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The effect of household processing on the decline pattern of dimethomorph in pepper fruits and leaves

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A B S T R A C T

The effects of various household processes, including washing, boiling, frying, parboiling, and drying under different conditions (water amount, boiling times, and temperatures) on the residual levels of dimethomorph were evaluated in pepper fruits and leaves grown under plastic greenhouse conditions. The original quick, easy, cheap, effective, rugged, safe (QuEChERS) method (after modification) and liquid chromatography–tandem mass spectrometry (LC/MS/MS) were used for extraction and analysis to determine the sample residues. The results of recovery tests in processed and unprocessed pepper fruits and leaves ranged from 73.6 to 106.2% with relative standard deviations of 1.62–12.4%. Among various processes, washing and parboiling (78.4–85.8% at single and 75.7–89.9% at double dose) and drying after washing and parboiling (95.3–97.3% at single dose) were the most effective household methods to attenuate the analyte residues in pepper fruits and leaves, respectively. We conclude that processing leads to extensive reduction of pesticide residue levels in pepper fruits and leaves, particularly following washing and cooking operations.

1. Introduction

Dimethomorph [(*E*,*Z*)-4-[3-(4-chlorophenyl)-3-(3,4-dimethoxy phenyl)acryloyl]morpholine, consists of *E* and *Z*-isomers in approximately equal proportions (Fig. 1). It is a local systemic fungicide that effectively controls late blight, downy mildew, and crown and root rot in vines, potatoes, tomatoes, and other crops (Cohen, Baider, & Cohen, 1995; Liu et al., 2012). Dimethomorph is necessary to prevent *Phytophthora* blight, a disease resulting in serious threats to pepper production (Hwang & Kim, 1995; Ristaino & Johnston, 1999). Pesticides are widely used in food production to increase food security, despite that they may have hazardous effects on consumers (Keikotlhaile, Spanoghe, & Steurbaut, 2010; Radwan, Abu-Elamayem, Shiboob, & Abdel-Aal, 2005).

Pepper is an annual herbaceous plant that is very popular vegetable worldwide because of its profitability for farmers and high nutritional value containing vitamins A, B, C, carotene, polyphenols, flavonoids, quercetin, and luteolin. Peppers are used as an ingredient in many regional cuisines because of their attractive color and unique spicy aroma (Kim et al., 2007; Minguez-Mosquera, JarBn-Galh, & Garrido-Fernhdez, 1994; Sousa et al., 2006). In Korean cuisine, the typical forms of consuming pepper and pepper leaf are “jjigae” which is made by boiling the washed pepper with vegetables in hot water; “bokkeum” in which the washed pepper is fried, or “namul” prepared by mixing parboiled leaves with several seasonings (Lee & Jung, 2009).

One of the most common routes of pesticide exposure is via consumption of both raw and processed foods (Han et al., 2014;

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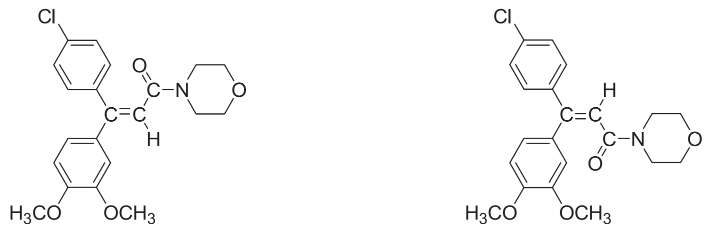

(E)-isomer (z)-isomer

Compound	M.W.	Precursor ion (m/z)	Product ion (m/z)	Cone (V)	Ce[b)] (V)	R.T.[c)] (min)
Dimethomorph	387	388	165[a)] 301	34	54 42	13.2

a) Quantitation ions

b) Collision Energy

c) Retention time

Fig. 1. Chemical structures and mass spectrometric parameters of dimethomorph.

Keikotlhaile et al., 2010). Various food processing operations can alter pesticide structure and result in a relative decrease and/or increase of residues in cooked foods (Bajwa & Sandhu, 2014; Holland, Hamilton, Ohlin, & Skimore, 1994; Park et al., 2011). Therefore, it is imperative to monitor and control the residues in processed as well as in raw foods to protect human health from the hazardous effects of pesticides (Park et al., 2011). The characteristics of pesticides, including solubility, hydrolysis rate constant, volatility, octanol–water partition coefficient, physical location of residues, and thermal degradation are very important to accurately estimate the effects of processing on the dissipation of residues in foods (Holland et al., 1994; Kaushik, Satya, & Naik, 2009). Common food processing operations along with the degree of residue removal in each process have been studied previously for pyridaben and tralomethrin in washed peppers (Valverde, Aguilera, Rodraguez, Boulaid, & Begrani, 2002), profenofos in washed, blanched and fried hot and sweet peppers (Radwan et al., 2005), and dichlofluanid, flusilazole, folpet, iprdione, λ-cyhalothrin, and lufenuron in washed, blanched and dried hot pepper leaves (Lee & Jung, 2009).

Literature considering the effects of processing on dimethomorph residue in sweet pepper and pepper leaves is very scarce. Therefore, the objectives of this study were to investigate the decrease of dimethomorph content in pepper fruits and leaves using various foods processing operations, including washing, boiling, frying, parboiling, and drying at different water volumes, times, and temperatures. The analyte was extracted with the QuEChERS method, which was modified in accordance with the analyte properties, matrix composition, equipment, and analytical techniques available in the laboratory (Anastassades, Lehotay, Stajnbaher, & Schenck, 2003; Lehotay et al., 2010; Park et al., 2011; Wilkowska & Biziuk, 2011).

2. Materials and methods

2.1. Chemicals and reagents

An assured standard of dimethomorph (purity: 99.8%) was provided by Dr. Ehrenstorfer GmbH (Augsburg, Germany). High performance liquid chromatography (HPLC)-grade acetonitrile (MeCN) was purchased from Burdick and Jackson (Ulsan, Republic of Korea). Anhydrous magnesium sulfate ($MgSO_4$) and sodium chloride (NaCl, purity: 99.5%) were supplied by Junsei Chemical Co. Ltd. (Kyoto, Japan). Formic acid was obtained from Daejung Chemicals & Materials (Siheung, Republic of Korea). Primary secondary amine (PSA) and C_{18} were purchased from Agilent Technologies (Palo Alto, CA, USA). All other chemicals were of analytical or HPLC grade.

2.2. Field trial

A field trial was conducted in a greenhouse located in the experimental plot of the Chonnam National University, Gwangju, Republic of Korea. Control samples were collected before pesticide application. Commercial dimethomorph (suspension concentrate, Festival®, 18% active ingredient, Dongbang Agro, Seoul, Republic of Korea) was sprayed on pepper plants at the single and double dose rate. Pepper fruit and leaf samples were collected at 2 days after application. Approximately 5 kg of pepper fruits and leaves were randomly collected from each plot in polyethylene bags, kept in ice, and transported to the laboratory for processing.

2.3. Pepper fruit and leaf processing

The samples were processed as follows to determine the changes in dimethomorph concentrations in pepper fruits and leaves: washing, boiling (after washing), stir-frying (after washing), parboiling (after washing), and drying (after washing and parboiling). All sample processing were carried out in triplicate, and the processed samples were blended, chopped, grinded, and frozen at −21 °C pending analysis.

2.3.1. Unprocessed samples

Impurities such as diseased or inedible parts were removed from samples. The pepper fruit and leaf samples were treated as described below for an analytical sample.

2.3.2. Washing

The pepper fruit and leaf samples (50 g each) were rinsed three times by distilled water immersion (pepper fruits, 200 mL; leaves, 1000 mL) in a stainless vessel (diameter/height, 24/8 cm for pepper fruits; 34/11 cm for leaves). The washed samples were left for 1 h in a colander to drain at room temperature.