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Fate of triadimefon and its metabolite triadimenol in jujube samples during jujube wine and vinegar processing

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ABSTRACT

Chinese jujube (*Zizyphus jujuba* Miller) is an indigenous fruit with Chinese characteristics in China which is widely used in traditional medicines and also consumed as a food material. Chinese jujube is subjected to wide varieties of pesticides like triadimefon which are harmful to humans. In present study, the fate of triadimefon and its metabolite triadimenol during jujube wine and vinegar fermentation processing was assessed. Jujube samples collected from plants sprayed with triadimefon from field trials. The analysis of triadimefon and triadimenol residues were carried out by gas chromatography–mass spectrometry (GC-MS) at different steps of the fermentation i.e fresh jujube, first and second jujube juice and pomace, jujube wine, and jujube vinegar. Processing factors (P*f*s), which is defined as the ratio of pesticide residues in jujube sample to that in jujube wine or vinegar samples, were lower than 1 for triadimefon, indicating that food processing could reduce the pesticide level. But triadimefon was metabolised to triadimenol during this process with the P*f*s of triadimenol in jujube wine and vinegar were 1.38 and 1.13, respectively, indicating that more attention is needed towards the metabolites during the processing. The study indicates the level of safety towards triadimefon in jujube beverage processing and allows the refining of the dietary risk analysis.

1. Introduction

Chinese jujube (*Zizyphus jujuba* Miller) is a fruit with Chinese characteristics and indigenous to China with a history of over 4000 years (Li, Fan, Ding, & Ding, 2007). Jujube fruit is commonly used as a crude drug in traditional Chinese medicine for the purpose of analeptic, palliative, antibechic and also increasingly consumed as fresh or used in food products as food additive and flavouring agent due to their potential nutritive value (Li et al., 2007). Jujube fruits also have been reported in several food processing products, including compotes, alcoholic beverages, cakes and bread (Shobha & Bharati, 2007). China shares 90% of the world jujube production and its production has increased substantially during the last decade (Zhao, Zhang, Liu, Xue, & Pan, 2014).

Triadimefon, a broad-spectrum fungicide, is one of the most important and widely-used pesticides for the control of fungus on jujube fruits in China (Zhao et al., 2014). Recent report showed that different pesticides were found in jujube ranged from 59.4 $\mu g\ kg^{-1}$ to 2945.0 $\mu g\ kg^{-1}$, of which triadimefon was found at a concentration of 1.0 $\mu g\ kg^{-1}$ in fruits and 94.5 $\mu g\ kg^{-1}$ in jujube soil (Liu et al., 2016). Triadimefon and triadimenol (Fig. 1) are structurally related systemic fungicides with its registered use in many countries. Their main action mode is by inhibiting ergosterol biosynthesis in fungi (Siegel, 1981). The JMPR (Joint Meeting on Pesticide Residues) concluded that the residue definition of triadimenol for plant matrices is the sum of triadimefon and triadimenol for both enforcement and risk assessment purposes. Triadimefon and triadimenol are in general stable to hydrolysis during pasteurization, baking and boiling conditions (Food and Agriculture Organization of the United Nations, 2007).

Several studies have investigated the level of reduction in the pesticide residues under different microbial fermentation process. In most cases, on analyzing the levels of pesticide residues even after fermentation process, only very few pesticides were degraded or adsorbed by the lactic bacteria during the fermentation process in wine (Cabras & Angioni, 2000; Cabras et al., 1999, 1994). However, Ruediger, Pardon, Sas, Godden, and

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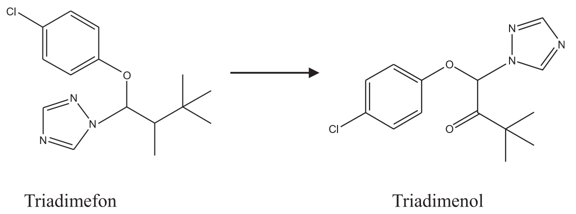

Fig. 1. Structure of triadimefon and triadimenol.

Pollnitz (2005) reported that malolactic fermentation by *Oenococcus oeni* resulted in significant reduction in chlorpyrifos and dicofol concentrations by 70% (at levels 1.0 and 0.1 mg kg^{-1}) and more than 30% (at levels 5.0 mg kg^{-1} and 2.0 mg kg^{-1}, respectively) in wine making process. Banna and Kawar (1982) investigated the change of parathion during apple juice processed into cider and vinegar. They showed that after 57 days of fermentation parathion was reduced to 5.1 mg kg^{-1} from 25 mg kg^{-1} with the residue levels of amino-parathion and 4-nitrophenol at 0.23 and 1.2 mg kg^{-1}, respectively in the vinegar, whereas in cider the level of parathion was reduced to 2.2 mg kg^{-1} with amino-parathion and 4-nitrophenol levels at 0.15 and 1.3 mg kg^{-1}, respectively. The fermentation process in meat products (fermented sausage) reduced the pesticide residues by 10% and 18% of DDT and lindane after 72 h from an initial level of 5 and 2 mg kg^{-1}, respectively and these reductions were due to the activity of meat starter (Abou-Arab, 2002). Studies have shown that the fate of triadimefon and triadimenol during food processing in apples, grapes, pineapples, tomatoes, coffee beans and barley is generally stable (Food and Agriculture Organization of the United Nations, 2007). Miyake, Tajima, & Ono (2003). observed that pesticides were persistent during storage of barley and concentration of metabolites of triademefon and triflumizole increased slightly during storage, but the concentration of residues of fenitrothion, phenthoate and triflumizole and its metabolites were considerably reduced. Kong et al. (2016) recently reported that triadimefon degraded to triadimenol during barley brewing by two different yeast strains, *Saccharomyces cerevisiae* IAPPST 1401 (Y1) and CICC 1202 (Y2), and found that Y2 promoted the degradation, and the processing factor value of >1 for triadimenol was also observed in malting and fermentation. The processing factor (P*f*) is the ratio of residue levels in processed products to their respective raw products (FAO/WHO, 2006; Gonzalez-Rodriguez, Rial-Otero, Cancho-Grande, Gonzalez-Barreioro, & Simal-Gandara, 2011). It is used to define refined dietary exposure assessments with primary processed products to assess consumer safety; establish maximum residue limits (MRLs) for processed commodities when the processing leads to an increase of the residue level and monitor compliance with the Raw Agricultural Commodities MRL.

Triadimefon was chosen as the model pesticide mainly because its wide use on jujube planting and its residue was usually detected. Till date, no study has been conducted or reported to evaluate the P*f*s of triadimefon in jujube during fermentation processing. There is only one study on the degradation kinetics of vitamin C in jujube fruit (Zhang, Cao, Cao, Wang, & Chen, 2008). The aim of the present work was to study the fate of triadimefon and its metabolite triadimenol in jujube during fermentation process and throw light on the processing factors of triadimefon and triadimenol in jujube wine and vinegar making process. The results would provide basic information about the risk of pesticides to jujube wine and vinegar, which would allow the establishment of best-management practices.

2. Materials and methods

2.1. Materials

Triadimefon standard (purity, 99.0%) and formulation were supplied by the Institute of Agro-Environmental Protection (Tianjin, China). Triadimenol, metabolite of triadimefon, was purchased from Standard Technology Development Co., Ltd. (Beijing, China). Chromatographic grade acetonitrile was acquired from Honeywell (Burdick & Jackson, USA), and ultra-pure water was obtained from a Milli-Q filtration system (Bedford, MA, USA). Multi-walled carbon nanotubes (MWCNTs) with average outer diameters of 10–20 nm, PSA, and GCB (40 μm particle size) were provided by Agela Technologies (Beijing, China). Analytical grade reagents were obtained from Sinopharm Chemical Reagent (Beijing, China).

2.2. Preparation of standards

Standard stock solutions (100 mg L^{-1}) of triadimefon and triadimenol were prepared in acetonitrile, respectively. Standard working solution (matrix-matched standard) was prepared fresh each day by adding appropriate volumes of the standard stock solution to a blank matrix extract.

2.3. Field trial

Field trials were conducted in a jujube orchard located in Lengquan Township (Beijing, China). Pesticides were applied to jujube trees at a rate 5× higher than the recommended commercial dosage (300 multiples of 20% triadimefon missible oil) to ensure to have ample amount of pesticide residues (OECD, 2008). Mature jujube (20 kg) was harvested in polyethylene bags and transported to the laboratory.

2.4. Sample preparations

The production procedures of jujube fermentation involve seven steps such as washing, sugaring, inoculating, and fermentation (Fig. 2). In this study, the samples were collected in different processing steps to determine the variation of triadimefon during the processing procedure (Vithlani & Patel, 2010). In step I, the fresh jujube samples were carefully washed, halved and stoned, with the edible portions (flesh and skin) been crushed. The jujube samples and water ($m: v = 1:1$) were added to the fermentation container in its ratio. In step II, sugar was added to it to make the solution at 210 g L^{-1}. In step III, the solution was inoculated with yeast (*Saccharomyces cerevisiae*) at 0.25 g L^{-1}. In step IV, on the 10th day, the juice was transferred to another container where the peel and core were separated. In step V, the juice was fermented at 20 ± 2 °C for 10 days to obtain jujube wine. In step VI, the solution was inoculated with 10% inoculum of *Acetobacter aceti* in Mannitol broth. In step VII, the wine was fermented at 30 ± 2 °C for 20 days to obtain jujube vinegar.

2.5. GC-MS condition

An Agilent 6890N Network GC system (Agilent Technologies Inc., California, USA) equipped with a 7683B Series splitless auto-injector, a 7683 Series Auto sampler, and a 5975B inter XL EI/CI MSD was used for pesticide analysis in selected ion monitoring mode. One quantitation ion and two identification ions were chosen for the determination of each analyte. Agilent Technologies Capillary Column HP-5 MS analytical column (30 m × 0.25 mm i.d. × 0.25 μm film thickness) was used for GC separation, with helium (99.99%) as the carrier gas (flow rate: 1.2 mL min^{-1}). The GC