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PYRIDALYL INSECTICIDE RESIDUES IN TOMATO PLANTS

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ABSTRACT

Field experiment was conducted to determine residues of pyridalyl insecticide on tomato leaves and fruits. Tomato plants were sprayed with the insecticide pyridalyl (Pleo 50% EC) at the rate of 100 ml/fad. on January, 2014. QuEChERS (catchers) method was used for extraction and clean-up of the samples. Residues were determined 2 hours, 1, 2, 3, 5, 7, 10 and 14 days post-treatment using UHPLC-UV. The recovery percentages were 89.29 and 96.73 % for leaves and fruits, respectively. The results revealed that the residue concentrations of pyridalyl on leaves and fruits, two hours after single application of the insecticide were 1.007 and 0.815 mg a.i./kg, respectively. The insecticide residues on fruits were 0.707, 0.569 and 0.474 mg a.i./kg after 1, 2 and 3 days and reached 0.2 mg a.i./kg after 14 days. The corresponding residues on leaves were 0.808, 0.646, 0.637 and 0.284 mg a.i./kg after 1, 2, 3 and 14 days. The rates of degradation (k values) were 0.100 and 0.115 on leaves and fruits, respectively. The corresponding half-life times (t 0.5) were 6.950 and 6.050 days on leaves and fruits, respectively. The residues on tomato fruits were below the maximum residual level (MRL) value reported by the European Food Safety Authority (EFSA, 2013). Thus, tomato fruits could be safely harvested for human consumption and for processing purposes.

Key words: Pyridalyl, Pleo, residues, QuEChERS, tomato, UHPLC.

INTRODUCTION

Pesticides from a broad range of classes that are widely used in various combinations and/or at different stages of cultivation, and during post-harvest storage to protect crops against pests, and/or to provide quality preservation. Pesticide residues that remain in the food supply could pose a risk for human health because of their potential subacute and chronic toxicity. Therefore, residues of pesticide could affect the ultimate consumers especially when freshly consumed (Abou-Arab, 1999). Moreover, Food Inspection Agencies require improved sensitive and confirmatory methods to monitor pesticide residues in fruits and vegetables to ensure the safety of food supply.

Tomato is one of the most important vegetable crops in Egypt, which considered the world's fourth largest producer of tomato (FAO, 2010). The average yield in Egypt per faddan is relatively low, this may be due to many factors, including insect infestation. Tomato used for consumption as fresh product produced under greenhouse conditions as well as in open fields (Ugurlu Karaagac, 2012).

Pyridalyl is an insecticide invented and developed by Sumitomo Chemical Co. Ltd. This insecticide exerts effective control against lepidopterous and thysanopterous pests on cotton, vegetables and fruits (Sakamoto *et al.*, 1995; Sakamoto and Umeda, 2003) Also, pyridalyl is safe for useful arthropods like parasitoids and predators, hence is a suitable tool for compositional management of pests as well as management of pest resistance. Due to its short occurrence period and low impacts on environment, pyridalyl may be used as a selective poison against most of pests without generating phytotoxic effects. Pyridalyl was registered in some Asian countries in 2002, including Japan (Sakamoto *et al.*, 2003;

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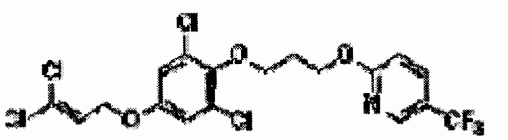
Sakamoto *et al.*, 2005; Sato, 2010), and it is permitted for use in Africa. The chemical starts to be broadly used in Egypt. The mode of action of pyridalyl is inhibition of cellular protein synthesis in insect, but not mammalian (Moriya *et al.*, 2008). Hrouzková *et al.* (2012) showed that the QuEChERS method is simple and exhibits acceptable levels of sensitivity and accuracy to fulfill the requirements of pyridalyl residue analysis.

The aim of the present study is to determine residues of the insecticide pyridalyl on tomato leaves and fruits at different intervals after application under open field conditions and calculate the rate of degradation to get data required for sanitary, phytosanitary standards as well as assessment the health risk of exposure. Thus, the safety of food supply could be ensured.

MATERIALS AND METHODS

Chemicals

Pyridalyl (Pleo® 50% EC) and analytical standard pyridalyl (95.3%) were kindly supplied by Sumitomo Chemical Co. Ltd.



IUPAC name: 2,6-dichloro-4-4 (3,3-dichloroallyloxy) phenyl-3-[5-(trifluoromethyl) - 2- pyridyloxy] propyl ether.

Other chemicals and reagents of analytical grade were used such as: acetonitrile, HPLC grade (POUCH SA, Gliwice, Poland); acetic acid (El Nasr Pharmaceutical Chemicals Co., Abu-Zaabal, Cairo, Egypt); primary secondary amine (PSA), graphitized carbon black (GCB), C18, anhydrous magnesium sulfate (MgSO4) and anhydrous sodium acetate for QuEChRs kits purchased from Agilent Technologies Co., USA).

Field Treatment and Sampling

Field trial was carried out under completely randomized blocks design with three replicates, plot dimensions were 6x7 m^2 at Dakados village, Mit Ghamr district, Dakahlia Governorate, Egypt on January 12, 2014. Tomato seedlings (*Lycopersicon esculentum* Mill.) cultivar 2006TY (Newstar Company) were transplanted in open field. Common agricultural and fertilization practices were used. At the beginning of fruits mature stage, the plants were sprayed with pyridalyl recommended rate (100 ml pyridalyl 50% EC/fad.) using backpack sprayer (capacity 20 l). After the insecticide application, tomato plants didn't receive any foliar applications until the end of experiment.

Representative leaf and fruit samples were collected randomly from the experimental plots at 0, 1, 2, 3, 5, 7, 10 and 14 days after insecticide application. The leaves collected from different levels of plant while fruit samples were also collected from mature fruits that represent the consumed edible part. Samples were collected for recovery test before pesticide application, then transferred to laboratory in one kg plastic bags. Each sample was blended. Ten grams of the blended sample was transferred to a 50 ml polypropylene centrifuge tube, labeled and stored at -18 °C.

Extraction and Clean up Procedure

Pyridalyl residues were extracted and cleaned up by QuEChERS modified method according to Lehotay (2007) and Raczkowski *et al.* (2011). In this method, 10 g of the blended sample were transferred to 50 ml polypropylene centrifuge tube, 15 ml of acetonitrile, containing 1% (*V/V*) of acetic acid, were added. The sample was shaken manually for one minute hardly and vortexed for 15 sec. Then extract powder include: 6 g magnesium sulphate and 1.5 g anhydrous sodium acetate were added to the centrifuge tube contents, mixed manually for one minute and vortexed for 15 sec, then centrifuged for 5 min at 4000 rpm. Eight milliliters of the resulted supernatant were transferred to a 15 ml centrifuge tube. This tube contains required materials for purifying including: 400 mg PSA and 1200 mg magnesium sulphate, in addition to, 10 mg GCB for leave samples, no GCB was add to fruit samples. Then the sample was shaken immediately manually for one min, vortexed for 30 sec and centrifuged for 5 min at 5000 rpm. Afterwards, 5 ml of the upper layer were taken by pipette and poured into a clean tube. These prepared samples were stored frozen until final quantitative determination.

Quantitative Determination Procedure

One microliter of the previously prepared sample was injected to a UHPLC-UV Agilent USA model 1290 infinity with binary pump, vwd, autosampler. The mobile phase consisted of 60% acetonitrile: 40% distilled water. Pyridalyl was detected at 208 nm (Farouk *et. al.*, 2014).

Recovery Assay

Recovery assay was performed using untreated tomato fruits and leaves. The samples were homogenized before being spiked with one mg/kg concentration. The samples were processed for extraction, clean up and quantitative final determination according to the above mentioned procedure.

The obtained recovery percentages were 89.29 and 96.73 % for leaves and fruits, respectively. The results were corrected according to the recovery values.

Kinetic Study

The rate of degradation and half-life period of pyridalyl was calculated according to Gomaa and Belal (1975), Ashour (1976) and Gomaa *et al.* (1979). The relationship between the logarithm of concentration of pyridalyl residues and time intervals were plotted. A straight line was fitted using excel trend line with intercept equal to logarithm of initial concentration, and the slope of the line was calculated. Accordingly, the rate of degradation (k) of pyridalyl and the half-life period (t 0.5) of the insecticide were calculated as follows:

$$\text{Rate of degradation (k)} = 2.303 \times \text{slope}$$

Finally, the half-life period (t 0.5) can be obtained from the following equation:

$$t_{0.5} = 0.693/k$$

RESULTS AND DISCUSSION

Pyridalyl residues on leaves and fruits after single application of the insecticide on the mature stage of tomato plants at the rate of 100 ml/fad. are presented in Table 1. The residue concentrations were 1.007 and 0.815 mg a.i./kg after 2 hours post-treatment on leaves and fruits, respectively. The percentages of dissipation on tomato leaves were 19.762, 36.743 and 54.618% after 1, 3 and 7 days from application, respectively. The corresponding percentages of dissipation on fruits were 13.251, 41.840 and 59.509%. Fourteen days after application, pyridalyl residues reached 0.284 and 0.200 mg a.i./kg on the tomato leaves and fruits, respectively. The corresponding percentages of dissipation were 71.797 and 75.460%.

The logarithms of pyridalyl residue concentrations on tomato leaves and fruits were plotted against time after application (Figure 1). The data felt very closely on straight lines, in accordance with the requirements of a first order reaction, in which the rate of reaction is directly proportional to the concentration of the insecticide. Accordingly, the slope value, rate of degradation (k) of pyridalyl and the half-life period (t 0.5) of the insecticide were calculated as mentioned before and presented in Table 2.

The k values were 0.100 and 0.115 on tomato leaves and fruits, respectively. The corresponding t 0.5 values were 6.950 and 6.050 days. The k value of the insecticide was lower on leaves than on fruits. Subsequently, the t 0.5 value was higher on leaves than on fruits. The higher deposits on leaves compared with fruits may due to larger exposed surface area on leaves than that on fruits as the later are always hidden under leaves. The rate of loss was higher on fruits in comparison to leaves. The differences in the loss of the initial residues on leaves and fruits reflect the titer of metabolizing enzymes in plants as well as the effect of growth dilution of the residues (Hill *et al.*, 1982).

In a study where Phe-^{14}C-pyridalyl and Pro-^{14}C-pyridalyl were applied to tomato plants (cultivar: Bush Beefsteak), 4 times at 224 g ai/ha (*i.e.*, 78 days, 43 days (5-7 leaves stage), 22 days and 1 day before harvesting, respectively). It was found that residues on the mature tomato collected 7 days after the final treatment were 0.085-0.172 mg/kg, and those after washed off were 0.056-0.135 mg/kg. Major ^{14}C residue on the mature tomatoes was the unchanged form pyridalyl metabolism in tomatoes (GLP study) (Anonymous, 2004). Hrouzková *et al.* (2012)

studied the dissipation of pyridalyl on spring onions and strawberries following an application of 238 ml a.i./ha and reported that initial deposits were less than 3 mg/kg, which declined to 1 mg/kg in 7 days, with half-lives of 0.27 and 5.99 days, respectively. The higher residues on strawberries were probably due to the difference in surface area. Spray retention on onion leaves can also be difficult because of the vertical nature of the plant. Yoon *et al.* (2013) studied the dissipation of pyridalyl on cauliflower following an application of 200 g a.i./ha. They reported initial deposits of 0.43 mg/kg, which declined to 0.12 mg/kg in 10 days, with half-life time of 7.74 days. Farouk *et al.* (2014) studied the dissipation of pyridalyl on tomato treated with the recommended dose. They reported initial deposits of 0.953 mg/kg, which declined to not detected in 14 days, with half-life time of 22.56 days.

Table 1. Residues of pyridalyl on tomato leaves and fruits

Hours or days after treatment	Leaves (mg a.i./kg)	Loss (%)	Fruits (mg a.i./kg)	Loss (%)
2 hours	1.007	0.00	0.815	0.00
1 day	0.808	19.762	0.707	13.251
2 days	0.646	35.849	0.569	30.184
3 days	0.637	36.743	0.474	41.840
5 days	0.519	48.461	0.378	53.620
7 days	0.457	54.618	0.330	59.509
10 days	0.398	60.477	0.254	68.834
14 days	0.284	71.797	0.200	75.460

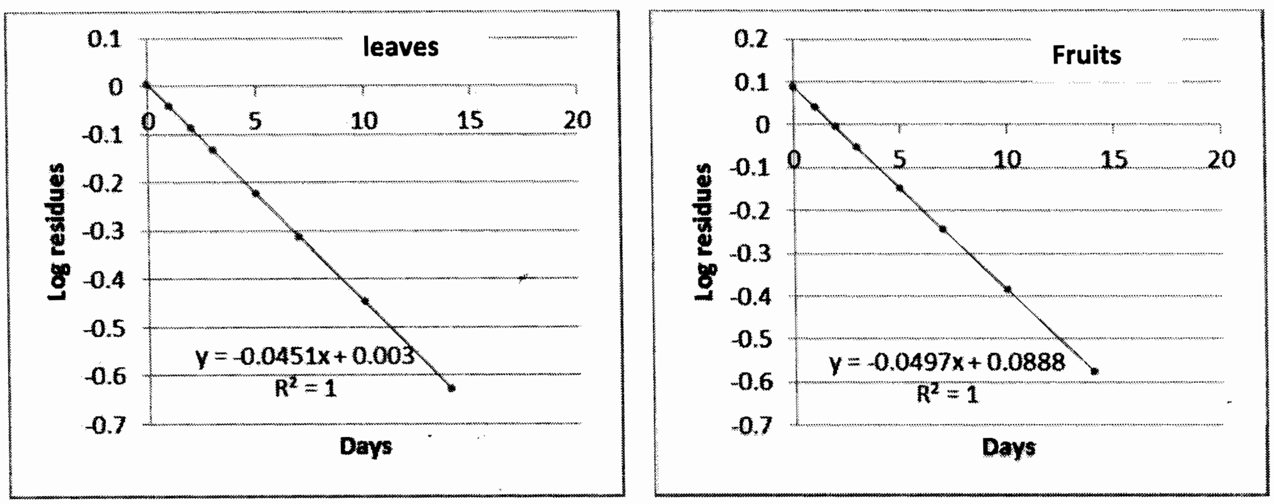


Fig. 1. Regression lines of logarithm pyridalyl residue concentrations versus days after application on tomato plant

Table 2. Slope, rate of degradation and half-life time of pyridalyl on tomato

Parameter	Leaves	Fruits
Slope	0.043	0.050
Rate of degradation (k)	0.100	0.115
Half-life t 0.5 (days)	6.950	6.050

Adverse effects on human health of pesticides residues remaining in food after application may be cause health risk due to pesticide residues in the diet. The lowest no observable adverse effect level (NOAEL) for pyridalyl was 2.80 mg/kg b.w./day, based on two-generations reproductive toxicity tests in rats. Therefore, a safety factor of 100 was applied to calculate ADI, thus yielding 0.028 mg/kg b.w./day (Anonymous, 2004).

Pyridalyl maximum residue limit (MRL) in tomato was 1.5 mg/kg according to European Food Safety Authority (EFSA) (2013). Regarding the data obtained from the present study, the residue concentration of pyridalyl on tomato fruits (0.707 mg a.i./kg) one day after single application at the recommended rate was below the above-mentioned EFSA MRL value. Thus, tomato fruits could be safely harvested for human consumption and for processing purposes.

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تقـدير متبقيـــات المبيد الحشري بيريدليل في الطماطم

محمود محمد رمضان - مصطفى عبدالحفيظ الطنطاوي
محمــد باسم علي عاشور – رفعـت مصطفــى شريف

قسم وقاية النبات - كلية الزراعة – جامعة الزقازيق – مصر

أجريت تجربة حقلية لتقدير متبقيات المبيد الحشري بيريدليل على أوراق وثمار الطماطم في يناير ٢٠١٤، تم رش النباتات مرة واحدة بمستحضر بيليو ٥٠% مركز قابل للاستحلاب بمعدل حقلي ١٠٠ مل/فدان، واستخدمت طريقة كاتشرز لاستخلاص وتنقية العينات المأخوذة على فترات ساعتين، ١، ٢، ٣، ٥، ٧، ١٠، و١٤ يوماً بعد الرش ثم قدرت باستخدام جهاز UHPLC-UV، حيث بلغت نسبة استرجاع المبيد ٨٩,٢٩ و٩٦,٧٣% علي كلٍ من عينات الأوراق والثمار على التوالي، وأوضحت النتائج أن كميات متبقيات مبيد البيريدليل على الأوراق والثمار بعد ساعتين من المعاملة كانت بمقدار ١,٠٠٧ و ٠,٨١٥ مليجرام مادة فعالة/كجم على التوالي، بينما كانت كمية المتبقي على الثمار ٠,٧٠٧، ٠,٥٦٩ و ٠,٤٧٤ مليجرام مادة فعالة/كجم بعد ١، ٢ و٣ أيام على التوالي، ووصلت إلى ٠,٢ مليجرام مادة فعالة/كجم بعد ١٤ يوماً من الرش، وعلى نفس الفترات كان متبقى المبيد على الأوراق ٠,٨٠٨، ٠,٦٤٦، ٠,٦٣٧ و٠,٢٨٤ مليجرام مادة فعالة/كجم بعد ١، ٢، ٣ و١٤ يوماً، على التوالي، وكان معدل تحطم المبيد ٠,١٠٠ و ٠,١١٥ على الأوراق والثمار على التوالي، وقدرت فترة نصف العمر بـ ٦,٩٥٠ و٦,٠٥٠ يوماً على الأوراق والثمار على التوالي، ولقد كانت المتبقيات على ثمار الطماطم أقل من الحدود المسموح بها طبقا للهيئة الأوروبية لسلامة الأغذية وبالتالي يُمكن أن تُحصد ثمار الطماطم بأمان للاستهلاك البشرى أو لأغراض التصنيع.

المحكمــــون:

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