprole is typically marketed and applied as the racemate as a member of the phenylpyrazole insecticide class. Many researchers have reported the enantioselective separation and enantiomeric analysis methods of fipronil in plants or soils (Jones et al., 2007; Qu et al., 2014; Nillos et al., 2009; Liu et al., 2008). The (*R*)-enantiomer degraded faster in Chinese cabbage, while the preferential degradation of (*S*)-fipronil in sediment and hyacinth plants. In addition, stereoselective toxicity has been reported for the fipronil enantiomers and the (*R*)-form was higher than that of the (*S*)-form in tubifex tissue. (Liu et al., 2008, 2006). Ethiprole has an ethylsulfanyl substituent that replaces the trifluoromethylsulfanyl moiety in fipronil. However, only a small number of traditional achiral methods have been investigated for ethiprole (Eitzer et al., 2013). Although ethiprole is widely used, limited studies have been conducted on the resolution of ethiprole enantiomers and their selective dissipation in environmental samples, which resulted in a lack of data during risk assessment (Zhang et al., 2012a). Therefore, it is necessary to develop enantioselective separation and enantiomeric analysis methods of ethiprole to provide more accurate data for evaluating environmental risks and food safety.

In this study, the stereoisomers of ethiprole were successfully separated by enantioselective HPLC on a carbamoyl-cellulose chiral stationary phase (cellulose tris (3-chloro-4-methyl phenyl carbamate)) in reversed-phase elution mode. The mobile phase systems were

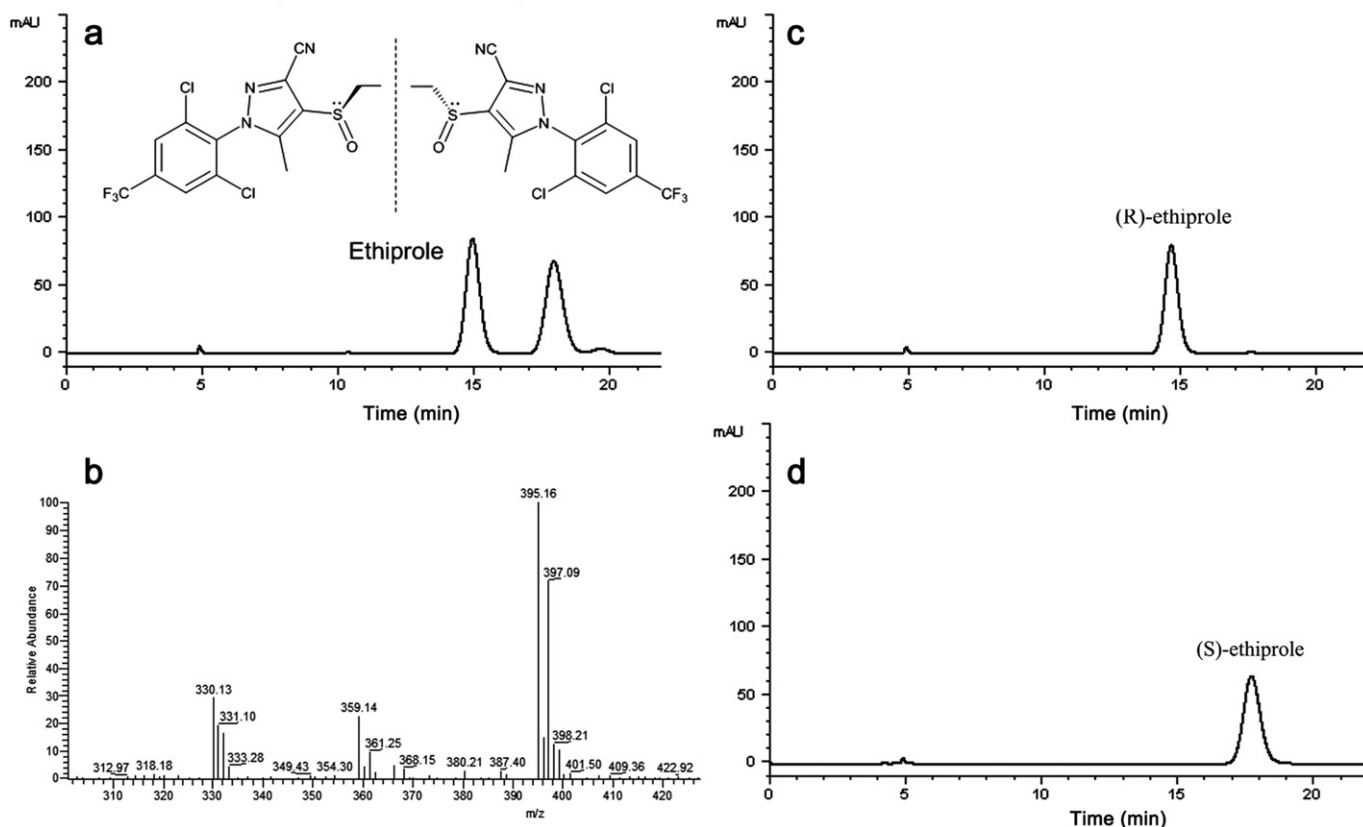


Fig. 1. Molecular structures, chromatograms and mass spectra of the ethiprole enantiomers: (a) HPLC chromatogram of racemic ethiprole; (b) mass spectra of ethiprole; (c) chromatogram of (*R*)-(+)-ethiprole; and (d) chromatogram of (*S*)-(-)-ethiprole.

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