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Residue behaviors and dietary risk assessment of dinotefuran and its metabolites in *Oryza sativa* by a new HPLC–MS/MS method

Ruijuan Li [a,1], Tongjin Liu [a,1], Shuhua Cui [b], Sicong Zhang [a], Jianlei Yu [a,*], Guochun Song [a,*]

[a] Institute of Plant Protection, Shandong Academy of Agricultural Sciences, Jinan 250100, China
[b] Inspection and Quarantine Technology Center of Shandong Exit Entry Inspection and Quarantine Bureau, Qingdao 266002, China

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ABSTRACT

In this study, we developed a new method to detect dinotefuran and its metabolites (UF and DN) in *Oryza sativa* (Rice) by HPLC–MS/MS in multiple reaction monitoring (MRM) modes. The recovery rates for dinotefuran, UF and DN were 82.3–85.8%, 83.7–89.0%, and 81.6–90.2%, respectively. The dissipation kinetics of dinotefuran in rice followed a combined first + first kinetic model, where the half-lives of dinotefuran and its metabolites were determined to be between 0.5 and 2.3 days. The dinotefuran residue in brown rice sampled at day 7, 14, and 21 after the last application was 0.4131 mg/kg with a very low risk quotient (RQ) value. We recommend that the safety interval of application for rice is 7 days. The method developed in this study is simple and rapid, with high accuracy and precision which meet the requirements for quantitative analysis of dinotefuran in rice.

1. Introduction

Rice is one of the main staple foods for humans that have been consumed throughout the world. Nearly half of the world's population, including almost the entire population of East Asia and Southeast Asia, consume rice. Besides being consumed as food, rice can also be used for wine production and as raw materials in the sugar industry. Currently, there are more than 250 types of rice pests, mainly planthoppers, *Chilo suppressalis*, and *Cnaphalocrocis medinalis,* which cause severe yield losses and quality decline of rice (Huang, Wang, Liu, Fu, & Zhu, 2013). An effective control of rice pests is of great significance for sustainable rice yields.

Dinotefuran ((*RS*)-1-methyl-2-nitro-3-(tetrahydro-3-furylmethyl) guanidine) (Fig. 1) is the third-generation of neonicotinoids developed by Mitsui Chemicals (Tokyo, Japan) (Wakita et al., 2003). It is the only member of the neonicotinoid family that does not contain chlorine substitutes and aromatic rings, enabling it to be effective to the pests which are resistant to the first- and second-generation neonicotinoids (Tomlin, 2011). The main mechanism of action is through the inhibition of the nerve conduction in insects by binding to nicotinic acetylcholine receptors (Mori, Okumoto, Kawahara, & Ozoe, 2002). Dinotefuran possesses stomach poisoning and contact poisoning, as well as characteristics of a high, durable and broad-spectrum insecticidal activity, yet highly safe to plants and animals (David, George, & Peter, 2007). Dinotefuran has been applied to prevent and control planthoppers, stink bugs, and Nephotettix cincticeps, in rice (Watanabe, Baba, & Miyake, 2011). Dinotefuran is widely used around the world, accounting for more than 25% of world's pesticides (van der Sluijs et al., 2013). Indiscriminate use of dinotefuran is inevitably generating residues in the environment and cereal grains, thus affecting the human health and quality of life. Besides, it also affects the biodiversity and reduces the role of natural enemies of the pests. Therefore, the understanding of the dissipation kinetics of dinotefuran and dietary intake risk are essential to human food safety and the balance of the paddy ecosystem.

A number of studies on dinotefuran in rice, apples, cucumbers, eggplant, ginger, onions, and other crops have been reported (Chen et al., 2012, 2015; Watanabe, Kobara, Baba, & Eun, 2015; Xie et al., 2011; Zhang et al., 2013). However, there are relatively few reports on both dinotefuran and its metabolites in crops. Watanabe et al. reported that the main dinotefuran metabolites in plants are 1-methyl-2-nitroguanidine (MNG), 1-methyl-3-(tetrahydro-3-furylmethyl)urea (UF), and 1-methyl-3-tetrahydro-3-furylmethyl)guanidine (DN) (Fig. 1) (Watanabe et al., 2011). These metabolites are toxic to bees, and exhibit higher mobility and durability than dinotefuran. Rahman et al. analyzed the residues of dinotefuran

* Corresponding authors at: 202 Gongye North Road, Jinan, Shandong 250100, China.
E-mail addresses: jlyu2010@163.com (J. Yu), songguochun2008@163.com (G. Song).
[1] These authors contributed equally to this work.

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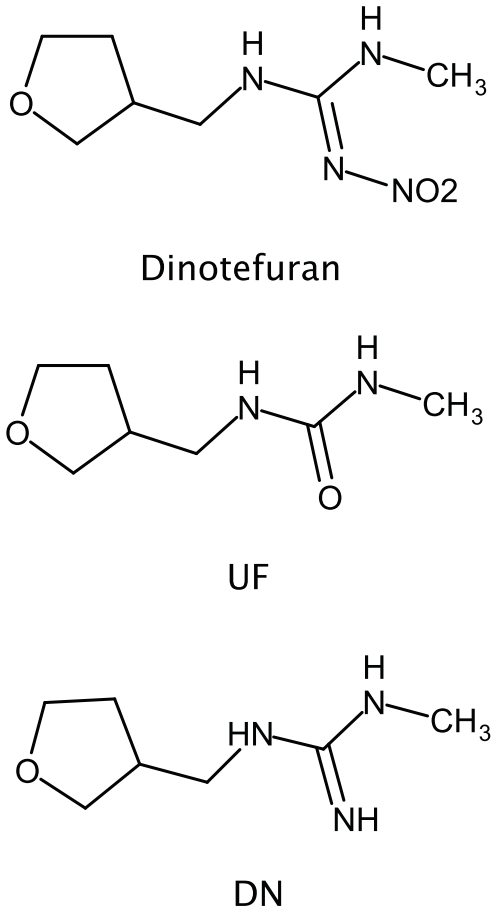

Fig. 1. Chemical structure of dinotefuran and its metabolites UF and DN.

and its metabolites (MNG, UF, and DN) in tea leaves and melons (Rahman et al., 2013, 2015), using a QuEChERS pre-treatment method, with 1–2% acetic acid in acetonitrile for extraction followed by purification by primary secondary amine (PSA), C18 and SPE C18 columns. Kamel analyzed the residues of dinotefuran and its metabolites (UF and DN) in honey, which used a similar QuEChERS method, with 2% triethylamine (TEA) in acetonitrile for extraction followed by purification by a C18 column (Kamel, 2010). However, both of these methods have a low DN recovery rate and relative poor reproducibility. Currently, there is still no report on the residues of dinotefuran and its metabolites in rice. The United States stipulates that the residues of dinotefuran are the sum of dinotefuran, UF, and DN, and the residue limit of Dinotefuran in rice is 9 mg/kg (https://www.globalmrl.com/). In this study, we developed a new method for simultaneous determination of the residues of dinotefuran and its metabolites (UF and DN) in rice. The results showed that our method is simple and rapid, and gives a great separation with high accuracy and precision that meets the requirements of quantitative analysis. Based on this new method, we further studied the dissipation kinetics of dinotefuran and assessed the dietary intake risk of the dinotefuran residue in rice.

2. Materials and methods

2.1. Reagents

The 50% dinotefuran soluble powder was provided by Anhui Yangzi Chemical Industry Co., Ltd. Dinotefuran (95.0% purity), UF (97.0% purity), and DN (97.9% purity) were provided by Beijing Qinchengyixin Technology Co., Ltd. HPLC-grade acetonitrile and methanol were provided by TEDIA company (Fair Field, Ohio, US). The other analytical grade reagents were provided by Sinopharm Chemical Reagent Co., Ltd.

A total of 50 mg of dinotefuran, UF, and DN standard were dissolved in methanol in 50-mL volumetric flasks to make standard stock solutions (1 mg/mL). The standard stock solutions were stored at −20 °C. A series of dinotefuran, UF and DN solutions were prepared by serial dilution. The concentrations of the dinotefuran and UF were 0.002, 0.01, 0.1, 1, and 10 μg/mL whereas the concentrations of the DN solutions were 0.01, 0.1, 0.5, 1, and 10 μg/mL. All standard solutions were stored in the dark at 4 °C.

2.2. Field trials

Field trials were carried out in research stations at three different locations, including Zibo of Shandong Province, Zhanjiang of Guangdong Province, and Hefei of Anhui Province from 2014 to 2015. Both dissipation kinetics and residue determination experiments were carried out in accordance with the Guideline on Pesticide Residue Trials (NY/T 788-2004, the Ministry of Agriculture of China) and Standard Operating Procedures on Pesticide Registration Residue Field Trials established by the Institute for the Control of Agrochemicals, Ministry of Agriculture (ICAMA). Six treatments were carried out, including 5 treatments at different doses of dinotefuran and a control treatment. Each experiment was carried out in three plots of 30 m^2 and was separated by a buffer zone. All areas were subjected to routine horticultural treatment.

The rice plants were applied with pesticides 20 days after the plants were transplanted to the trial plots. The 50% soluble powder of dinotefuran was evenly sprayed at 180 g/ha (1.5 times the recommended high dose) by a knapsack sprayer, and the control was sprayed with water. The plant samples were collected at the 2nd hour, day 1, 3, 5, 7, 14, 21, 28, and 35 after the application of the pesticide. The rice plants were applied with pesticides during the late growth phase for the final residue trials. The 50% soluble powder of dinotefuran was evenly sprayed at 120 g/ha (the recommended high dose) to 180 g/ha (1.5 times the recommended high dose) for 3 to 4 times with a 7-day interval between sprays. The rice plants and grains were sampled at day 7, 14, and 21 after the last pesticide application.

2.3. Sample preparation

The collected rice plant samples were cut into small pieces (<1 cm^3). The evenly mixed samples were dispensed into two sets of 100-g samples by using the coning and quartering method. The threshed rice grain samples were shelled with a shelling machine. After the brown rice and rice hulls were mixed separately, two sets of 100-g samples of brown rice and a sufficient amount of rice hulls were dispensed separately into sample bags with proper labeling. All packaged and labeled samples were stored at −20 °C.

2.4. Extraction and purification

A total of 5 g processed rice sample was placed in a 50-mL centrifuge tube and mixed with 3 mL acetic acid followed by addition of 10 mL acetonitrile. The mixture was vortexed at 3000 r/min for 1 min followed by ultrasonic extraction for 15 min. The mixture was then added with 5g anhydrous magnesium sulfate and vortexed at 3000 r/min for 1 min followed by centrifugation at 5000 r/min for 5 min. Two-milliliter supernatant was transferred into a 15-mL centrifuge tube containing 0.03g PSA and C18 each, and 0.2g MgSO4. The mixture was vortexed and centrifuged at 5000