ASSESSING THE DISTRIBUTION OF PERMETHRIN RESIDUE IN TREATED CEREAL GRAINS USING COLD SOLVENT EXTRACTION COUPLED WITH UV-VISIBLE SPECTROPHOTOMETRY

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Abstract: The residual levels of permethrin, a pyrethroid insecticide, in two different parts of treated cereal grains have been evaluated. The parts of the grains studied include the husk/bran and the endosperm. In this research, two commonly used fresh grains, millet and corn, were obtained from Dawanau market of Kano State. The fresh grains were spiked with permethrin pesticide commercially known as coopex dust at 10 g sample/33 mg dust. After extraction, detection of the residual level was carried out using UV spectrophotometric analysis at 290 nm. Results indicated higher permethrin residue accumulation in the husk/bran for millet sample with 25.37% recovery as against 17.09% recovered in the endosperm. Similar trend was observed for corn sample with 26.01% and 17.85% recoveries in the husk/bran and the endosperm, respectively.

Keywords: Distribution, extraction, grain, permethrin residue, UV-spectrometry

Introduction

Cereal grains constitute a large part of the global diet and play a significant role in world trade (Richard, 1985). Under suitable conditions of low moisture, these grains can be kept for long period of time without noticeable chemical or biological decay. However during storage, the grains are susceptible to deterioration by insects, rodent and bird pests. Therefore, control of such deteriorating agents has become a challenging issue. One method of controlling grain insect pests is through the application of insecticides used as residual protectants (Sowunmi and Agboola, 1982).

In many developing countries, pesticides are used as a quick and ready answer to the numerous pest problems, which abound in arable and cash crop farming and in the control of endemic and epidemic diseases like malaria, typhoid fever, filariasis, etc. (Atuma, 1985).

Permethrin is a broad spectrum non-systematic pyrethroidinsecticide (Arayne *et al*., 2011) with chemical formula $C_{21}H_{20}Cl_2O_3$ and chemical (IUPAC) name (3-phenoxyphenyl)methyl-3-(2,2–dichloroethenyl)–2,2–dimethylcyclopropanecarboxylate, was registered with the U.S Environmental Protection Agency (EPA) as a grain pest control insecticide and first marketed in 1977. It is a synthetic chemical similar to the natural insecticide pyrethrin which comes from the chrysanthemum plant, but it remains effective for long period of time (Mitchell, 1998).

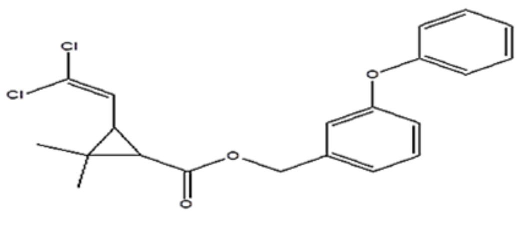

Fig. 1: Structure of Permethrin (Charles and Raymond, 1991)

Permethrin, a synthetic pyrethroid has become very popular and it is the constituent of many household and agricultural insecticidal formulations. It has also been used to impregnate army battle-dress uniforms as insect repellant in the field (Wilfred, 1995). Formulation for impregnation is usually 0.5% aerosol spray, which provides protection against insects for about six washings, or about six weeks of use (Clark and Matsumura, 1982).

Literature on the level of residual permethrin in wheat grains treated at a rate of 0.5-5.0 mg/kg revealed a residue level of 0.36-4.5 mg/kg after 9 months of storage (Halls, 1981). Another study found that residues (10-20% of the amount initially applied) of cyfluthrin, deltamethrin, cypermethrin, fenvalarate and permethrin remain effective for a long period of time in grains (over 10 months), with minimal losses even after milling and baking (Dicke *et al*., 1988).

One effect of treating foodstuffs such as grain with a pesticide must be the probability of residues surviving in the end food product as pesticides often leave some of their residues on food with which they are treated (Sowunmi and Agboola, 1982). High pesticide residues are hazardous to human and animal (Thomas and Lafontine, 1985).

Permethrin has low to moderate toxicity to humans for short-term exposures. Results on human subject suggest that human newborns may be more sensitive to permethrin than adults (Mitchell, 1998). Permethrin acts similarly to the insecticide pyrethrum (from the chrysanthemum plant). Pyrethrum can cause skin or respiratory reactions in people with hay–fever or in people who are sensitive to rag weed and pollen. These reactions may include irritation or inflammation of the skin (contact dermatitis) or sneezing, nasal stuffiness, or asthmatic breathing (Contalamessa, 1997). Although there is no clear evidence that pyrethroids (such as permethrin) cause allergic–type reactions, it is important to recognize this possibility (Wagner, 1994). Exposure to permethrin may occasionally produce numbing, tingling, and burning sensations of the skin. These sensations are reversible and usually go away within 12 hours (FMC, 1995). Permethrin has been found to be highly toxic to fish and bees but it is of low toxicity to birds (WHO, 1990). Different techniques including high performance liquid chromatography and spectrophotometric determination (Kazemipour, 2002; Niazi *et al*., 2008) have been described for the determination of permethrin.

The main significance of the present work is to investigate the portion of grain where storage pesticides may likely accumulate so as to promote public awareness through various media which can reduce the danger of chemical ingestion by the end users.

Materials and Methods

Reagents: All solvents (hexane, methanol and xylene) were of analytical grade supplied by Sigma Aldrich (Madrid, Spain) and used without further purification. High purity deionized water was obtained from a Milli-DI water purification system

(Molsheim, France). Permethrin standard was supplied by Gongoni Nigeria Ltd (Kano, Nigeria).

Instrumental conditions

The absorbance measurements, by UV spectrophotometric analysis of the extracts were carried out at 290 nm using a Unicam UV 1 Spectrophotometer Model NC 9423 UV 1000E equipped with digital display. In this work, 290 nm was chosen because previous work indicated that permethrin absorbs UV radiation strongly in the range of 279 to 290 nm (Kazemipour, 2002).

Sampling and sample admixture

Dried and fresh millet and corn samples were obtained after harvest period, between September and November from Dawanau market, Kano-Nigeria in two different containers. 10 g of the samples were subsequently admixed with 33 mg of commercial coopex dust (permethrin) in the laboratory and stored in an air tight polyethylene bag in a dark wardrobe for 60 days prior to analysis.

Dehulling and extraction

Prior to extraction, the samples de-hulled to separate the husk or bran from the main grain or endosperm using mortar and pestle. The two components were then extracted separately by transferring 2.50 g of each sample into a 100 mL conical flask. 15 mL of methanol was added and the flask placed on a shaker for one hour of continuous shaking. This was allowed to stand for about 3 min and filtered. The flask was then rinsed with 2 mL of methanol; the washing was added on to the filter paper. The washing procedure was repeated with further 2 mL of methanol. The obtained filtrates were then transferred into a 30 mL beaker. All samples were extracted in triplicates. Each extract obtained was evaporated to remove the methanol using a water bath at 55^{o}C. The flask was then cooled and 5 mL of methanol was added to dissolve the residue. The solution obtained was filtered again through a filter paper and the filtrate analysed for permethrin residue.

Results and Discussion

Optimization of extraction solvent

Permethrin has been reported to be soluble in many organic solvents like acetone, ethanol, ether, xylene etc. Therefore three different organic solvents namely methanol, xylene and hexane were tested as extraction solvents. In this case, best extraction efficiency was achieved using methanol as extraction solvent as shown in Fig. 2.

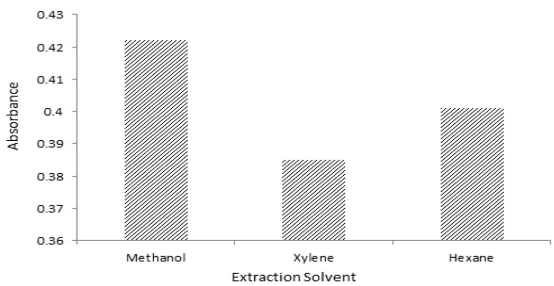

Fig. 2: Effect of extraction solvent on permethrin

Optimization of extraction time

Different extraction times in the range of 20-100 min were examined to configure the time at which equilibrium is reached. Highest extraction efficiency was achieved at 60 min (Fig. 3). There was increase of extraction efficiency from 20 min up to 60 min suggesting continuous mass transfer of the analyte. The efficiency fairly remains constant from 60-100 min and therefore 60 min was chosen as the extraction time.

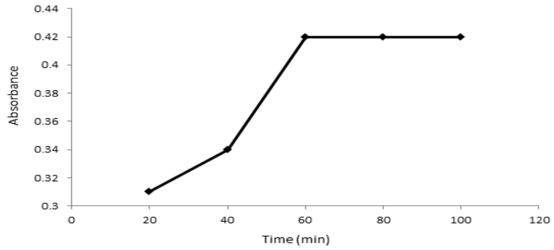

Fig. 3: Effect of extraction time on permethrin)

Scanning of absorption wavelength for permethrin:

In investigating the wavelength of UV/visible radiation at which permethrin gives the highest absorbance, solutions of different concentrations of permethrin in methanol were prepared and their absorbance values measured using UV spectrophotometer. In each case, scanning was carried out against the solvent as blank. All results indicated that permethrin absorbs most at 290 nm.

Distribution of permethrin residue in the components of treated grains

Results from Table 1 show that permethrin residue accumulated more in the husk than the endosperm of grains treated with the pesticide. This could be due to higher exposure or contact time of the pesticide with the outer part of the grain (predominantly the husk). These findings are in agreement with a previous work (Audu and Musa, 2007) in which permethrin residue was found to accumulate in the husk of two grains obtained from Kwasangwami and Aujarawa villages of Kano State.

Table 1: The distribution of permethrin residue in the components of treated grains

Sample	Component	Recovery(%)
Millet	Dehulled millet (endosperm)	17.09
	Husk of millet	25.37
Corn	Dehulled corn (endosperm)	17.85
	Husk of corn (HC)	26.01

Conclusion

The levels of residual permethrinin both treated grains were considerably low in the endosperm compared with what was recorded in the husk of the two grains. Generally permethrin residue accumulates more in the husk or bran of treated grains than in the other parts. Therefore dehulling the grains before consumption will reduce the risk of pesticide ingestion.It is recommended that further work should consider more storage time for the investigation possibly from six months to two years in order to ascertain the stability of the residue.

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