

Cypermethrin Residues on *Jambal Roti* Product of Giant Catfish (*Arius thalassinus* Ruppell)

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Abstract: Cypermethrin is synthetic pyrethroid insecticide, having toxic effects and harmful to humans. It is commonly used by farmers to control pests on cotton and vegetables, but now it used by *Jambal Roti*'s producer to depress the damage of the products. The aim of study was to determine the concentration of cypermethrin residues on products of *Jambal Roti* made from Giant Catfish (*Arius thalassinus* Ruppell). Samples of *Jambal Roti* were taken from the small, medium and large-scale producer in Lamongan District, East Java with *Accidental Sampling Technique*. Cypermethrin residues were analyzed using gas chromatography. The results showed that products of *Jambal Roti* on a small scale producer contain cypermethrin of 1.491-2.124 mg/kg, medium scale of 0.298-0.830 mg/kg and large scale processing 0.027-0.257 mg/kg. This concentration is over the maximum residue limits permitted by the SNI (Indonesian National Standard) and the Codex of Alimentarius Commission of 0.05 mg/kg.

Key words: cypermethrin, giant catfish, jambal roti, residues.

Introduction

Pesticide residues are the remaining pesticides in food and affect the food safety and harm the health of human beings. Hardinsyah and Pranadji ^[1] suggest that the era of globalization would affect the systems of food security and safety. Safe food is the consumer demands which will compete in the global market. Hariyadi ^[2] stated that the availability of safe food can minimize the cases occurrence of foodborne disease. It also presses the cost of foodborne disease cases and creates healthier and more productive human beings.

The Law of Republic of Indonesia No. 7 of 1996 about food and No. 38 of 2009 about health arranged the availability of food and the requirement on safe food production for humans and the environment; from production to distribution. It is a main prerequisite to the systems that provides protection for the good health and functioned in increasing the prosperity and welfare of the people.

Cypermethrin is synthetic pyrethroid insecticide and an active material that used in formulation of aerosol insect repellent which have the effects of stomach and contact toxic ^[3]. The chemical structure of cypermethrin contains α -siano-3-fenoksibensil ^[4]. Cypermethrin is heavy liquid, foul-smelling, relatively unevaporate, steady to heat, and soluble in non-polar solvents (acetone, alcohol, xylene, and chloroform), and

have a low solubility in water of 0.009 ppm ^[5]. Cypermethrin residue analyzed and separated by gas chromatography equipped with a DB-5 column and electron capture detector ^[6].

Cypermethrin is generally used to control pests on agricultural activities due to its effectiveness and cheaper price ^[4]. The residue that remains in the product due to inappropriate use of cypermethrin threaten the food safety for consumers ^[5]. Cypermethrin is a poison that attacks the organs and the nervous system. Cypermethrin also inhibits the formation of antibodies against diseases that caused by microbes and suppress the immune system. Based on SNI 7313:2008 ^[7] and Codex Alimentarius Commission ^[8], the maximum limits of residue insecticide made from active cypermethrin on agricultural products of poultry meat is 0.05 mg/kg.

Jambal roti is one of favorite dried salted fish products in Indonesia, especially Java. *Jambal roti* generally made from Giant Catfish (*Arius Thallasinus*) through the process of salting, fermenting and drying. It is called *Jambal Roti* because the texture of the flesh that are easily crushed after being fried like toast with a distinctive flavour ^[9]. The distinctive flavours, soft and compact texture produced by proteolytic reaction which occurs because of the fermentation process. During the fermentation process, fish protein will hydrolyzed into amino acids and peptides, and then the amino acids will break down further into other components that functioned in the formation of the products' taste ^[10]. Cypermethrin used in fishery products to prevent damage due to fly.

Many researches have been conducted on various active materials in pesticide residues on agriculture and husbandry. Some researchers also found pesticide residues in fisheries (Table 1).

Table 1. Research on Pesticide Residues

No.	Object of Research	Researcher
1	Metidation pesticide residues on tomatoes	Atmawidjaja <i>et al.</i> ^[11]
2	Cypermethrin residues in the milk of dairy cows	Sassine <i>et al.</i> ^[12]
3	Pesticide residues of organochlorine (OC) and organophosfat (OP) in fresh milk and feed from some areas in Java	Indraningsih and Sani ^[13]
4	Organochlorine pesticide residues in beef from Bandung	Isnawati and Mutiatikum ^[14]
5	Pesticide residues of organochlorine with active material Gamma BHC, Aldrin and endosulfan in carrots	Sinulingga ^[15]
6	Pesticide residues in the brain tissue of dairy cows in Lembang, West Java	Indraningsih and Sani ^[16]
7	Pesticide residues in cayenne, lettuce, and red onion	Miskiyah and Munarso ^[17]
8	Pesticide residues of cypermethrin and permethrin in cabbage	Loekman <i>et al.</i> ^[18]
9	Organophosfat insecticide residues in vegetable	Harsojo and Chairul ^[19]
10	Residues of dichlorodiphenyltrichloroethane (DDT) and its metabolites on cocoa beans from three ecological zones of cocoa in Nigeria	Paul <i>et al.</i> ^[20]
11	Organochlorine residues on all samples of beef from animal slaughterhouse of Kumasi and Buoho in Ghana	Darko and Acquaaah ^[21]
12	The presence of organochlorine pesticide residues in fish caught in the Oueme Republic of Bénin River	Pazou <i>et al.</i> ^[22]
13	The presence of organochlorine pesticide residues in fish taken from Densu River valley, Ghana	Afful <i>et al.</i> ^[23]

14	The presence of pesticide residues in dried salted fish in traditional market, Makassar	Said ^[24]
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However, research on the presence of cypermethrin residues in fishery products is rarely done, while its presence in the product affect the food safety that cause interference to the humans health. Therefore, we conducted the research about cypermethrin residues on *Jambal Roti* product of Giant Catfish (*Arius thalassinus* Ruppell).

Materials and Methods



Figure 1. *Jambal Roti* of Giant Catfish (*Arius thalassinus* Ruppell)

Jambal Roti of Giant Catfish (*Arius thalassinus* Ruppell) (Fig. 1) were taken from some producer in Lamongan District, East Java. The sampling used *Accidental Sampling* techniques ^[25]. Producer of *Jambal Roti* were categorized into small, medium and large scale producing according to its outcome per month.

Characteristics and nutritional value of *Jambal Roti* were analyzed in the Laboratory of Quality Testing and Food Safety, Faculty of Agricultural Technology, University of Brawijaya. Analysis of pesticide residues used gas chromatography in the Laboratory of Pesticides and Fertilizers Testing, *UPT* (Technical implementation unit) Plant Protection and Horticulture of Surabaya. The assessment refers to the procedures that set by the General Directorate of Food crop production ^[26] through the following stages.

Extraction

Total of 5 g *Jambal Roti* samples were crushed and put into the lid Erlenmeyer to be added by Acetone: Dichloromethane (50:50). The mixture was left for one night for a static extraction process. The crude extract filtered through a funnel with a cotton or glass wool that has been cleaned with a mixture of Petroleum Ether and Acetone (4:1) for eight soxhlet hours. Total of 25 mL organic phase were pipetted into the round flask. It concentrated in *Rotary Evaporator* on the temperature of water bath 40°C, until almost dry, and then dried using nitrogen gas. The residues dissolved in 5 mL of Isooctane and Toluene (90:10) to get the extract.

Purification

Total of 20 mL extract evaporated until almost dry by using *Rotary Evaporator* on the temperature of water bath at 40°C. The residues dissolved in 20 mL n-Hexane that contained 1 g of analytical samples. Glass wool, 5 mL of n-Hexane and 1 g of activated silica gel were added consecutively. The mixture stirred until homogenous. The inner wall of the column was rinsed with 2 mL of n-Hexane, til its meniscus just above the silica gel. A total of 2 mL extract concentrates (equivalent to 1 g analytical samples) putted in the column, and then rinsed with 3 x 1 mL n-Hexane, til its meniscus just above the silica gel. Next, we eluted the mixture with 20 mL of eluent A (a mixture of ethyl acetate and n-Hexane, 0.2:99.8). The first eluate (contained internal standard) was taken for 10 mL and we discarded the eluate residues. Meanwhile, pyrethroids were eluted with 35 mL eluent B (mixture of ethyl acetate and n-Hexane, 10:90) resulting eluate to be collected in round flask and added with 10 mL of first eluate which contained the internal standard, and then evaporated until dry. The residue was dissolved in n-decane to the volume of 1 mL.

Determination

Total of 1-2 μL extract was injected into the gas chromatography with Electron Capture Detector (ECD) equipped with RTX-1 column, 30 m x 0.25 mm. Temperature of injector and detector were set at 280°C, oven temperature at 255°C, carrier gas of Nitrogen flowed 30 ml/min. The content of the tested substance were determined by comparing the width of peak area on the substance component to the area of the standard reference. The amount of residues contained in the sample is formulated as follows ^[26].

$$R = \frac{\frac{A_2}{A_1} \times V_{i1} \times K \times \frac{V}{V_{i2}}}{W}$$

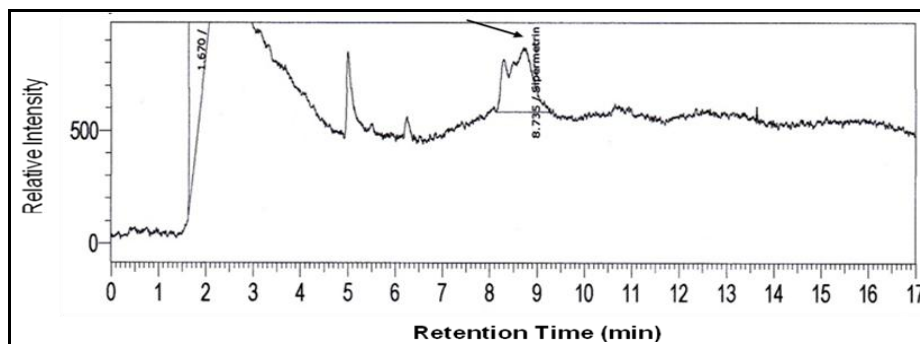
Description :

- R = residues on sample (mg/kg)
 A₂ = sample area
 A₁ = standard area
 V_{i1} = standard injection volume (μl)
 V_{i2} = sample injection volume (μl)
 K = standard solvent concentration (ng/ μl)
 V = last volume of concentration (μl)
 W = weight of sample (g)
 ng/g = 1000 = mg/kg

Results and Discussion

Retention Time

The presence of cypermethrin residues in the sample determined by the specified retention time of standard reference on cypermethrin using the same methods and conditions of tested sample. The retention time of standard cypermethrin is presented in the form of chromatogram (Figure 2).



Description :

→ : retention time of Cypermethrin

Figure 2. Retention Time Chromatogram of Standard Cypermethrin

Gas chromatography result showed that *Jambal Roti* products of Giant Catfish taken from Lamongan District, East Java are positively contained the active material of insecticide residues, i.e. Cypermethrin. It is implied in the retention time of the sample is not much different from the standard cypermethrin (Figure 3). Cypermethrin concentration on product is in the amount of 0.027–2.124 mg/kg. Concentration of Cypermethrin on some samples was above the permitted Maximum Residue Limits based on SNI 7313:2008 ^[7] and Codex Alimentarius Commission ^[8]. The sample's chromatogram demonstrates that the retention time.

Concentration of cypermethrin is different based on their processing scale. Concentration of cypermethrin on small scale processing is 1.491-2.124 mg/kg, while medium scale processing of 0.298-0.830 mg/kg, and large scale processing of 0.027-0.257 mg/kg. Comprehensively, the result indicates that all

producers conduct malpractice using cypermethrin without considering the harms to consumer's health. Purnomo *et al.* [27] suggests that several factors caused the malpractice among the producers and traders of fish and fishery products, i.e. technical, economic, social cultural and institutional factors. The cause were such as follows: unavailability of alternative preservatives materials that are safe, more effective, more practical, and cheap to reduce the cost of production; the lack of socialization in the form of counseling and guidance about the food safety from institutions/related agencies; both of the producers and the consumer were lack of knowledge about food safety; dietary habits did not concerning the food safety for their health; the lack of regulation; lack of law enforcement; and ineffective role of related institution, e.g. YLKI and BPOM. In agriculture and husbandry, Loekman *et al.* [18] found cypermethrin residue of 2.08 mg/kg in cabbage. Chandra *et al.* [28] also found cypermethrin residue 0.002 mg/kg in cauliflower and 0.003-0.012 mg/kg in brinjal. Cypermethrin residue was also found in C4 rice that has been sold in the Gentan market of 0.07 mg/kg and in Rejodani Market of 0.005 mg/kg [29]. Total of 0.001 mg/kg cypermethrin residue was detected on okra leaves and fruits [30] and 0.0989 – 0.2456 mg/kg α -cypermethrin residues were detected in onion [31], while 0.010-0.168 mg/kg found in the milk of a lactating dairy cows [12]. However, these contents are still under the limit of allowed concentration of cypermethrin, i.e. 5 mg/kg.

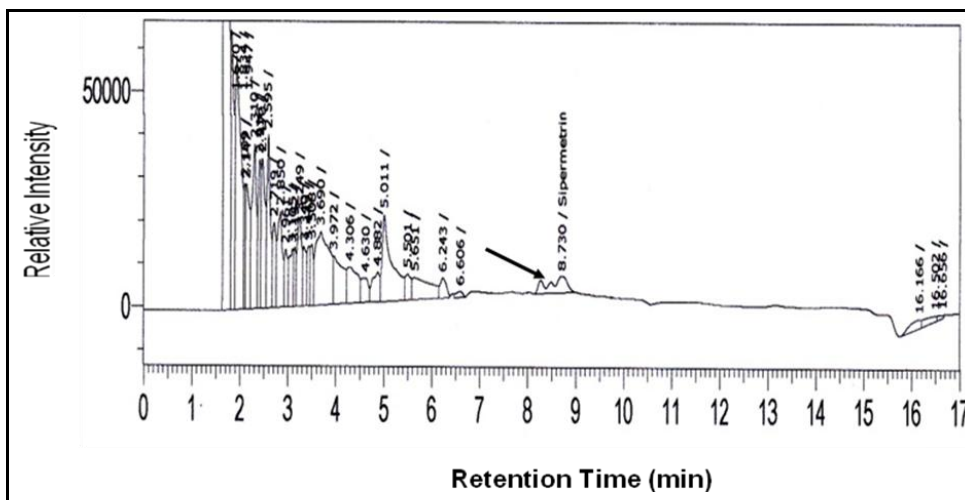


Figure 3. Retention Time Chromatogram of Sample

Description :

→ : retention time of cypermethrin

Cypermethrin Concentration

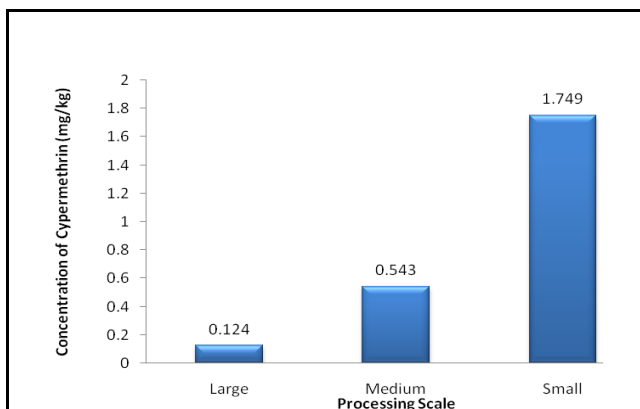


Figure 4. Concentration of Cypermethrin on *Jambal Roti*

The results indicated that the average of cypermethrin concentration on small scale producer is larger than medium and large-scale processing (Fig. 4). The high average of cypermethrin concentration on small scale processing was caused by greater intensity of cypermethrin usage. Product of *Jambal Roti* were taken

from the small scale processing were usually marketed after several times of the production. The existence of waiting period before marketed triggered the great intensity use of cypermethrin. As for medium and large scale, the resulting products are directly marketed every one or two times of the production, thus need less cypermethrin. Application of cypermethrin focused on decreasing product damage due to flies or other insects. Cypermethrin was sprayed on the product or dipping the product within^[33]. Producers also use cypermethrin by dipping the fish into cypermethrin solution before drying. Narwanti *et al.*^[31] suggests that cypermethrin is non-systemic pesticide, broad spectrum of pest control, has insecticidal activity which quickly knocks down the insects. Cypermethrin is very effective as a contact and stomach poison in pest control, targets at relatively low application rate, e.g. flies^[32].

Conclusion

Jambal Roti product of Giant Catfish (*Arius thalassinus* Ruppell) taken from Lamongan District, East Java were positively contained cypermethrin. *Jambal Roti* production on small scale processing contains higher cypermethrin than medium and large scale production. The three concentrations are above the maximum residue limits that permitted by the SNI and the Codex Alimentarius Commission (0.05 mg/kg).

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