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Stereoselective bioactivity, acute toxicity and dissipation in typical paddy soils of the chiral fungicide propiconazole

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ABSTRACT

Propiconazole is a widely used systemic agricultural triazole fungicide with two chiral centers. In the present study, systemic assessments of propiconazole stereoisomers are reported for the first time, including absolute configuration, stereoselective bioactivity toward pathogens (*Ustilaginoidea virens, Magnaporthe oryzae, Fusarium moniliforme, Thanatephorus cucumeris,* and *Rhizoctonia solani*), and stereoselective acute toxicity toward aquatic organisms (*Scenedesmus obliquus*, and *Daphnia magna*). Moreover, the stereoselective dissipation of propiconazole in three types of paddy soil under laboratory-controlled conditions (aerobic, anaerobic and sterile) was investigated. The degree of bioactivity and acute toxicity of the propiconazole stereoisomers differed depending on the type of target pathogens and non-target organisms. There were 2.43–23.47 and 1.48–2.13 fold differences between the best and worst stereoisomer in bioactivity and toxicity, respectively. Under aerobic conditions, (*2S,4S*)-propiconazole and (*2S,4R*)-propiconazole were preferentially degraded in the three types of soils. However, no significant stereoselectivity was observed under anaerobic and sterile conditions. Propiconazole was configurationally stable throughout the study. In comprehensive consideration of bioactivity, toxicity and environmental behavior, using stereoisomer mixture rather than pure stereoisomer may help to control more species of disease in practical application, and the stereoselectivity should be taken into consideration in risk assessment.

1. Introduction

An increasing number of chemical pesticides are being used to increase food yield due to their high effectiveness and low cost [1–4]. It has been estimated that 25% of pesticides currently sold are chiral, and this figure is estimated to be over 40% in China with increasingly complex compounds registered for use [5,6]. In general, enantiomers of a chiral chemical have identical physicochemical properties while often showing obviously different bioactivity, metabolism, non-target toxicity, and environmental behavior when exposed to chiral conditions, including enzymes and biological receptors [7–12]. In most cases, only one enantiomer of a chiral compound has the desired effect on the target organism(s), whereas the other enantiomers are not only inactive against the targets but also an unwanted burden on the environment [11,13]. In addition, the degradation of chiral compounds in soil is enantioselective, and enantioselectivity often varies with the type of soil [14,15]. Increasing evidence indicates that racemates cannot adequately describe their actual biological activity, ecological risks and environmental fate [16–19]. Thus, treating chiral pesticides as single compounds in traditional risk evaluation may be inappropriate and incomplete. Unfortunately, until now most chiral pesticides are produced and released into the environment in the form of racemates due to commercial benefits and the state of chemical synthesis technology. Consequently, it is of great significance to study the biological activity, ecological risks and environmental fate of pure enantiomers to provide more accurate data for evaluating the environmental risks and public health, and further guide the appropriate use of chiral pesticides to reduce environmental risks.

Propiconazole, (1-[[2-(2,4-dichlorophenyl)-4-propyl-1,3-dioxolan-2-yl]methyl]-1H-1,2,4-triazole), is a broad spectrum systemic triazole fungicide used to control fungal diseases on fruits, cereals, vegetables, hardwoods, and other field crops. Like many other triazole fungicides,

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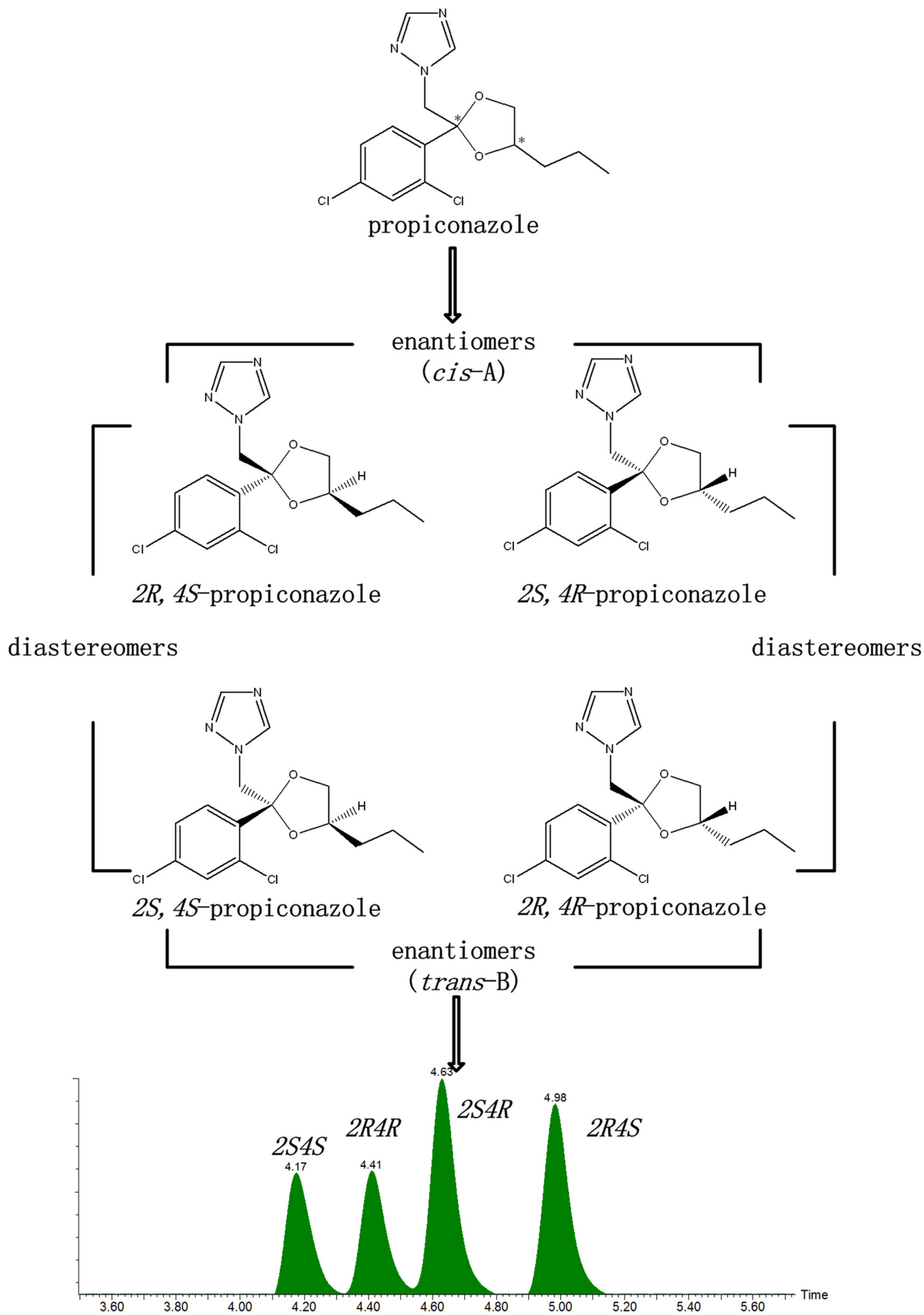

Fig. 1. The chemical structure of propiconazole stereoisomers.

propiconazole acts by interfering with ergosterol biosynthesis and inhibiting steroid demethylation [20]. It has been reported that propiconazole exposure was related to an increase in the incidence of hepatocellular adenomas and carcinomas in a group of male mice in a long-term feeding study [21,22]. Compared to other triazole fungicides, propiconazole is difficult to degrade and exhibits relatively high acute toxicity in a wide range of aquatic organisms [23]. Furthermore, propiconazole is widely used on crops, especially rice. Hence, pollution of surface aquatic ecosystems caused by propiconazole would become a significant environmental stress. In addition, propiconazole has two asymmetrically substituted C atoms, resulting in two pairs of enantiomers and two pairs of diastereomers for a total of four stereoisomers. The four stereoisomers are defined as *cis* A [(*2R,4S*) and (*2S,4R*)] and *trans* B [(*2S,2S*) and (*2R,2R*)] (Fig. 1). Pioneer studies