

Dissipation and Residues of Lufenuron in Grape Fruits

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Abstract The main objective of this study was to understand the residue and persistence behavior of lufenuron insecticide in grape fruit samples. The residues were analyzed by HPLC and it dissipated in grape fruit following first order kinetics. The average initial deposit of in grape fruit was observed to be 1.85mg kg⁻¹ at single application rate. The recoveries of lufenuron on grape fruit were observed from 91.97% to 95.25% at fortification levels of 0.1, 0.5 and 1.0mg kg⁻¹. The reported limit of quantification (LOQ) was found to be 0.01mg kg⁻¹. The dissipation experiments showed the half-lives (T_{1/2}) of lufenuron were around 2.79 days. According to the maximum residue limit (MRL) the pre-harvest interval (PHI) of lufenuron on grape was 3 days after the treatment.

Keywords: Lufenuron, Residues, Dissipation, Grape

1. Introduction

Pesticides will continue to be used in the production of food and fiber especially in the developing countries. Drastic reductions of pesticide usage will increase the production cost and lower the quality of the agriculture productivity. It is well recognized that there are risks attached to the consumption of pesticide-treated crops because of the presence of residues on them [1,2]. Therefore, the rational recommendation of a pesticide requires that it must not only provide an effective control of pests but at the same time its residues on the commodity must also be toxicologically acceptable. Lufenuron (RS)-1-[2,5-dichloro-4-(1,1,2,3,3,3-hexafluoropropoxy) phenyl]-3-(2,6 difluorobenzoyl) urea (Figure 1), is a benzoylphenylurea insecticide whose mode of action is known to be the inhibition of chitin synthesis in the cuticle of insects [3]. It shows relatively low toxicity to mammals since the activity is highly specific to immature insect at the molting stage. Grape (*Vitis vinifera*) is one of the most widely-grown fruit crop in the world. Thompson Seedless grape cultivar ranking as the most important table grape variety grown in Egypt. Worldwide, the planted areas of grapes are estimated by 24 million feddan and the total yield exceeds than 60 million ton annually. In Egypt, the grape is planted in different type of soils and represents the second position between fruit crops after citrus. In the earliest writings and archives associated to all sorts of agricultural and religious activities, grapes and its products were given a significant place [4]. The grape 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 severe damage. Very limited data have been reported concerning the dissipation of benzoylphenylurea insecticides in agricultural products [5,6,7] and, as a result, no published data are available concerning the fate of lufenuron in grape. Therefore, the aims of the present study were to evaluate the dissipation of lufenuron residues as a function of time and to calculate the PHIs on treated grape.

Table 1. Recoveries and relative standard deviations for lufenuron in grape at various fortification level

Fortified level (mg kg ⁻¹) (n*=5)	Lufenuron	
	Grape Fruits	
	Recovery	RSD
1	92.64	5.7
0.5	95.25	6.2
0.1	91.97	3.8

* Number of replicates

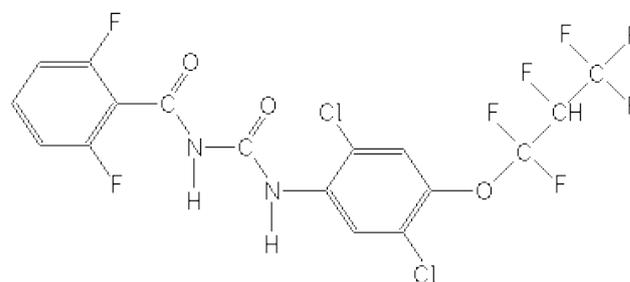


Figure 1. molecular structural of lufenuron

2. Material and Method

Lufenuron analytical standard and the formulation (5% EC) were kindly supplied by Syngenta (Cairo, Egypt). All

organic solvent were HPLC grade and supplied by Merck Ltd. Deionized water was prepared by a Milli-Q water purification system. Primary secondary amine (PSA, 40 μm Bondesil) was purchased from Supelco (Supelco, Bellefonte, USA). Anhydrous magnesium sulfate was of analytical grade and purchased from Merck Ltd. Sodium chloride was analytical grade and purchased from El Naser pharmaceutical chemical Com. (Egypt). Anhydrous magnesium sulfate and Sodium chloride were activated by heating at 250°C for 4 h in the oven before use and kept in desiccators. A high-performance liquid chromatography (Agilent 1100 HPLC system, USA), with quaternary pump, manual injector (Rheodyne), thermostat compartment for the column and photodiode array detector was used. Zorbax XDB C18 (250 \times 4.6mm, 5 μm film thicknesses) was used as an analytical column for lufenuron. Grape trees were cultivated in plots, each plot contained 20 vines. Plots were arranged in complete randomized block design at Quesna district, El-Menofia Governorate, Egypt. Common agricultural and fertilization practices were used. No insecticide sprays were applied to the test plots prior to or during this experiment. Mature plants were sprayed in June 13th, 2010 by commercial formulation of lufenuron (Match[®] 5% EC) at the recommended dose (40cm³/100L) using knapsack sprayer motor. The spray solution was prepared in accordance with the manufacture recommendation. 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 25 to 39°C. Sampling was performed by randomly collecting from various places of the experimental plots according to the FAO/WHO recommendations [8]. Three replicates were made and fruit samples were taken 0, 1, 2, 3, 7, 10, 14, 17 and 21 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 (10g) of each was then placed into 50mL polyethylene tube. Samples were extracted and cleaned up immediately after sampling using QuEChERS methodology [9]. 10mL of acetonitrile was added into each tube. The samples were well shaken using a vortex mixer at maximum speed. Afterwards, 4g of anhydrous magnesium sulfate and 1g of sodium chloride were added, then extract by shaking vigorously on vortex for 5min and centrifuged for 10min at 4,000rpm. An aliquot of 1mL was transferred from the supernatant to a new clean 15mL centrifuge tube containing 25mg PSA and 150mg anhydrous magnesium sulfate. The samples were again vortexed for 3min and then centrifuged for 10min at 4,000rpm. An aliquot of 1mL was concentrated to dryness. The residue was redissolved in 1mL of methanol and filtered through a 0.2 μm PTFE filter (Millipore, USA) prior to HPLC. An aliquot (20 μL) of the final extract was injected into the HPLC with photodiode array detector as described by Gamon et al.[10] with the following modifications: The mobile phase was methanol: water (80/20 v/v) at a flow rate of 0.8mL/min. Detection wavelength for detection of lufenuron was set at 245nm. The retention time of lufenuron was about 11.1min. Residues were estimated by comparison of peak area of

standards with that of the unknown or spiked samples run under identical conditions. Untreated grape samples were homogenized before begin spiked with lufenuron. Recovery assays were performed in the 0.1–1.0mg kg⁻¹ range. The samples were processed according to the above procedure. At each fortification level, five replicates were analyzed. Statistical analyses were done using the Statistical Package for Social Sciences (SPSS 10.0).

3. Result and Discussion

A standard calibration curve of lufenuron was constructed by plotting analyte concentration against peak area. The detector response was linear in the range of analysed lufenuron by the given method with correlation coefficients [0.999]. Blank grape samples were used to establish the detection (LOD) and quantification (LOQ) limits for lufenuron by HPLC. The LOD and LOQ were determined as the sample concentration of lufenuron at signal to noise ratio of 3:1 and 10:1, respectively. The LOD and LOQ were estimated to be 0.02 and 0.04mg kg⁻¹, respectively. Recovery results are shown in Table 1. The recoveries obtained from grape ranged from 91.97% to 95.25%. The relative standard deviation (RSD) was <7.5%. These results demonstrate the good performance of the method.

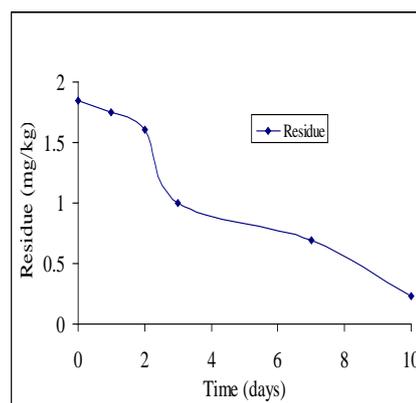


Figure 1. Dissipation of lufenuron in grape fruits

The initial deposit of lufenuron on and in grape fruits as determined one hour after application was 1.85mg kg⁻¹ as shown in Figure 2. Residue of lufenuron decreased to 1.76mg kg⁻¹ one day after treatment with 4.86% loss of the initial deposits. The residues decreased to 1.61mg kg⁻¹ two days after treatment with a loss of 12.97% of the initial deposits. The decline in the amounts of lufenuron continued after 7 and 10days of application to be 0.695 and 0.23mg kg⁻¹ with 62.43 and 87.57% loss, respectively. Finally, the residue of lufenuron in grape was below 0.04mg kg⁻¹ 14 days after the treatment. The dissipation of the pesticide in/on crops depends on the climatic condition, type of application, plant species, dosage, the interval between application, and harvest [7]. Half-life value ($T_{1/2}$) for degradation of lufenuron on grape fruits was calculated [11] and observed to be 2.79 days, at the recommended dosage. While the FAO/WHO has not established MRLs for lufenuron, European Union MRL for lufenuron in grape was 1 mg kg⁻¹. Residues of lufenuron on grape fruits

were less than its MRL value after 3 days of its application at the recommended dosage. The result reported by [12] whose study indicated that the half-lives of lufenuron was 3.06 – 3.45 days in cotton leaves. It suggested the half-lives varied with different plants, location of application and growth dilution factor.

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