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Estimation of Etofenprox Residues in Tomato Fruits by QuEChERS Methodology and HPLC–DAD

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Abstract Etofenprox residues were estimated by employing standardized QuEChERS technique in tomato following one application of Trebon® 20 % EC. The average recoveries of etofenprox on tomato for fortification levels 0.01, 0.1 and 0.5 mg/kg were observed to be 87.5 %, 89.7 % and 92.2 %, respectively, with relative standard division of 3.50, 4.11 and 3.20. The LOQ for tomato was found to be 0.01 mg/kg. The average initial deposit of etofenprox on tomato was observed to be 0.783 mg/kg, at single application rate. This etofenprox residue dissipated below its LOQ of 0.01 after 15 days at a single dosage. Half-life of etofenprox was observed to be 2.15 days, at the recommended dosage. These data could provide guidance for the proper and safe use of this pesticide on tomato in Egypt.

Keywords Tomato · Etofenprox · QuEChERS · Dissipation

Tomato (*Lycopersicon esculentum*) is one of the most popular vegetables in Egypt. Annual tomato production in the country is estimated to be seven million metric tones and area under cultivation about 221 thousand hectares which represent about 34 % of the average area of vegetable in Egypt. Tomato is considered to be an important crop and basic component of diet and is used almost daily in Egypt. It is consumed in raw form as salad, home-cooked or processed as a sauce, juice or paste. The tomato crop is frequently infested by a number of diseases at all stages of its development. The crop is often applied with chemical pesticides to offer protection from sever damage.

Etofenprox, 2-(4-ethoxyphenyl)-2-methylpropyl-3-phenoxybenzyl ether (Fig. 1), which belongs to the pyrethrin group, is widely used because of its properties of broad-spectrum insecticide control, high insecticidal activity, and safety to plants. It is usually employed to prevent and control insects with sucking mouth parts, particularly planthopper, leafhopper, aphid, and thrips on crops such as tomato, fruit trees, cotton, and rice (Cao et al. 2010). As a systemic insecticide, it can be absorbed by roots and leaves and transmitted to the plant tissues. Therefore, etofenprox might cause food contamination and is a potential threat to human health (Qian et al. 2011). Since agricultural use of etofenprox to control these insects has increased, appropriate maximum residue limit and pre-harvest interval measurements are required to ensure food and environmental safety at harvest time. Consequently, field dissipation studies on the persistence of the pesticide in tomato are needed. To our knowledge, limited studies have been published on the determination or dissipation of etofenprox. Therefore the present investigation was carried out with the objective to study the dissipation pattern and residue levels of etofenprox in tomato fruit.

Materials and Methods

Etofenprox standard (purity at 98.0 %) was purchased from Dr. Ehrenstorfer GmbH (Augsburg, Germany). All organic solvents were HPLC grade and supplied by Alliance Bio, USA. Primary secondary amine (PSA, 40 μm Bondesil) sorbents was purchased from Supelco (Supelco, Bellefonte, USA). Anhydrous magnesium sulfate was of analytical

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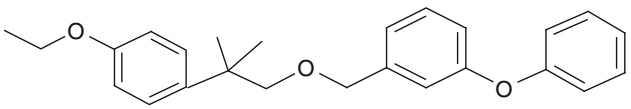

Fig. 1 Molecular structure of etofenprox

grade and purchased from Merck Ltd. Sodium chloride is analytical grade and was purchased from El Naser pharmaceutical chemical Com., (Egypt). Anhydrous magnesium sulfate was activated by heating at 400°C for 4 h in the muffle furnace, cooled and kept in desiccators before use. The physical and chemical properties of etofenprox are as follows: vapor pressure of 32 mPa (100°C); solubility in water of <1 mg/kg (25°C); logPow of 7.05 (25°C). It is stable in acidic and alkaline conditions.

The stock solution containing 100 µg/mL of analyte was prepared using acetonitrile as solvent. The standard solutions used for fortification of the matrices and instrument calibration purposes were prepared by serial dilution. All standards were stored at 4°C before use. Standard calibration curve of etofenprox was constructed by plotting analyte concentrations versus peak area (Fig. 2).

Tomato plants were cultivated in plots consisting of eight rows. Plots were arranged in complete randomized block design at El-Hakimayia village, Miet-Gamer Province, El-Dkahlyia Governorate, Egypt, on 2 August 2011. Common agricultural and fertilization practices were used. Mature plants were sprayed by etofenprox (Trebon 20 % EC) at the recommended rate of application i.e. 150 g a.i. ha^{-1} using knapsack sprayer motor. The control plots were left unsprayed. There was no rainfall at any time during the experimental period. The average daily temperature during the experiment was from 27 to 39°C.

Sampling was performed by randomly collecting from various places of the experimental plots according to the FAO/WHO (1986) recommendations. Three replicates were made and fruit samples were taken 2 h after pesticide application. After words, the fruits were collected randomly after 1, 3, 7, 10 and 15 days after application. Random samples of about 1 kg were collected from each plot and the samples were transferred immediately to the laboratory in an ice box. The samples were comminuted using the laboratory blender and representative homogenized (15 g) of each was then placed into 50 mL polyethylene tube. Samples were extracted and cleaned up immediately after sampling. 15 mL of acetonitrile was added into each tube. The samples were well shaken using a vortex mixer at maximum speed (Anastassiades et al. 2003). Afterwards, 6 g of anhydrous magnesium sulfate and 1.5 g of sodium chloride were added, then extract by shaking vigorously on vortex for 5 min and centrifuged for 10 min at 4,000 rpm. An aliquot of 4 ml was transferred from the supernatant to a new clean 15-mL centrifuge tube containing 100 mg PSA and 600 mg anhydrous magnesium sulfate. The samples were again vortexed for 3 min and then centrifuged for 10 min at 4,000 rpm. An aliquot of 2 mL was filtered through a 0.2 µm PTFE filter (Millipore, USA). The sample was then ready for the final analysis in LC system. HPLC analysis was performed with an Agilent 1100 HPLC system (USA), with quaternary pump, manual injector (Rheodyne), thermostat compartment for the column and photodiode array detector. The chromatographic column was C_{18} Zorbax XDE (250 mm × 4.6 mm, 5 µm film thickness). The column was kept at room temperature. Flow rate of mobile phase (methanol/water = 92/8 v/v) was 0.8 mL/min., and injection volume was 20 µL. Detection wavelength for detection of etofenprox was set at 220 nm. The retention time of etofenprox was about 12.5 min. Residues were estimated by comparison of peak area of standards with that of the unknown or spiked samples run under identical conditions.

In order to estimate the efficiency of the method, a recovery experiment was conducted by fortifying untreated samples with analytical grade etofenprox standard at the rate of 0.01, 0.1 and 0.5 mg kg^{-1}. Each fortification level was replicated five times. Extraction of control samples was performed as mentioned earlier. Results of recovery study are shown in Table 1. Satisfactory results were achieved at three spiking levels with recoveries ranges between 87.5 % and 92.2 % with RSD ranged from 3.2 to 4.11. The LOD and LOQ were determined as the sample concentration of etofenprox at signal to noise ratio of 3:1 and 10:1, respectively. The LOD and LOQ were estimated to be 0.003 and 0.01 mg kg^{-1}, respectively.

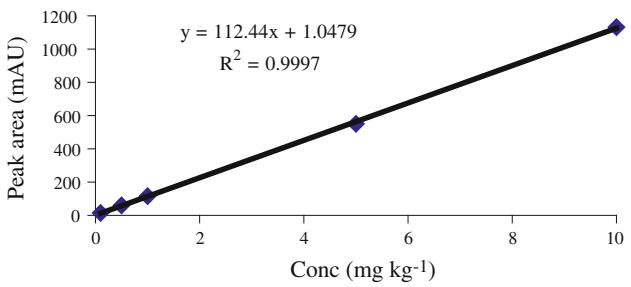

Fig. 2 Linearity correlation for etofenprox calibration curves

Table 1 Recoveries and relative SD for etofenprox on tomato at various fortification level

Fortified level (mg/kg) (n* = 5)	Recovery	RSD
0.01	87.5	3.50
0.1	89.7	4.11
0.5	92.2	3.20

* Number of replicate

Table 2 Residues of etofenprox (mg kg^{-1}) in tomato

Time (days)	Residue level (mg kg^{-1}) Mean* ± SD	Dissipation %
Zero	0.783 ± 0.014	0.00
1	0.537 ± 0.096	31.4
3	0.318 ± 0.010	59.3
7	0.20 ± 0.004	74.4
10	0.02 ± 0.009	97.4
15	ND**	–
K ($days^{-1}$)	0.32	
$t_{1/2}$ (days)	2.15	

* n = 3

** Not detectable

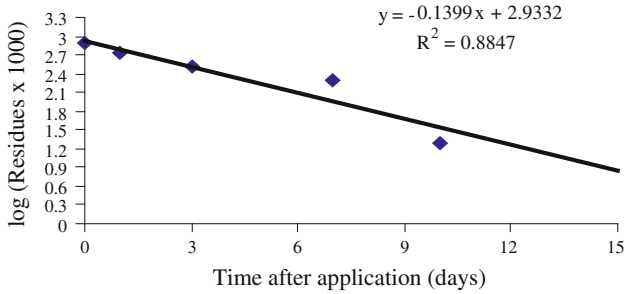

Fig. 3 Semi-logarithm graph showing dissipation kinetics of etofenprox on tomato fruit

Data were statistically evaluated by one-way analysis of variance (ANOVA). All statistical analysis was done using the statistical package for social sciences (SPSS 16.0) program.

Results and Discussion

The residual data at different day's intervals, dissipation pattern percentage, and half-life values in tomato fruits for etofenprox has been presented in Table 2. Following single application of Trebon 20 % EC @ 150 g a.i. ha^{-1} resulted in the initial deposits of 0.783 mg kg^{-1} in tomato fruit. These deposits dissipated to 0.318 mg kg^{-1} after 3 days of their application, thereby, showing a loss of about 59.38 %. The residues of etofenprox on tomato reached below the LOQ of 0.01 mg kg^{-1} in 15 days after application at the recommended dosage.

The results are in disagreement with Sun et al. (2011) who studied the dissipation behavior of etofenprox in cabbage differed in two different locations (Beijing and Kunming in China) and reported initial deposits of 4.37 mg kg^{-1} in Beijing and 4.05 mg kg^{-1} in Kunming following application at the rate of 120 g a.i./ha. Thereafter, analysis of samples collected after 10 days in Beijing and after 14 days in Kunming from application did not reveal the presence of etofenprox.

Half-life values calculated from the best fit lines of the log of residual concentration versus time period, suggested first order reaction kinetics with respect to dissipation of residues of etofenprox (Fig. 3). The rate of degradation (K) and half-life ($t_{1/2}$) values were obtained from the following equation of Gomaa and Belal (1975).

$$\text{Rate of degradation (K)} = 2.303 \times \text{slope} \quad (1)$$

$$\text{Half-life } (t_{1/2}) = 0.693/\text{K} \quad (2)$$

Half-life of etofenprox calculated was observed to be 2.15 days when applied @ 150 g a.i. ha^{-1}.

Nakamura reported that etofenprox is characterized by high stability against light, acids, and bases and has an extremely high bioconcentration factor of 1.6 × 106, which is higher than that of DDT by a factor of about 10 (Nakamura et al. 2002). Because of the high bioconcentration, etofenprox may remain in living bodies or plants for a long time. However, in our study, the half-life of etofenprox in tomato was notably short, indicating that the bioconcentration did not play a significant role on the dissipation of etofenprox in tomato. These data could provide guidance for the proper and safe use of this pesticide on tomato in Egypt.

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