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RESIDUES OF INSECTICIDES FOR GUMMOSIS CONTROL IN PINEAPPLE

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ABSTRACT

Without labeled insecticides, such as toxaphene, Puerto Rico pineapple growers are unable to control the larvae of *Batrachedra comosae* Hodges, a moth causing the dreaded gummosis. Pineapple production of 68,753 metric tons valued at $19.5 million in 1987-88 may be in jeopardy.
For several years up to and following the US EPA cancellation of toxaphene labels, field and residue trials were conducted to evaluate the effects of other insecticides for gummosis control. Insecticides with active ingredients acephate, fenvalerate and esfenvalerate were effective when applied during bloom 60-80 days before harvest.
In several trials insecticide residue levels in the pineapple crown, stump, foliage, whole fruit, pulp and bran were barely detectable and ranged from 0.01 to 0.08 ppm. On basis of current data, EPA has granted a Section 18 emergency exemption registration for one year for the use of esfenvalerate on pineapples grown in Puerto Rico. A tolerance and full label will be granted after additional residue data is provided from samples of pineapple juice and bran.

Keywords : Pesticide residues, insecticide residues, pineapples.

RESUME

LES RESIDUS INSECTICIDES ET LE CONTROLE DE LA GOMMOSE DES ANANAS

A Porto Rico les planteurs d'ananas, s'ils ne peuvent utiliser d'insecticides du type toxaphène, sont dans l'incapacité de contrôler la teigne *Batrachedra comosae* Hodges responsable de la gommose. Dans ces conditions la

production d'ananas qui était en 1987-88 de 68753 T et représentait une valeur de 19,5 millions de $ pourrait se trouver en péril.
Depuis quelques années, à la suite de l'annulation par l'E.P.A. de la dérogation d'utilisation du toxaphène, des essais ont été effectués pour évaluer le taux des résidus et l'efficacité au champ d'autres insecticides. Certains de ceux-ci, à base notamment d'acephate, fenvalerate et esfenvalerate, se sont montrés efficaces appliqués à la floraison 60 à 80 jours avant la récolte.
Dans divers essais insecticides les analyses de résidus effectuées alors dans différentes parties de la plante (couronne, souche, feuille, fruit, pulpe...) ont montré que ceux-ci étaient difficilement détectables puisque compris entre 0,01 et 0,008 ppm. A la suite de ces résultats l'E.P.A. a accordé (Section 18) aux planteurs d'ananas de Porto Rico une dérogation d'une année pour l'utilisation de l'esfenvalerate.
L'homologation définitive pourrait être accordée à la suite d'analyses de résidus complémentaires qui seraient à effectuer notamment à partir d'échantillons de jus et d'écorce d'ananas.

INTRODUCTION

There are about 2,430 hectares in Puerto Rico planted to pineapple cultivars such as Red Spanish, Smooth Cayenne, PR 1-67, Bullhead, Champaca, Mariota (PR 1-56), and others.

In 1987-88, pineapple production was 68,753 metric tons with a farm value of $19.5 million (Personal communication, 1989). About 90 % was processed into pineapple juice and other by-products, and only 10 per cent was sold as fresh fruit.

Of all the weed, nematode, disease and insect problems impacting on pineapple production in Puerto Rico, a disease like condition called gummosis may be the most serious. Caused by the larvae of the moth *Batrachedra comosae* Hodges, gummosis affects the external appearence at the lower portion of the fruit, and subsequently the quality of the juice. In other countries such as Trinidad, Costa Rica, Venezuela, Brazil and Mexico, gummosis of the fruit is caused by the Lepidoptera species *Tmolus echion* L. = *Techla basilides* Seyer (Pye, 1987). One of the most popular pineapple cultivars, the Red Spanish, is susceptible to gummosis whereas others such as Smooth Cayenne, PR 1-67 and Bullhead are less susceptible.

Pérez-Escolar conducted extensive studies dealing with the biology of *Batrachedra comosae* and the evaluation of chemical compounds for

prevention of pineapple gummosis in Puerto Rico (Pérez, 1957 ; Pérez-Escolar, 1959). His studies resulted in the US federal registration of the insecticide toxaphene as a foliar spray, at the rate of 3.5 liters per hectare applied 2-3 times during blossoming to control *B. comosae*. Toxaphene, a camphene derivative, was used from 1965 until 1985 when the US Environmental Protection Agency cancelled all labels due to suspected carcinogenic properties. From 1978 to 1988, Inglés conducted several field trials to evaluate potential insecticides for gummosis control such as diazion, methomyl, acephate, carbaryl, oxamyl, and the pyrethroids fenvalerate, esfenvalerate, permethrin and others (Inglés, 1989). His research led to the federal registration of the biological insecticide Dipel 2 x (Bacillus thuringiensis) and the issuance of one-year emergency registration (Section 18) for the insecticide esfenvalerate.

This paper reports results and findings on pesticide residues of acephate (O, S-dimethyl acetylphosphoramithioate), fenvalerate (Cyano (3-phenoxyphenyl) methyl 4-chloro-a(1-methylethyl) benzeneacetate) and its most insecticidally active isomer, esfenvalerate, on pineapple samples from Puerto Rico.

MATERIALS AND METHODS

General Aspects

Insecticide needs for pineapples were identified by the Puerto Rico IR-4 Liaison Representative with the assistance of researchers of the College of Agricultural Sciences of the University of Puerto Rico-Mayaguez Campus ; pineapple growers,
and representatives of pesticide manufactures. High priority needs identified by scientists at the Puerto Rico Agricutural Experiment Station, were submitted as pesticide clearance requests (PCR) through the IR-4 regional office (University of Florida, Gainesville, Florida) to IR-4 National Headquarters at Rutgers University, New Brunswick, New Jersey, or to the research and development representative of pesticide companies. Details requested in each PCR and the operation of the IR-4 program to expand pesticide labels for food uses has been described priviously (Montalvo-Zapata et al., 1987 ; Meister, 1984).

After screening, both at the IR-4 Regional Office and National Headquarters, each PCR was examined to determine compliance with specific criteria. With the help of the requester and industry, a research test protocol was developed by IR-4 to generate performance data : efficacy, effect on yield and quality of commodity, and residue data.

Each field trial was established following IR-4 or pesticide company guidelines for experimental design, plot size, treatments, rates, frequency, method of application, harvesting, field sampling and shipment of samples to U.S.

Acephate Experiment

This experiment was established on at a commercial planting owned by the Land Authority Pineapple Program at Sabana Seca, Manati, Puerto Rico. Pineapple cultivar Red Spanish was planted on July 3, 1983. Seed selection, planting, fertilization, and weed control followed standard practices of the Puerto Rico Land Authority-Pineapple Program. Other materials used and their dates of application included were as follows : D-D- as a soil-applied treatment before plantin ; Karmex,as preemergence herbicide treatment (July 3, 1983); and a tank mix of Ametryne-Atrazine, as a postemergence treatment on October, 1983. Acephate (Orthene 75S at 0, 1.68 and 2.56 kg a.i.ha-1 was applied as a foliar spray on July 19 and 26, 1984 when the pineapple was blooming. The insecticide was applied with a hand sprayer having an 8004 nozzle tip. The spray volume was 1 liter/plot. The experiment design was a randomized complete block with four replications. Whole mature fruits and other pineapple parts were harvested at random 82 days after the last treatment, i.e., in October 16, 1984. All samples were transferred immediately to the AES Pesticide Laboratory at Rio Piedras, where crown and peel (bran) were removed, stored at -20°C, then packed in appropriate bags and shipped frozen in containers with dry ice by air freight to Ortho/ Chevron Pesticide Laboratory, Richmond, California.

Acephate and methamidophos residues were extracted from each sample with ethyl acetate, cleaned on a silica gel column using 10 % methanol in ethylether as the eluant, and determined by thermionic GLC (Chevron Chemical, 1972). Programmed-temperature gas-liquid chromatography, with a termionic detector, and GLC column containing 1 % Reoplex 400 on 100-120 mesh Gas-Chron Q, was used for the quantitave determination.

A second experiment following the same protocol, experimental design, harvesting and shipment guidelines was conducted during 1984-85.

Fenvalerate Experiment

This experiment was also established at a commercial planting owned by the Land Authority-Pineapple Program. Pineapple cultivar Red Spanish was planted on March 1984 and harvested on October 24, 1985. Fenvalerate (Pydrin 2.4 EC formulation) at 0,0.14 and 0.28 Kg a.i.ha-1 was applied three times as a foliar spray on the following dates : July 26, August 1, and August 7, 1985. The insecticide was applied with a hand sprayer (3.8 1 capacity)

having an 8004 nozzle tip. The spray volume was 1 1/plot. The experimental design was a partially balanced incomplete block design with four replications.

Mature fruits randomly selected from center rows of each treatment were harvested 78 days after the last treatment, and taken to the AES Pesticide Laboratory at Rio Piedras. Samples of pulp, bran and crown from each replicate were prepared, packed in appropriate bags, frozen and stored in a walk-in freezer and later shipped in containers with dry ice by air freight to the IR-4 Pesticide Research Laboratory, University of Florida, Gainesville, Florida.

Fenvalerate residue determinations were made following the gas chromatographic method of Lee, Wescotte and Reichle (Lee et al., 1978). Residues were extracted with hexane and the organic extract concentrated using a roto-evaporator. Esfenvalerate residues were then determined in a Hewlet Packard GC, model 5840 A, equipped with a Ni63 election capture detector. A glass column 160 cm x 2 mm packed with 3 % OV-101 on 100/120 mesh Gas Chrom G was used for identification and quantification. Other chromatographic conditions were as follows : oven and injector (225°C), and argon-methane as carrier gas with a flow 40 ml/min.

Esfenvalerate Experiment

This experiment was established at the Hill Farm, Manati municipality. The pineapple cultivar Red Spanish was planted on July 24, 1985 and harvested on October 10, 1986. Esfenvalerate (Asana 1.9 EC formulation) at 0, 0.28 and 0.05 kg a.i.ha-1 was applied as a foliar spray on the following dates : July 14 and 23, August 13 and 22, 1986. The insecticide plus Triton B spreader-sticker was applied with a hand sprayer (3.8 1 capacity) with an 8004 nozzle tip. The spray volume was 1 1/plot. The experimental design was a partially balanced incomplete block with four replications.
Four mature fruits randomly selected from center rows of each treatment, 59 days after the last treatment, were collected and taken of the AES Pesticide Laboratory at Rio Piedras. Samples of pulp, peel (bran) and crown from each replicate were prepared, frozen and stored in a walk-in freezer. Samples were then packed in appropriate bags and shipped in containers with dry ice by air freight to the IR-4 Pesticide Research Laboratory, Univerisity of Florida, Gainesville, Florida.

Esfenvalerate residue determinations were made following the gas chromatographic method of Lee, Wescotte and Reichle (Lee et al., 1978).

RESULTS AND DISCUSSION

A. Pesticide Residue Data

Acephate and methamidophos residues - Maximum residues of acephate and its metabolite methamidophos (O, S-dimethyl phosphoramidothioate) resulting from foliar sprays of Orthene 75s on pineapple are shown on Table1. For the 1983-84 trial acephate residues in fruit without crown and collected 80 days after the last spray, were 0.06 as compared to 0.03, 0.04 and less than 0.01 ppm in the crown, foliage and stump, respectively. Data obtained from the 1984-85 field trial revealed that the highest concentration of acephate in the fruit was 0.03 ppm as compared to 0.02 ppm in the crown, less than 0.02 ppm in the foliage and less than 0.01 ppm in the stump. In both trials methamidophos residues were not detected in any fruit part at the level of instrumental sensitivity (0.01 ppm).

Fenvalerate residues - Table 2 shows fenvalerate residues on the pulp, crown and bran of pineapples treated with three sprays of the Pydrin 2.4 EC formulation at the rate of 0.28 kg a.i.ha-1. Fenvalerate residues were less than 0.05 ppm in the bran and pulp, respectively, and 0.06 ppm in the crown of fruits collected 78 days after treatment.

Esfenvalerate residues - Table 2 shows esfenvalerate residues in the fruit, crown and bran or peel of pineapple, treated with four foliage sprays of esfenvalerate at a rate of 0.056 kg a.i. ha-1. Maximum detectable residues of esfenvalerate (0.08 ppm) were found in the crown as compared to 0.02 and 0.01 ppm in the bran and fruit, respectively.

B. Regulatory status

IR-4 has submitted to US EPA tolerance petitions for the insecticide acephate in or on the raw agricultural commodity pineapples at 0.1 ppm and for methamidophos at the same level. However, acephate is under Special Review and US EPA has requested more data concerning toxicological aspects of the insecticide.

Trial on fenvalerate were discontinued due to its phytotoxicity effects on other crops grown in USA. The manufacturing company has developed a new formulation called Asana which contains esfenvalerate and does not contain the isomer causing damage to plants.
Based on residue data, IR-4 has submitted a proposal to EPA requesting a tolerance of 0.05 ppm be set for esfenvalerate in pineapple juice. In addition, US EPA has granted an specific exemption under Section 18 of FIFRA for the use of esfenvalerate for gummosis control in pineapples grown in the

Table 1. Maximum residues of acephate and methamidophos resulting from foliar applications of Orthene 75s on pineapple samples collected in Puerto Rico.

Year	Spray X treatment (Kg a.i./ha^{-1})	Pre-harvest interval (days)	Plant Part	Maximum Residues (ppm) Acephate	Methamidophos
1983-1984	2 x 1.68	82	Fruit (w/o crown)	0,06	< 0,01
			Crown	0,03	< 0,01
			Foliage	0,04	< 0,01
			Stump	< 0,01	< 0,01
1984-1985	2 x 1.68	80	Fruit	0,03	< 0,01
			Crown	0,02	< 0,01
			Foliage	< 0,02	< 0,01
			Stump	< 0,01	< 0,01

Table 2. Fenvalerate and esfenvalerate residues resulting from foliar application of Pydrin 2.4 EC and Asana 1.9 EC, respectively, on pineapple samples collected in Puerto Rico.

Pesticide	Year	Spray X Treatment(Kg a.i./ha^{-1})	Pre-harvest interval (days)	Plant Part	Maximum detectable Residue (PPM)
Fenvalerate	1984-1985			Crown	0,06
				Bran	< 0.05
				Pulp	< 0.05
		3 x 0.28	78	Crown	0,06
				Bran	0,05
				Pulp	0,05
Esfenvalerate	1985-1986	0		Crown	0,02
				Bran	0,02
				Fruit	0,01
		4 x 0.056	59	Crown	0,08
				Bran	0,02
				Fruit	0,01

northern part of Puerto Rico. Additional field trials are underway to collect samples of whole fruit with crown removed, juice and bran in order to complete all residue data to obtain a tolerance and a special local need registration for esfenvalerate on pineapples.

C. Persistence of insecticides and potential residues on pineapple fruits

Esfenvalerate is a synthetic pyrethroid, non-systemic, has a low vapor pressure, is stable to sunlight and has low water solubility (about 2 ppb). This insecticide is applied at blooming of the pineapple plant, has a half life of 5 to 10 days, and hence, negligible residues could be expected when fruits are harvested around 70 to 90 days after the last spray treatment.

Acephate is a systemic organophosphorus insecticide which is more soluble in water and has a longer half life (10-15 days) than esfenvalerate. It is expected that residues of acephate and its metabolite methamidophos would be extremely low when mature pineapples are harvested either for the fresh market or pineapple juice and other by-products.

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