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Residue and risk assessment of pyridaben in cabbage

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ABSTRACT

The dissipation and residue of pyridaben in cabbage under field conditions were investigated. A sensitive, simple, and fast method for determining pyridaben in cabbage was established by high-performance liquid chromatography tandem mass spectrometry. The average recoveries were in the range of 90.29–95.00% with relative standard deviations ranging from 1.72% to 6.39%. The field results showed that pyridaben dissipated rapidly in cabbage and had a half-life of 2.8–3.5 d. During harvest, the terminal residues of pyridaben were 0.01–0.80 mg/kg. Given that no maximum residue limit (MRL) has been set for pyridaben in cabbage, risk assessment was evaluated by using the risk quotient (RQ). Results indicated that the RQ value was significantly lower than RQ = 1. Thus, the effect of pyridaben in cabbage at the recommended dosage was negligible to humans. This study could provide guidance for the safe and reasonable use of pyridaben as a broad-spectrum acaricide and serve as a reference for the establishment of an MRL in China.

1. Introduction

Pyridaben (2-*tert*-butyl-5-(4-*tert*-butylbenzylthio)-4-chloropyridazin-3(2*H*)-one; Fig. 1) is a novel broad-spectrum acaricide that exhibits high potency and low toxicity. Pyridaben was first reported by Hirata et al. and was subsequently discovered and introduced by Nissan Chemical Industries Ltd. Pyridaben was first marketed in Belgium as a pesticide in 1990 (The e-Pesticide Manual Version 3.0, 2003–2004).

Pyridaben has protective and therapeutic effects on different growth periods of leaf mites and *Aculops lycii*. Pyridaben can also be applied to various fruits, vegetables, and economic crops (Li, Yang, & She, 2007).

Several studies have recently reported analytical methods for measuring pyridaben. To date, pyridaben residue analysis is mainly performed via gas chromatography (GC) (Boulaid, 2005; Jun & Bin, 2008), high-performance liquid chromatography (HPLC) (Yu, 1996), GC coupled with mass spectrometry (GC–MS) (Garrido-Frenich, 2003), and HPLC coupled with mass spectrometry (HPLC–MS) (Sannino, Bolzoni, & Bandini, 2004).

Few studies have investigated the dissipation of pyridaben. Zhang, Shang, Chen, and Wu (2005) studied the dynamic variation of pyridaben residues in citrus fruits and indicated that the half-life of pyridaben in orange ranged from 11.9 to 24.9 d in different experimental areas. Ma et al. (2007) studied the residue dynamics of pyridaben in apples and showed that the half-life of pyridaben in apple was 7.3 d. Chen, Cai, Guo, and Yang (2011) determined the dissipation dynamics of pyridaben residues in bananas and found that half-life ranged from 2.8 to 2.9 d. To our knowledge, no study has been conducted on the dissipation of pyridaben on cabbage under field conditions.

Cabbage is one of the most widely grown vegetables for human consumption. However, some diseases and pests can cause problems during the growth of cabbage. Thus, pyridaben is used to protect cabbage from *Phyllotreta striolata*. Field dissipation studies on pesticide persistence in foodstuffs and pesticide residue behaviour in agricultural fields are necessary to ensure food safety and protect the environment (Liang et al., 2011). The maximum residue limit (MRL) is enforced to protect humans from the harmful effects of pesticides and to maintain pesticide residues below the proposed MRL during harvest (Karmakar & Kulshrestha, 2009). However, the MRL of pyridaben in cabbage is not regulated in China and other countries and organizations.

A simple HPLC–MS/MS method was established to detect pyridaben residues in cabbage. A field study was also conducted to investigate the dissipation of pyridaben in cabbage under field conditions. Given that China has not set an MRL value for pyridaben in cabbage, risk assessments based on field trial data are necessary for pyridaben in cabbage after the harvest season. This study could help the government establish the MRL of pyridaben in cabbage and provide guidance on the proper and safe use of pyridaben.

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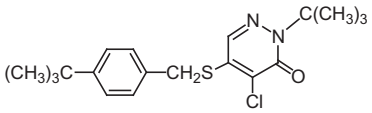

Fig. 1. The chemical structure of pyridaben.

2. Materials and methods

2.1. Field experiment design and sampling

A field experiment was conducted in 2011 in Beijing, Guangzhou, and Wuhan, according to the NY/T 788-2004 (*Guideline on Pesticide Residue Trials*) issued by the Ministry of Agriculture of the People's Republic of China.

A formulation of 40% pyridaben wettable powder (WP) was applied on cabbage samples at a dosage of 202.5 g ai/ha to study the dissipation behaviour of pyridaben. Three replicate plots were prepared, and each plot had an area of 15 m^2. A buffer area was also employed to separate each plot. Cabbage samples were collected 0, 1, 3, 7, 10, 14, 21 and 28 d after pyridaben spraying.

To study the terminal residues of pyridaben, 40% pyridaben WP was applied on the cabbage samples at a dosage of 135 (recommended dosage) and 202.5 g ai/ha (1.5 times the recommended dosage). Each dosage application was sprayed three and four times. Three identical procedures were conducted at each treatment and a buffer area was set to separate each plot. The spraying interval was 7 d. The cabbage samples were collected 3, 5 and 7 d after spraying. Approximately 2.5 kg of cabbage were collected and homogenised with a blender for every sampling from each plot. All samples were stored at −20 °C for the analysis.

2.2. Standards and reagents

Analytical grade (99.5%) pyridaben was obtained from the National Research Center for Certified Reference Materials (Beijing, China). Acetonitrile (chromatographically pure) was obtained from Fisher Scientific (Pittsburgh, PA). Anhydrous magnesium sulfate and sodium chloride (analytical reagent) were purchased from Beijing Chemical Reagents Company (China). High-speed centrifuge (RJ-TDL-40B) was obtained from Beijing Medicine Centrifuge Factory (China).

2.3. Extraction procedure

Ten grams of a previously homogenised cabbage sample was weighed in a 50 mL Teflon centrifuge tube. An aliquot of 10 mL acetonitrile was added as the extraction solvent, and the resulting mixture was vortexed for 1 min. Roughly 4 and 1 g of anhydrous magnesium sulfate and sodium chloride were subsequently added, respectively. The sample was mixed further by vortexing for 1 min and centrifuging for 5 min at 3800 rpm. Thereafter, 1 mL supernatant was filtered using a 0.22 μm filter membrane and transferred into the autosampler vial for HPLC–MS/MS analysis.

A blank sample was collected at the control area of field experiment; the extraction and clean-up procedure was as same as for the field sample.

2.4. HPLC–MS/MS analysis

A high-performance liquid chromatograph (LC-20A; Shimadzu, Kyoto, Japan) equipped with an API4000 mass spectrometer (Applied Biosystems, Foster City, CA) and an electrospray ion source was used to analyse the pyridaben residues. Chromatographic separation was performed on an Agilent Zorbax SB-C18 column (100 mm × 1.8 mm × 2.1 mm) with acetonitrile/water (0.1% formic acid) (v/v = 70/30) as the mobile phase at a flow rate of 0.3 mL/min. The injection volume was 10 μL. Electrospray ionisation and multi-reaction monitoring mode were used. Nitrogen (99.99%) was used as the drying gas at a flow rate of 8 L/min. The pesticide was analysed in positive ion mode. For quantification the transformation m/z 364.8 → 147.1 was measured, with the transformation m/z 364.8 → 309.2 being used for confirmation. Mass spectrometric conditions were 110 V declustering potential, 10 V entrance potential, 34 and 18 eV collision energies for m/z 147.1 and 309.2, 12 V collision cell potential. The relevant chromatogram is shown in Fig. 2.

2.5. Calculations

The dissipation of pyridaben in cabbage was fitted to an exponential model by using the following equations: $C_t = C_0 e^{-kt}$ and $t_{1/2} = ln\,2/k$, where C_t (mg/kg) is the pesticide concentration at time t (d), C_0 (mg/kg) is the initial concentration, k is the rate constant and $t_{1/2}$ is the half-life of dissipation.

Dietary exposure calculation and risk assessment were calculated by using the following equations:

$$\mathrm{EED\ (mg/kg,\,bw)} = \mathrm{CRL\ (mg/kg)} \times FI\ \mathrm{(kg)} \div \mathrm{bw(kg)},$$

$$\mathrm{RQ} = \mathrm{EED\ (mg/kg,}bw) \div \mathrm{ADI\ (mg/kg,}bw).$$

where EED is the estimated exposure dose, CRL is the calculated residue level, FI is the food intake, RQ is the risk quotient and ADI is the acceptable daily intake. According to a summary report of China Health and Nutrition Survey, the average standard vegetable intake of an adult per day is 276.2 g (Wang, 2005). The ADI for spirodiclofen is 0.01 mg/kg/d based on the National Food Safety Standard of China (GB2763-2012: MRLs for pesticides in food).

An RQ value that is higher than RQ = 1 indicated that the risk of pesticide for humans is unacceptable. A citrus fruit is not safe for human consumption if pyridaben is used as the pesticide. By contrast, an RQ value that is less than RQ = 1 represents minimal risk to humans (Zhang et al., 2009).

3. Results and discussion

3.1. Linearity, recovery and detection limits

For the fortified recovery study, standard pyridaben was spiked at three different levels with five replicates for each level. The results were 91.0–95.0% in cabbage with relative standard deviations ranging from 1.72% to 6.39% (Table 1). The calibration curves for pyridaben were obtained by plotting the peak area against the concentration of the matrix-matched standards from 0.001 to 1.0 mg/kg with a linearity equation of $y = 2E{+}06x + 32192$. The results showed good linearity with a correlation coefficient of 0.997 in cabbage.

The limit of detection for the test compound was determined by using a signal-to-noise ratio of three with reference to the background noise obtained for the blank sample, whereas the limit of quantification was defined as the lowest spiked level (Table 1).

3.2. Dissipation of pyridaben in cabbage

Fig. 3 shows the dissipation of pyridaben residue in cabbage under field conditions. The initial concentrations of pyridaben in cabbage were 4.92, 4.16 and 0.88 mg/kg with corresponding half-lives of 2.8, 2.8 and 3.5 d for Beijing, Wuhan and Guangzhou, respectively. The half-life ($t_{1/2}$) and dissipation equation of pyridaben in cabbage are summarised in Table 2.