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Dissipation kinetics and effect of processing on clothianidin residues in cardamom (*Elettaria cardamomum* Maton)

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ABSTRACT: The dissipation behaviour of clothianidin (Dantop 50% WDG), a neonicotinoid insecticide, in fresh and cured cardamom capsules was studied following-application at 20 and 40 g a.i. ha^{-1}, respectively, in the plantation of Indian Cardamom Hills (ICH), Idukki, Kerala, India. A single laboratory UPLC-MS/MS method was developed and validated for the estimation of residues of clothianidin in fresh and cured cardamom. The recovery experiments were conducted at fortification levels of 0.01, 0.05 and 0.1µg g^{-1}.The average recoveries obtained were 91.04 to 94.44 and 89.22 to 91.41 % for fresh and cured cardamom, respectively. The LOD and LOQ in both fresh and cured cardamom were found to be 0.005 and 0.01µg g^{-1}, respectively. The initial deposits of clothianidin on fresh and cured cardamom were 1.96 and 5.24 µg g^{-1}, respectively, following application at the lower dose while the corresponding deposits were 4.13 and 10.61µg g^{-1} at the higher dose. For fresh and cured cardamom, the residues dissipated below the quantitation level of 0.01µg g^{-1} after 21 and 28 days at both the doses, respectively. The half-life of clothianidin in fresh and cured cardamom was 3.40 and 3.11 days at the lower dose and 3.42 and 3.45 days at the higher dose, respectively. The waiting periods of clothianidin on fresh and cured cardamom at the lower and higher doses were 18.41 and 22.09 days, and 21.16 and 27.54 days, respectively. The processing factor was evaluated at the lower dose and the mean processing factor was 2.90.

KEYWORDS: cardamom, clothianidin, dissipation, processing factor

INTRODUCTION

Cardamom (*Elettaria cardamomum* Maton), the queen of spices, is one of the most exotic and highly prized spices in the world. It thrives well in the tropical rain forests of Western Ghats of India. India accounts for the largest area under cardamom cultivation yet the productivity is low mainly due to the attack of diverse pests and diseases in all stages of the crop growth, necessitating frequent application of pesticides for their timely control (Kumaresan, 2008). It is reported that around 650 tons active ingredients of different pesticides were applied during 2009 season in Indian cardamom hills (Murugan *et al*., 2011). The residues of pesticides deposited during plant protection operations are a major concern and pesticide residue in spices have affected our exports (Bhardwaj *et al*., 2011). Management of pests in cardamom largely depend on the use of conventional, neurotoxic, broad-spectrum, synthetic chemical pesticides, such as organophosphates, carbamates, synthetic pyrethroids and a number of new chemical classes, such as neonicotinoids. Exposure to pesticides, both

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occupationally and environmentally, poses a range of adverse effects. The resistance build-up by pests to conventional pesticides demands the use of newer and safer products with low dose requirement and different modes of action (Sreelekshmi, 2014; Aravind *et al.,* 2015).

Neonicotinoids are relatively new class of insecticides with novel mode of action and chemistry. They act as agonists, which play an important role in synaptic transmission in the central nervous system of insects. Clothianidin ((E)-1- (2-chloro-1,3-thiazol-5-ylmethyl)-3-methyl-2-nitroguanidine) is a second generation neonicotinoid insecticide with excellent plant systemicity, broad-spectrum activity and high crop safety, was discovered by the Agro Division of the Sumitomo Chemical Co. Ltd. (formerly Takeda Chemical Industries, Ltd.), and was co-developed with Bayer CropScience (Uneme, 2011). It acts selectively on insect nicotinic acetylcholine receptors (Thany, 2009). This pesticide is highly effective in controlling hemipterous insects coleopterous, thysanopterous, and certain lepidopterous pests (Chen *et al*., 2005). Being the member of biggest selling insecticide class worldwide, it is important to find out the residue dynamic characteristic of clothianidin in various agricultural and environmental commodities. However, studies on the residue and dissipation of clothianidin are limited. Uneme and co-workers (Uneme *et al.,* 2006) studied the efficacy of clothianidin against several pests including hemipterous, coleopterous, thysanopterous, dipterous and some lepidopterous in different crops including tea.

The monitoring studies of pesticide residues in market samples of cardamom in Kerala analyzed by Pesticide Residue Research and Analytical Laboratory of Kerala Agricultural University, Kerala, India indicated a high level of contamination with pesticides including neonicotinoid group insecticide; imidacloprid indicates the use of relatively new class of such insecticides. Since no information is available on the persistence of clothianidin in cardamom, the present study was undertaken to standardise the protocol for estimation of residues, assessment of dissipation kinetics and effect of curing on level of residues of clothianidin after application at the fruit maturing stage of cardamom.

MATERIALS AND METHODS

Analytical standard (≥ 95.0% purity) of clothianidin was procured from M/s. Sigma-Aldrich, USA. Dantop 50% WDG, formulation from Nagarjuna Agrichem Ltd, Hyderabad, acetonitrile of HPLC grade (LiChrosolv), magnesium sulfate, sodium chloride, sodium sulphate of GR grade from Merck (Mumbai) and methanol of HPLC grade (LiChrosolv) were procured and the solid reagents were activated before use. Primary secondary amine (PSA), endcapped C18 and graphitized carbon black (GCB) from Agilent Technologies, USA. The 0.22 µm pore sized polyvinylidene fluoride (PVDF membrane) syringe filters (Rankem, New Delhi) were used to filter the extracts. All the glasswares were thoroughly washed as per the standard operating procedure to avoid the interferences from any contaminant during analysis. The suitability of the solvents and other chemicals were ensured by running reagent blanks before actual analysis.

Preparation of standard solution:

A standard stock solution of clothianidin (1,000 mg L^{-1}) was prepared in methanol and stored at -20 °C. The working standard solutions were prepared by serially diluting the standard stock solution to obtain the suitable dilutions required for plotting a calibration curve (1.0, 0.50, 0.25, 0.10, 0.075, 0.05, 0.025, 0.0l and 0.005 µg mL^{-1}) and were used for studying the linear dynamic range of the UPLC–MS/MS analysis, preparing matrix-matched calibration standards and spiking samples. The working solutions were stored in refrigerator at 4 °C. The recovery study with the fresh and cured cardamom capsules were carried out at 0.01, 0.05, and 0.10 µg g^{-1} with five replications at each level. Matrix matched calibration standards, prepared by adding the extract of blank samples, were in the range of 0.01–1 µg mL^{-1} for the compounds under study.

Validation of analytical methods:

Single laboratory method validation was done to standardize the procedure for residue estimation of fresh and cured cardamom capsules. For method validation, the multiresidue estimation procedure recommended for fruits and vegetables using Quick, Easy, Cheap, Effective, Rugged and Safe (QuEChERS) method as per AOAC Official Methods of Analysis (2007) was adopted for residue estimation in cardamom with slight modifications so as to suit the changed matrix. Control samples of fresh and cured cardamom with no history of pesticide application were collected and used for spiking insecticides at the three different levels. The samples were finely ground from which 12.5 g fresh and 5 g cured samples were taken and spiked with clothianidin at 0.01, 0.05 and 0.1µg g^{-1} levels in a 50-mL centrifuge tube. For cured cardamom, 4 g of sodium chloride and 5 mL water were added. The samples were mixed thoroughly in a vortex for 5 min. and 25 mL acetonitrile was added and kept in freezer at -20 °C for 20 minutes. The samples were homogenized (Heidolph Silent Crusher-M) at 14,000 rpm for 3 min. Sodium chloride (5 g) was added to the homogenized sample and thoroughly vortexed for 2 min. followed by centrifugation at 2500 rpm for 5 min. An aliquot of 12 mL of clear supernatant was transferred in to a 50-mL centrifuge tube prefilled with 6 g anhydrous sodium sulphate and mixed well for 2 min. for removing traces of moisture, if any. The extract was cleaned up by dispersive solid phase extraction (DSPE). For this, 8 mL of the supernatant was transferred to a 15-mL centrifuge tube containing 0.1 g primary secondary amine (PSA) sorbent and 0.6 g anhydrous magnesium sulfate, 0.05 g endcapped C18 and 0.025 g GCB. The mixture was again vortexed for 1 min. and centrifuged for 3 min. at 2,500 rpm. Five mL of the supernatant was transferred to a turbovap tube and evaporated to dryness under a gentle stream of nitrogen using the TurboVap set at 40 °C and 8 psi nitrogen flow. The residues were then reconstituted in 2 mL of methanol and filtered through 0.22µm polyvinylidene fluoride (PVDF) syringe filter for UPLC-MS/MS analysis.

Ultra Performance Liquid Chromatography (UPLC):

The residues of clothianidin were estimated using an Acquity UPLC (Waters, USA) - API 3200 MS/MS (AB Sciex) system by using a reversed phase 2.1 mm × 100 mm i.d. column (Atlantis d C18, Waters, USA) with 5 micron particle size in a column oven at 40 ^{o}C. The compound was separated in one single gradient run. The operation of the LC gradient involved the following two eluents: A: 10% methanol in water + 0.1% formic acid + 50 mM ammonium acetate; B: 10% water in methanol + 0.1 % formic acid + 50 mM ammonium acetate. The gradient elution followed was: 0 min. isocratic 5 % B, 0.0–3.0 min. linear from 5 % to 80 % B, 3.0 – 5.0 min. linear from 80 % to 100 % B, 5.0 - 7.0 min. linear from 100% to 50% B, 7.0 - 9.0 min. linear from 50% to 30 % B with 9.0 – 10.0 min. for initial conditions of 5 % B. The flow rate remained constant at 0.8 mL/min. and injection volume was 10 µL. The retention time of clothianidin was 1.65 min. (Fig. 1).

Mass spectrometry:

The effluent from the LC system was introduced into Triple quadrupole API 3200 MS/MS (AB Sciex) system. Analyte was detected by multiple reaction monitoring (MRM) using electrospray ionization mass spectrometry (ESI -MS) operating in the positive ion mode. The source temperature was 550 °C. Other important source parameters were; Ion source gas (GS1) 25 psi, ion source gas (GS2) 40 psi, ion spray voltage 2800 V and curtain gas 30 psi. For clothianidin, two MRM transitions were monitored and the quantitative and qualitative ion pairs selected were 250>169.1 and 250>132, respectively (Fig. 2). The parameters like declustering potential (DP), entrance potential (EP), collision cell entrance potential (CEP), collision energy (CE) and collision cell exit potential (CXP) for the quantitative ion pair were 45, 5, 18, 20 and 1, respectively. The corresponding values in the case of qualitative ion pair were 45, 5, 18, 23 and 1, respectively.

Field Experiment and sample collection:

The field experiment was conducted in a full bearing stage cardamom plantation in a randomized block design (RBD) replicated thrice with a plot size of 3 x 3 m^2 at the plantation of Indian Cardamom Hills (ICH), Idukki, Kerala, India. The site is situated at an altitude of 1,068 m above mean sea level at 9° 472’ 273” N latitude, and 77° 092’ 283” E longitudes and enjoys humid tropical climate with an average rainfall of 92.9 mm and relative humidity of 88.6 %. A single spray of clothianidin (Dantop 50 % WDG) was applied at two doses of 20 and 40 g a.i. ha^{-1} using a Knapsack sprayer. Despite the lack of label claim of clothianidin in cardamom, the dosage has been fixed based on the recommendation of clothianidin 50 % WDG against jassids and whiteflies of cotton (www.cibrc.nic.in). The control plots were sprayed with water. Three replicates of 100 g each fresh cardamom capsules from the treated and control plots were taken at intervals of 0 (2 hours), 1, 3, 5, 7, 10, 14, 21, 28 and 35 days after application. The samples were divided into two equal portions of which one portion (50 g) was used for estimation of residues on fresh capsules and the other portion was set apart for curing. The curing process included drying of fresh cardamom capsules at 50 °C for 36 h and then keeping at room temperature for 6 h. The capsules were again dried at 70 °C for 3 h and then polished for removing the perianth parts. The samples were crushed well using a blender. In the case of fresh samples, 12.5 g each was used for the estimation of residues, while only 5 g was used in the case of cured samples. Residues were extracted, cleaned up, and analysed following the method described earlier.

The residue data obtained at different intervals were subjected to statistical analysis to determine the half-life ($t_{½}$) values as per the procedure outlined by Hoskin (1961). The waiting period of clothianidin in fresh and cured cardamom was calculated based on the EU MRL value of 0.05 μg g^{-1}. The processing / dehydration factor (PF) was calculated as

$$PF = \frac{\text{Residues in cured cardamom } (\mu g\ g^{-1})}{\text{Residues in fresh cardamom } (\mu g\ g^{-1})}$$

RESULTS AND DISCUSSION

Efficiency of the method:

The efficiency of the method was evaluated by carrying recovery experiment. The modified QuEChERS method was suitable for the residue estimation of clothianidin from fresh and cured cardamom which indicated good recovery and high sensitivity. To minimise the matrix effect, quantitation of residues was conducted using matrix matched calibration curves. The instrument response was linear in the range 0.01 to 1 μg g^{-1} levels with a correlation coefficient (r) of above 0.999. The limit of detection (LOD) and limit of quantification (LOQ) of the analyte in both fresh and cured cardamom were found to be 0.005 μg g^{-1} and 0.01 μg g^{-1}, respectively.

To evaluate the accuracy and precision, fortified recovery experiments at three levels (0.01, 0.05, 0.10 μg g^{-1}) were done for both fresh and cured cardamom. In fresh cardamom recovery of clothianidin ranged between 91.0 and 94.4 %, with relative standard deviation of repeatability (RSDr) between 3.3 and 6.2 (Table 1). The mean percentage recovery from cured cardamom ranged from 89.2 to 91.4 %, and RSDr from 5.1 to 8.1. All of these values of recovery indicated good method accuracy and repeatability, and are within the accepted range for residue estimation.

Persistence of clothianidin in fresh cardamom:

The data on the persistence of clothianidin residues in fresh cardamom capsules when applied at 20 and 40 g a. i. ha^{-1} revealed the persistence up to 21 days (Table 2). No residue of clothianidin was detected in control sample. When applied at the lower and the higher dose, clothianidin resulted in an initial deposit of 1.96 and 4.13 μg g^{-1}, respectively. The mean deposit at 1, 3, 5, 7, 10, 14 and 21 days after treatment were 1.57, 1.12, 0.93, 0.61, 0.26, 0.11 and 0.03 μg g^{-1}, respectively, when applied at the lower dose of 20 g a. i. ha^{-1}, while the corresponding levels were 3.26, 2.21, 1.92, 1.35, 0.61, 0.19 and 0.05 μg g^{-1} when applied at the higher dose. On the 5th day after application, clothianidin

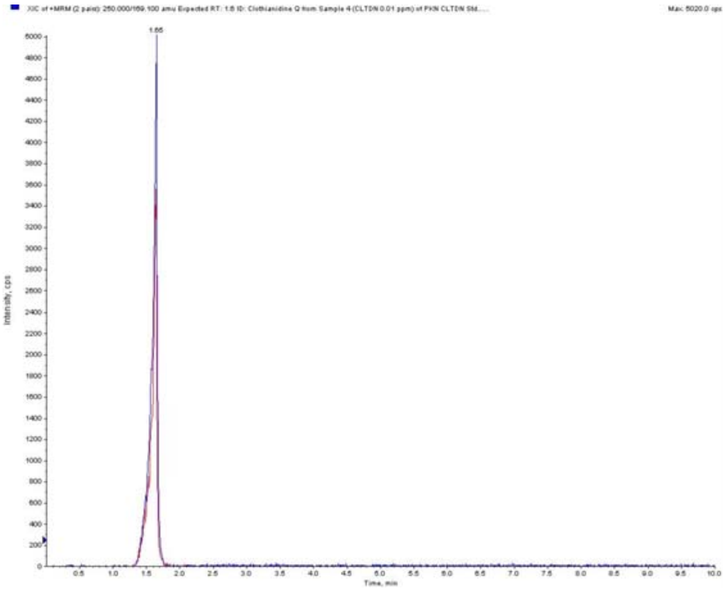

Fig. 1 LC-MS/MS MRM chromatogram of clothianidin in standard solution of 0.01 µgmL^{-1}

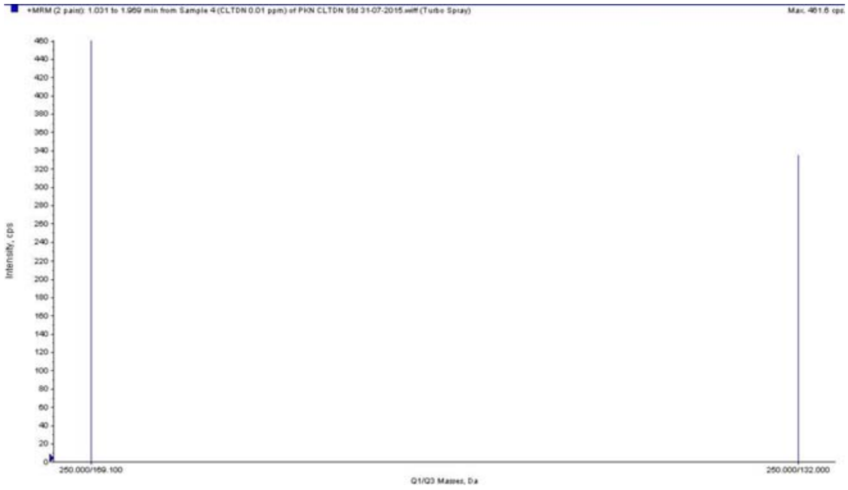

Fig. 2 MS/MS spectra of clothianidin

Table 1. Fortification and recovery in fresh and cured cardamom

Compound	Fortification level (µg g^{-1})	Fresh cardamom		Cured cardamom	
		Mean % recovery	RSDr	Mean % recovery	RSDr
Clothianidin	0.01	91.1	6.2	89.2	8.1
	0.05	94.4	5.8	90.1	6.9
	0.10	91.0	3.3	91.4	5.1

RSDr- Relative Standard Deviation of repeatability (n = 5)

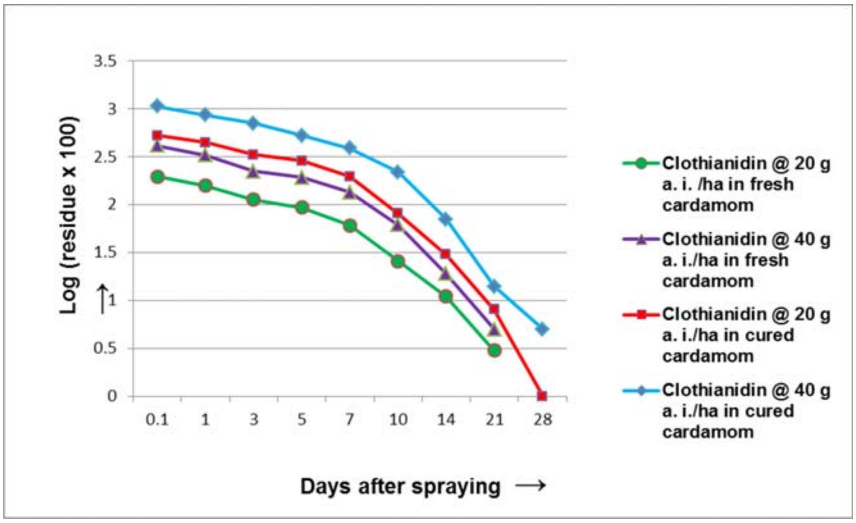

Fig. 3 Dissipation curve of clothianidin applied @ 20 and 40 g a.i. ha^{-1} in fresh and cured cardamom

showed more than 50 per cent dissipation at both the doses. Residues of clothianidin in fresh cardamom reached below the quantitation limit of 0.01 µg g^{-1} on the 28th day at both the lower and higher dosages (Fig. 3).

Persistence of clothianidin in cured cardamom

The data on the persistence of clothianidin residues in cured cardamom capsules when applied at 20 and 40 g a. i. ha^{-1} revealed the persistence up to 28 days which recorded 0.01 and 0.05 µg g^{-1}, respectively (Table 2). When applied at the lower and the higher doses, clothianidin resulted in an initial deposit of 5.24 and 10.61 µg g^{-1}, respectively. The mean deposits of 1, 3, 5, 7, 10, 14 and 21 days after treatment were 4.45, 3.30, 2.85, 1.95, 0.80, 0.30 and 0.08 µg g^{-1}, respectively, when applied at the lower dose of 20 g a. i. ha^{-1} while the corresponding levels were 8.56, 7.01, 5.23, 3.85, 2.17, 0.70 and 0.14 µg g^{-1} when applied at the double dose. In both the concentrations, the level of clothianidin residues dissipated on the fifth day was more than 45 per cent i.e., 45.61 and 50.71 %. Residues of clothianidin in cured cardamom reached below the quantitation limit of 0.01 µg g^{-1} on the 35th day at both the dosages (Fig. 3). A similar dissipation trend was reported by Pratheeshkumar and Chandran (2015) that the residues of acetamiprid, a neonicotinoid, reached below the quantitation limit of 0.01 µg g^{-1} within 28 days in both fresh and cured cardamom following the application of 10 and 20 g a. i. ha^{-1}.

Half-life and waiting period of clothianidin on fresh and cured cardamom:

The data on the level of residues of clothianidin in fresh and cured samples of cardamom is subjected to regression analysis for arriving half life ($t_{1/2}$) and pre harvest intervals. Accordingly, half life of clothianidin applied at 20 and 40 g a.i. ha^{-1} were 3.40 and 3.42 days, respectively, for fresh cardamom while the corresponding values were 3.11 and 3.45 days for cured cardamom (Table 2). Pesticide dissipation was reported to be dependent on physical and chemical factors, including environmental conditions, mode of application, plant species and growth rate, dosage, interval between applications and time of harvest (Khay *et al.,* 2008). The half-life values of clothianidin in tomato ranged between 7 and 11.9 days (Li *et al.,* 2012) whereas, Chen *et al.,* 2008 reported 1-2 days in cabbage. Thus, the half-life of clothianidn is influenced by the type of crop. The waiting period calculated for fresh and cured cardamom was 18.41 and 21.16 days and 22.09 and 27.54 days, respectively, for the lower and the higher doses. Pratheeshkumar and Chandran (2015) have reported waiting periods of 11.65 and 17.35 days and 14.86 and 20.40 days for acetamiprid in fresh and cured cardamom,

Table 2. Persistence of clothianidin residues in/on fresh and cured cardamom and processing factor

Days after spraying	Fresh cardamom				Cured cardamom				Processing Factor (Lower dose)
	Lower dose (20 g a.i. ha^{-1})		Higher dose (40 g a.i. ha^{-1})		Lower dose (20 g a.i. ha^{-1})		Higher dose (40 g a.i. ha^{-1})		
	Mean residue ± SD (µg g^{-1})	Dissipation %	Mean residue ± SD (µg g^{-1})	Dissipation %	Mean residue ± SD (µg g^{-1})	Dissipation %	Mean residue ± SD (µg g^{-1})	Dissipation %	
Before	BQL		BQL		BQL		BQL		
0 (2 hr after)	1.96 ± 0.132		4.13 ± 0.264		5.24 ±0.321		10.61± 0.624		2.67
1	1.57± 0.084	19.89	3.26 ± 0.202	21.06	4.45 ± 0.114	15.08	8.56 ± 0.551	19.32	2.83
3	1.12 ± 0.086	42.85	2.21 ± 0.133	46.49	3.30 ± 0.124	37.02	7.01 ± 0.451	33.93	2.95
5	0.93 ± 0.052	52.55	1.92 ± 0.101	53.51	2.85± 0.152	45.61	5.23 ± 0.217	50.71	3.06
7	0.61 ± 0.032	68.87	1.35 ± 0.092	67.31	1.95 ± 0.104	62.79	3.85 ± 0.103	63.71	3.20
10	0.26 ± 0.012	86.73	0.61 ± 0.044	85.23	0.80 ± 0.054	84.73	2.17 ± 0.106	79.55	3.08
14	0.11 ± 0.008	94.39	0.19 ± 0.008	95.40	0.30 ± 0.011	94.27	0.70 ± 0.031	93.04	2.73
21	0.03± 0.001	98.47	0.05 ± 0.003	98.79	0.08 ± 0.005	98.47	0.14 ± 0.007	98.68	2.67
28	BQL	-	BQL	-	0.01± 0.001	99.81	0.05 ± 0.002	99.53	-
35	BQL		BQL		BQL		BQL	BQL	-
Mean Processing Factor									2.90
Half life	3.40 days		3.42 days		3.11 days		3.45 days		
Waiting period	18.41 days		21.16 days		22.09 days		27.54 days		
Integrated rate equation	log ct = 2.3276 - 0.2037 t/2.303 R2= 0.99		log ct = 2.6666 - 0.2142t/2.303 R2= 0.98		log ct = 2.8378 - 0.2229 t/2.303 R2= 0.98		log ct = 3.1003 - 0.2007 t/2.303 R2= 0.99		

BQL – Below quantitation limit (0.01 µg g^{-1}), SD – Standard Deviation
log Ct = logarithm concentration of residue at 't' time; t - time in days

respectively, after application at 10 and 20 g a. i. ha^{-1}. Celik *et al*. (1995) concluded that under natural field conditions volatilization is the main process that affects pesticide dissipation. Huang *et al.,* 2010 reported that in agricultural fields, the growth dilution of treated plants may play a significant role in the diminution of pesticides in crop plants.

Effect of processing in dissipation of clothianidin in cardamom:

The initial deposit of clothianidin at the lower dose on fresh cardamom was 1.96 µg g^{-1} while it was 5.24 µg g^{-1} after curing registering a processing factor of 2.67. The processing factors arrived for 1, 3, 5, 7, 10, 14 and 21 days after treatment were 2.83, 2.95, 3.06, 3.20, 3.08, 2.73, and 2.67, respectively (Table 2). The residues were found to get magnified during drying presumably due to dehydration during curing/processing after accounting for the dissipation losses. During the curing process, 75–79 % of moisture got depleted which would have resulted in an accumulation of residues and a portion of residues also would have dissipated due to the effect of heat and rubbing. The mean processing factor 2.90 indicates that application of clothianidin in fresh cardamom followed by curing as per the farmers adopted practice followed by polishing resulted in 2.90 times more residues in the cured cardamom. A higher value of processing factor for clothianidin indicates its relatively high stability to dissipation during curing and that it cannot be dislodged easily by the action of curing. Pratheeshkumar and Chandran (2015) reported a mean processing factor of 2.77 for acetamiprid in cardamom after the application of 10 g a. i. ha^{-1}. George *et al.* (2013) reported that by the processing of cardamom, the residues of chlorpyrifos got magnified to the tune of 3.24-3.68 times and that of lambda-cyhalothrin to 2.98-3.46 times of initial residues, consequent to loss of weight due to dehydration during curing.

The information generated in the present study indicate moderate rate of dissipation of clothianidin on both fresh and cured cardamom capsules. As no Codex/FSSAI MRL is available for fresh or cured cardamom capsules, EU MRL of 0.05 mg kg^{-1} for dry cardamom is taken in to account for the calculation of pre harvest interval. Thus a pre harvest interval of 18.41 and 21.16 days are recommended for fresh cardamom for the lower and higher doses, respectively, while 22.09 and 27.54 days are recommended for the lower and higher doses, respectively, in cured cardamom. As the capsules are consumed after curing, waiting periods of 22.09 and 27.54 days may be followed to avoid the risk in terms of harvest time residues in the produce.

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