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Behavior of β-Cyfluthrin after Foliar Application on Chickpea (*cicer aretinium* L.) and Pigeon Pea (*cajanus cajan* L.)

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β-cyfluthrin is a mixture of two enantiomers, S- (α-cyano-4-flouro-3-phenoxybenzyl (1R) cis 3-(2,2-dichlorovinyl)-2, 2-dimethylcyclopropane carboxylate) and the corresponding (R) and (1S) cis isomer and (S) (1R) trans and (R) (1S) trans isomers in 1:2 ratio of the parent compound cyfluthrin. This photostable synthetic pyrethroid (Nauman, 1998) has an ester and ether linkage in addition to a dichlorivinyl group attached to a cyclopropane moiety (Fig. 1I). β-cyfluthrin is unique among the synthetic pyrethroids (Leicht et al., 1996) because of the presence of fluorine atom in the molecule, which imparts special character to the compound. It is a nonsystemic, contact insecticide with a wide spectrum of activity against Lepidoptera, Coleoptera, and Hemiptera in cotton, fruits, vegetables, and cereals. The residues of β-cyfluthrin have been estimated on various crops such as eggplant (Sinha and Gopal, 2002), okra (Dikshit et al., 2002), tomato (Dikshit et al., 2003), mustard (Gopal et al., 2002), sorghum (Berg and Rensberg, 2001), and cotton (Mukherjee et al., 2001). Laboratory studies have indicated that, because of to low mobility, the residues do not transport beneath the subsoil surface (Gupta and Gajbhiye, 2001). The compound is also being used in the area of public health for the control of houseflies and cockroaches (Zhuang, 1996), mosquitoes (Yap et al., 1997). There are, however, no reports of the behavior and persistence of β-cyfluthrin on pulse crops such as chickpea (c*icer aretinium* L) and pigeon pea (*cajanus cajan* L). The pulse crop is infested by a large number of insect pests, such as pod borers, aphids, jassids, and pod flies, which results in a reduction of crop yield. The synthetic pyrethriods have proved to be effective in the control of resistant insect pests of pulse crops. The consumption of synthetic pyrethroids has increased significantly with the decline in the use of organochlorine pesticides such as lindane and endosulfan, which were used for the control of insect pests of pulses. The synthetic pyrethroids represent the most popular class of insecticides today. The presence of pesticides residues in vegetables, fruits, and green leaves above the maximum limit is of concern to human health because of the toxic nature of the pesticides. Hence, it is imperative to evaluate the pesticidal schedule on edible crops for quantification of residues. This article presents the behavior of β-cyfluthrin in chickpea and pigeon pea.

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Materials and Methods

All of the chemicals were obtained from SD Fine Chem Ltd. (Mumbai, India). Solvents included acetone, hexane, and dichloromethane. Adsorbents included neutral alumina and Florisil. Drying agent included anhydrous sodium sulfate. The solvents were distilled before use. NMR was recorded on Varian model NMR (60 Hz) and FT-IR on Impact 400-Nicolet. Analytical standard of β-cyfluthrin (97.8%) was procured gratis from Bayer India Ltd. The stock solution of β-cyfluthrin was prepared in hexane at 1mg mL^{-1} and was stored at 4°C. Working standards were prepared by appropriate dilutions.

A field trial was conducted in a randomized block design during 2002–2003. Pigeon pea (var Pusa 22) and chickpea

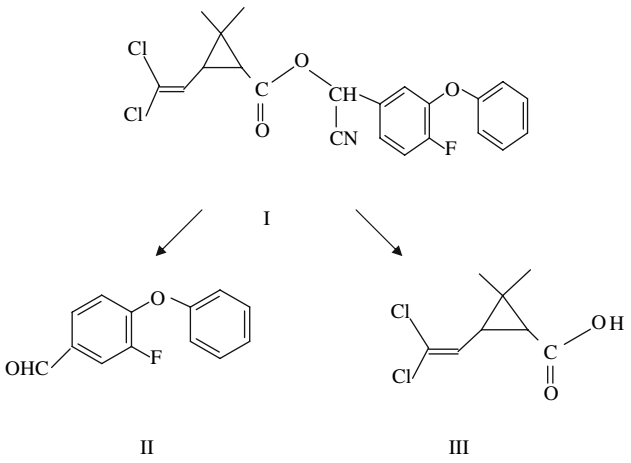

Fig. 1 *β*- cyfluthrin (I), 4-fluoro-3- phenoxybenzaldehyde (II), and 3-(2, 2- dichlorovinyl)-2,2-dimethylcyclopropane carboxylic acid (III)

crop (var Pusa 203) were raised in the fields of Indian Agricultural Research Institute, New Delhi, following the good agricultural practices of the region. The plot size was 6 m^2 for each replicate. Pigeon pea was grown during *Khariff* season, whereas chickpea was grown in the *Rabi* season. *β*-cyfluthrin formulation was obtained from M/s Bayer India Ltd. for the experimental study. *β*-cyfluthrin (Bulldock 025 SC) was applied @ 12.5 and 25 g a.i. ha^{-1} in 750 L water (Treatment T1 and T2) at 50% pod formation stage in both chickpea and pigeon pea. The experiment was performed in triplicate for each crop and a control plot was kept aside in which no pesticide was applied.

The maximum temperature during chickpea crop was 27.2°C and 12.0°C, respectively, with a relative humidity of 32%. Average sunshine hours recorded was 9.50. There was no rainfall during the period of study. In the case of pigeon pea, the maximum and minimum temperatures were 29.8°C and 16.9°C, respectively, with relative humidity of 69%. Average sunshine hours recorded was 5. The rainfall recorded during the period was 68.6 mm.

Green pod samples of both chickpea and pigeon pea were collected one hour after application of the pesticide, and subsequently at periodic intervals of 1, 3, 5,7, 10, and 15 days and grains at harvest. 50-g samples of green pods and grains were spiked in triplicate at two concentrations: 0.5 and 1.0 μg g^{-1} level. 50-g representative subsamples of green pods were extracted with acetone (3 × 50 mL) in a Waring blender. The extract was concentrated under reduced pressure and was transferred to a separatory funnel, and saline water (10%, 150 mL) was added. The pesticide was exchanged into organic phase by liquid–liquid partitioning with dichloromethane (3 × 30 mL). The organic solvent was concentrated under reduced pressure and then was subjected to clean up. The harvest time grain samples were extracted in a Soxhlet extractor for 4 hr with 300 mL of a mixture of hexane–acetone (1:1). The extract of the grain sample was evaporated completely under vacuum, was dissolved in hexane (40 mL), and was then exchanged into acetonitrile (3 × 40 mL) to remove the oil from the grains. The acetonitrile portion was further diluted with saline water (2%, 600 mL) and was then partitioned into dichloromethane (3 × 30 mL).

The organic solvent was evaporated (dissolved in) hexane-acetone (9 + 1) and was subjected to clean up. The concentrate (5 mL) was subjected to column clean up. The glass column (1.5 mm × 45 cm) was packed with anhydrous sodium sulfate (1g) + neutral alumina (2g) + Florisil (1g) + anhydrous sodium sulfate (1g). The column was prewashed with hexane (30 mL). The concentrate was loaded onto the column and was eluted with a mixture of hexane–acetone (1 + 1). The eluant was concentrated to dryness under a rotary vacuum evaporator and made up in hexane before analysis by GLC.

β- cyfluthrin (1g) was dissolved in methanol (30 mL) and was refluxed with aqueous sodium hydroxide (100 g L^{-1}, 20 mL) for 2 hr. The reaction mixture was cooled and extracted with dichloromethane. The crude mixture showed two products on TLC. Column chromatography over silica gel, and successive elution with hexane and mixture of hexane:acetone yielded pure two compounds. 4-fluoro-3-phenoxybenzaldehyde (Fig. 1, II, Rf 0.28), IR ν cm^{-1} 1725(s, C = O); NMR-$CDCl_3$ δ: 6.76 (m, 5H, Ar-H, C-5, C-2′, 3′, 4′, 5′, and 6′), 7.52 (dd, J = 2Hz, 2H, C-2, and 4), 7.63 (s, 1H, C-6), C-9.85 (s, 1H, D_2O, CHO), m/z 243.

3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid (Farkas acid, Fig. 1, III, Rf 0.13), IR: ν cm^{-1} 1780,COOH, 3200 (b, OH); NMR-$CDCl_3$ δ: 1.22 (s, 6H, 3 × CH_3), 1.72 (s, 1H, CH-C), 2.22 (s, 1H, CH-COOH), 5.65 (s, 1H,C=CH), 10.0(s, 1H, D2O exchangeable), m/z 208.

The quantitative estimation of *β*-cyfluthrin was carried out using Hewlett Packard gas liquid Chromatograph series II (model 5890) equipped with Ni ^{63} electron capture detector. The column BP-5 was megabore (12 m × 0.52 mm i.d × 1 μ) and was used for the estimation of *β*-cyfluthrin in crop samples. Another column [megabore BP-5 30 m × 0.52 mmi.d × 1 μ] of varying length but same polarity was used, to ascertain the identity of the pesticide. *β*-cyfluthrin was determined by HPLC (Merck-Hitachi), consisting of an L-7100 (computer operated dual pump), an L-7400 (UV detector), and an L-7200 (Auto sampler). The column used was Lichrospher, RP-18 (30 cm × 5 μm). The concentration of *β*-cyfluthrin was calculated on the basis of a peak area from the calibration curve. Standard solutions of different concentrations 0.1, 0.2, 0.5, 1.0, 1.5, and 2.0, μg mL^{-1} of *β*-cyfluthrin were injected in the GLC, and a calibration curve was drawn by plotting peak area vs concentration. Each injection was made thrice for all the

Table 1 Residues of β-cyfluthrin in chickpea and pigeon pea

Days	Treatment (g a.i. ha^{-1})	Average residues * (mg kg^{-1}) in chickpea	% Dissipation in chickpea	Average residues* (mg kg^{-1}) in pigeon pea	% Dissipation in pigeon pea
0	12.5	4.83	—	6.88	—
	25	7.34	—	14.92	—
1	12.5	3.11	35.6	5.65	17.8
	25	5.98	18.5	13.73	7.9
3	12.5	2.12	56.1	4.92	28.4
	25	3.98	45.7	11.18	25.0
5	12.5	1.95	59.6	3.09	55.0
	25	3.25	55.7	7.32	56.9
7	12.5	1.02	78.8	2.15	68.7
	25	2.27	69.0	5.28	64.6
10	12.5	0.93	80.7	1.83	73.4
	25	1.22	83.3	3.45	76.8
15	12.5	0.26	94.6	0.73	89.3
	25	0.39	94.6	0.91	93.9
Harvest grains	12.5	ND	—	ND	—
	25	ND	—	ND	—

*Average of three replicates, ND < 0.01 mg kg^{-1}

concentrations so as to obtain the linearity range of the pesticide.

The GC column temperature was 250°C, and injector port and detector were set at 270°C and 300°C, respectively. β-cyfluthrin eluted at 5.23 min under these conditions. The temperatures conditions maintained for the confirmation was 280°C column, injector port 290°C, and detector 350°C. The retention time of β-cyfluthrin was 3.73 min. The mobile phase in HPLC used was a mixture of acetonitrile–water (70: 30, v/v), was used as the mobile phase, with a flow rate of 0.5 mL min^{-1}. The injection volume was 10 μL, and the wavelength was set at 250 nm. β-cyfluthrin eluted at 4.52 min under these conditions. Thin layer chromatography was carried out on silica gel G coated glass plates using acetone–benzene (1 + 9) as the developing solvent. Iodine was used as a visualizing agent.

Results and Discussion

The identity of β-cyfluthrin was confirmed by using two columns of varying dimensions. An HPLC of β-cyfluthrin was performed to confirm the identity of the sample in the crop sample. The samples were analyzed on megabore column 12m in length.

The initial residues of β-cyfluthrin on chickpea were 4.83 and 7.34 mg kg^{-1} at the recommended and double the recommended dose of application (Table 1). The residues dissipated slowly by day 1 to 35.6% in the recommended treatment, and thereafter followed fast dissipation to 78.8 by day 7 and further to 94.6% by day 15. A similar trend of dissipation was recorded in double dose of application, recording 94.6% dissipation by day 15. The initial residues recorded on pigeon pea were 6.68 and 14.92 mg kg^{-1}, respectively, at the recommended and double dose of application. The residues dissipated to 5.65 and 13.73 mg kg^{-1} by day 1 (Table 1), and the corresponding percent dissipation was 17.8 and 7.9. The residues of β-cyfluthrin dissipated slowly initially and then recorded fast dissipation by day 15 to 89.3 and 93.9% in the two doses of application: recommended and double dose. The initial residues of β-cyfluthrin recorded on pigeon pea were higher than that observed on chickpea, which may be caused by the hairy surface of chickpea pods that prevents the adherence of the pesticide (Fig. 2). There is significant loss of both the pulse crop as a result of insect infestation, and pulses are a main source of food in the Indian diet.

Green chickpea pods are consumed raw or as cooked food, similar to *dal*, whereas pigeon pea is mostly consumed cooked as *dal*. The data indicate that the residues dissipated with time, following a first order dissipation, with a half life of 3.7 days in chickpea and 4.3–5.0 days in pigeon pea. Similar trends of dissipation have been observed during study of persistence of synthetic pyrethroids, namely tau-fluvalinate, fenvalerate, and lambda-cyhalothrin on eggplant, tea, and chickpea (Mukherjee and Gopal, 1992, Gopal et al., 1987, Gopal and Mukherjee, 1995). The two degradative products were synthesized in the laboratory to serve as authentic samples for quantification in the crop samples.

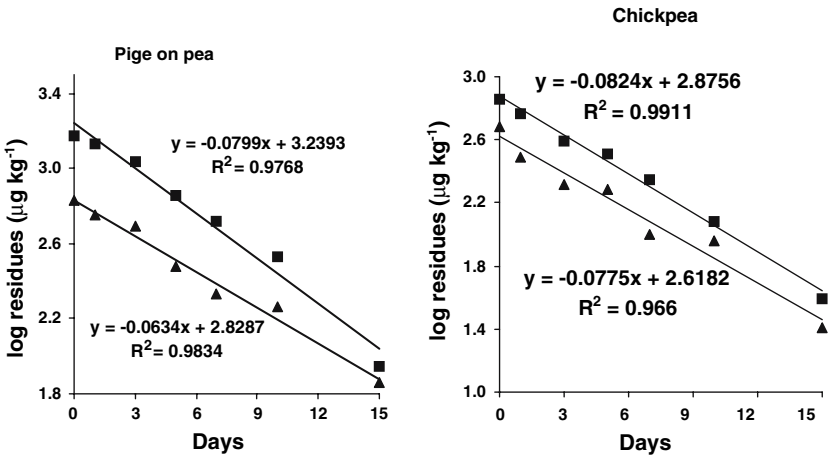

Fig. 2 First order dissipation of β-cyfluthrin in chickpea and pigeon pea

Two metabolites of β-cyfluthrin were detected that appeared below the spot of β–cyfluthrin on TLC, which were identified as 4-fluoro-3-phenoxybenzaldehyde (Fig. 1, II, Rf 0.58) and 3- (2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylic acid (Fig. 1, III), Rf 0.13), as are supported by the IR and NMR spectra (Saikia and Gopal, 2004). The metabolite 4-flouro-3-phenoxybenzaldehyde was not detected on TLC at spray levels of 12.5 and 25 g a.i. ha^{-1} in both chickpea and pigeon pea. This may be attributed to the fact that the aldehyde may have been oxidized into the corresponding acid and further conjugated in the crop. However, the metabolite, 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropane carboxylic acid was detected in day 7 and day 10 samples on TLC, at spray levels of 12.5 and 25 g a.i. ha^{-1}.

The acceptable daily Intake (ADI) of β-cyfluthrin is 0.02-mg kg^{-1} body weight (Tomlin, 1994), toxicity class, WHO-II, EPA-II. Considering the body weight of an average Indian person as 50 kg, MPI (maximum permissible intake) of β-cyfluthrin is 1.0 mg $person^{-1}$ day^{-1}. Further, considering 200 g as vegetable consumption for an Indian balanced diet, and maximum residues on day 7 is 1.95 mg kg^{-1}, in the case of recommended dose (12.5 g a.i. ha^{-1}), the TMRC is found at 0.32 mg $person^{-1}$ day^{-1}, whereas the residues on day 15 are 0.26 mg kg^{-1}, the TMRC is found at 0.052 mg $person^{-1}$ day^{-1}, and both these values are low as compared to MPI value of 1.0 mg $person^{-1}$ day^{-1}. Therefore, β-cyfluthrin treatment at recommended dose appears safe in plant protection schedules. Hence, if applied at 12.5 g a.i. ha^{-1} as foliar spray, this will not result in residue accumulation. However, even if a higher dose (25 g a.i. ha^{-1}) is also intended, the TMRC (0.078 mg $person^{-1}$ day^{-1}, residues on day 15 being 0.39 mg kg^{-1}), values are lower than MPI and hence the insecticide will not cause adverse effects after consumption of such chickpea green pods. TMRC for the recommended dose calculated in harvest grains of both chickpea and pigeon pea is 0.02 mg $person^{-1}day^{-1}$ (residue on grains at harvest is nondetectable, which is <0.01 mg kg^{-1}). As the theoretical residue contribution (TMRC) was found to be less than the toxicological estimated MPI value of 1.0 mg $person^{-1}day^{-1}$, it can be concluded that the rate of application of β-cyfluthrin at both the doses was safe from the crop protection point of view.

The pulses are a rich source of protein, are consumed almost twice daily, and are a regular part of Indian diet, and the MRL of β-cyfluthrin on brassica crops is 0.50 mg kg^{-1} (Codex, 1997), and the residues recorded in harvest grains were below the 0.01 mg kg^{-1}, thus indicating the spray schedule is not hazardous to the consumer health and environment. This study highlights the utility of these new insecticides over conventional insecticides (Mukherjee and Gopal, 1997, Mukherjee and Gopal, 1998) wherein synthetic pyrethroids were found superior to organochlorines from the residues angle. This observation gains significance in the light of safer alternative as certain conventional insecticides are under review or may be categorized as being under restricted use.

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