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Determination of Actual Chemical Composition of a Locally Formulated Pesticide Product in a Nigerian Market

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ABSTRACT

A locally formulated pesticide product with a trade name FIACO sold in a Nigerian market was investigated for the actual chemical composition aimed at specifying the number of chemical constituents and the actual active ingredient(s) present in the pesticide product. Gas Chromatography - Mass Spectrometry (GC-MS) technique was used for the analysis. Results indicated that the pesticide product contains nine (9) chemical constituents with percentage compositions as follows: Toluene (5.48%), Cumene (5.88%), 1,2,3-Trimethyl- Benzene (8.99%), Decane (6.09%), Undecane (6.25%), Dichlorvos (50.96%), Dodecane (8.02%), 11, 12-Dibromo- tetradecan-1-ol acetate (3.2%) and Pentadecane (5.13). Results equally pointed out that one of the identified components named Dichlorvos is a pesticide active ingredient which confirms its presence in the product. The identities of the chemical constituents in the product were revealed by mass spectra data. Therefore, it is a matter of public health significance and environmental sustainability to frequently monitor labeled and unlabeled pesticide products sold in the Nigerian markets in order to ascertain their true chemical composition.

Keywords: *locally formulated, chemical composition, pesticide, GC-MS, environmental sustainability.*

1. INTRODUCTION

In nature, there seems to be no pest(s). Humans label as "pests" any plants or animals that endanger food supply, health, or comfort. To manage these pests we have "pesticides" (Benbrook, 1991). The biological activity of a pesticide be it chemical or biological in nature, is determined by its active ingredient (AI - also called the *active substance*). Pesticide products very rarely consist of pure technical material. The AI is usually formulated with other materials and this is the product as sold, but it may be further diluted in use. Formulation improves the properties of a chemical for handling, storage, application and may substantially influence effectiveness and safety (Burges, 1998). Pesticides are substances or mixture of substances intended for preventing, destroying, repelling or mitigating any pest (US-EPA, 2007). A more elaborate definition of pesticide by Food and Agriculture Organization (FAO) is- "any substance or mixture of substances intended for preventing, destroying or controlling any pest, including vectors of human or animal disease, unwanted species of plants or animals causing harm during or otherwise interfering with the production, processing, storage, transport or marketing of food, agricultural commodities, wood and wood products or animal feedstuffs, or substances which may be administered to animals for the control of insects, arachnids or other pests in or on their bodies. The term includes substances intended for use as a plant growth regulator, defoliant, desiccant or agent for thinning fruit or preventing the premature fall of fruit. Also used as substances applied to crops either before or after harvest to protect the commodity from deterioration during storage and transport (FAO, 2010)."

They include herbicides, insecticides, rodenticides, fungicides, molluscides, nematicides, avicides, repellants and attractants used in agriculture, public health, horticulture, food storage or a chemical substance used for a similar purpose (NAFDAC, 1996).

Most people eat food grown in a system that uses pesticides and many individuals use pesticides in the house or garden. In places where there are insects whose bites can be a nuisance or a hazard, insecticides are used to make life safer or more comfortable. Yet there is little acknowledgement of the important beneficial role that pesticides play in world agriculture, or in parts of the world where flies and other arthropod vectors spread dreadful diseases (WHO, 2004).

For all pesticides to be effective against the pests they are intended to control, they must be biologically active, or toxic. Because pesticides are toxic, they are also potentially hazardous to humans, animals, other organisms, and the environment. Pesticides are distributed in the environment by physical processes such as sedimentation, adsorption, and volatilization. They can then be degraded by chemical and/ or biological processes. Chemical processes generally occur in water or the atmosphere and follow one of four reactions: oxidation, reduction, hydrolysis, and photolysis. Biological mechanisms in soil and living organisms utilize oxidation, reduction, hydrolysis and conjugation to degrade chemicals. The process of degradation will largely be governed by the

compartment (water, soil, atmosphere, biota) in which the pesticide is distributed, and this distribution is governed by the physical processes already mentioned (Clark, 1994).

The four main groups of pesticides such as the organochlorine, organophosphate, carbamate, and pyrethroid insecticides (Smith, 2002; Ahmed, *et. al*; 2000) are of particular concern because of their toxicity and persistence in the environment; however several of the banned pesticides are still used on a large scale in developing countries and continue to pose severe health and environmental problems. Farmers in developing regions seem to treat pesticides as substitutes for fertilizers and there is a need to create awareness among the farmers on Integrated Pest Management (Sanzidur, 2003). Pesticide toxicity can result from ingestion, inhalation or dermal absorption. Therefore, people who use pesticides or regularly come in contact with them must understand the relative toxicity, potential health effects, and preventative measures to reduce exposure to the products they use (Eric, 2009).
Some locally made pesticides had caused the death of so many Nigerian families in recent times (Olebunne, 2009) and worldwide (USEPA, 2007), specifically through food contamination (Akunyili, 2007). Children are especially prone to accidental poisoning of this product (Okeniyi, *et. al*; 2007). Also most pesticide preparations include carriers' substances in addition to the active ingredients and also solvents and compounds that improve absorption, etc. these "inert ingredients" are not usually included in any discussion of the effects on health although they frequently comprise a large part of a commercial pesticides product, and their adverse effects may exceed those of the active ingredients without being mentioned on the product label.

Local pesticide makers in Nigeria emphasized the potency of their pesticides by the word "*Ota-piapia"* indicating that such products will completely take care of our little pest problem (Mortui, 2006). Its acceptance and wide spread proliferation in Nigeria have been due solely to its cheap production, efficacy, accessibility and affordability (Essiet, *et. al*; 2009). The product is still not registered with NAFDAC (Akunyili, 2007), but have been commonly used as insecticide, especially for mosquitoes (Foll et al, 1965), food storage, such as grains and preventing insect infestation (FAO, 2001). This is the trend of application in Nigeria. The local formulation of *Ota-piapia* is thought to entails repackaging into a small (about 10 - 15 mL) retail bottle of an active ingredient which is unspecified pesticides from those imported, which include cypermethrin, *dichlorvos*, gammalin 20, gammalin super, lindane, capsitox 20 (PAN, 2007). Some may contain homemade cocktail of kerosene, oil, alcohol and any suitable solvent with the pesticide.

Therefore, there is need to analyze locally formulated pesticide products both labeled and unlabelled in a Nigeria market to determine their actual chemical constituents.

2. MATERIALS AND METHODS

2.1 Equipment

Gas Chromatography – Mass Spectrometry Machine, GC – MS QP2010 PLUS SHIMADZU, JAPAN.

2.2 Samples and Reagents

A pesticide product was purchased from Eke-Awka local market of Anambra State, Nigeria. The choice of the brand was based on the highest consumption among those available in the market. All reagents, chemicals and solvents such as n-hexane used were purchased from Bridge Head Market Onitsha, Anambra State, Nigeria.

2.3 Sample Preparation

Approximately 0.5ml of the product was dissolved in a proper amount of n-hexane which was made up to 100mL in a volumetric flask at room temperature to obtain a clear solution resulting to a stock concentration of 0.5ml/100mL (5mg/L or 0.5% v/v). Pesticide product solution obtained was transferred into 5 ml glass vial and was taken to Zaria, Kaduna State, Nigeria for Gas Chromatography – Mass Spectroscopy (GC-MS) analysis.

2.4 Gas Chromatography Mass Spectrometric (Gc–Ms) Analysis Of Samples (Instrumentation)

This is a two technique method that is combined to form a single method of analyzing mixtures of compounds. It is used in determination of molecular masses of the sample mixture and their fragmentation patterns. The machine used is a GC-MS QP2010 PLUS SHIMADZU, JAPAN.

3. RESULT AND DISCUSION

Figure 3.1 shows that there are nine (9) peaks which represent nine (9) components present in the product (FIACO). Each component has its own mass spectrum and their respective matched spectrum and mass profile of a known compound recommended by GC – MS Library for component identification.

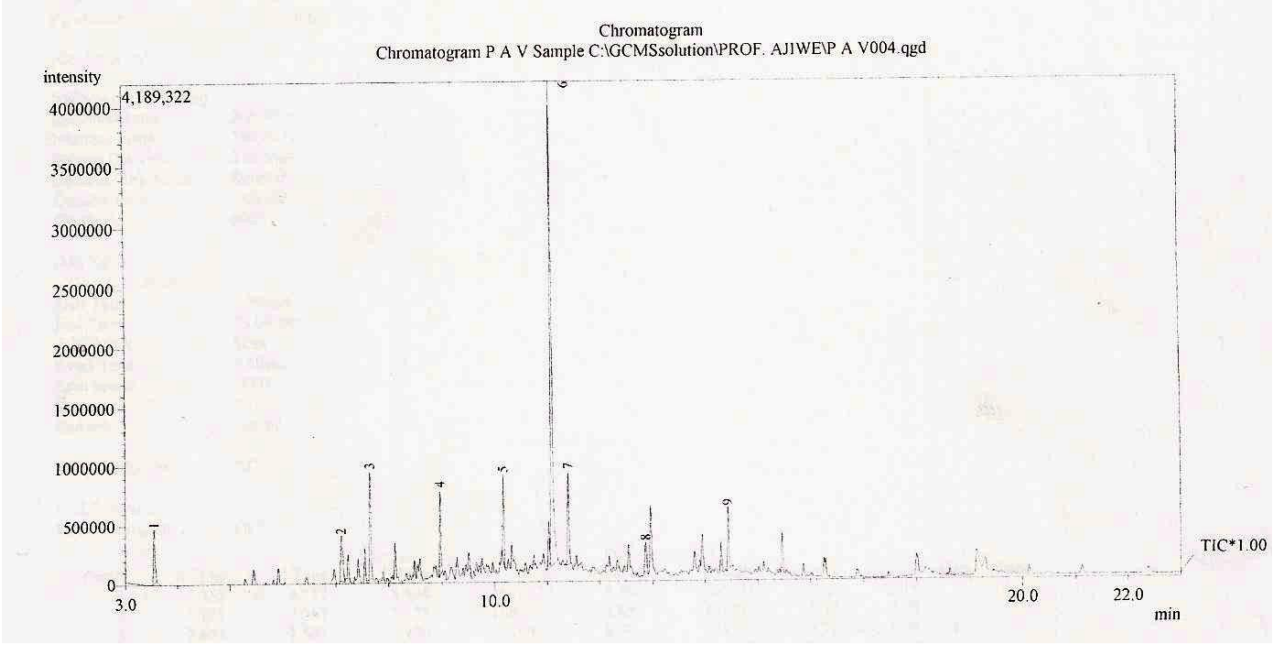
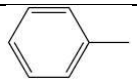
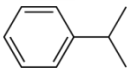
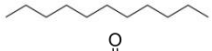
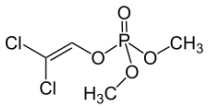
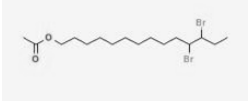
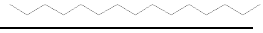


Figure 3.1: Gas Chromatograph of the product (FIACO)

Table 3.1 shows the observed retention time and percentage area of each component in the product (FIACO) for determining the amount of each identified component and also it includes molecular formula, compound name and the molecular structure of each component identified from Gas Chromatography – Mass Spectrometry (GC-MS) Analysis. The Gas Chromatography – Mass Spectrometry (GC-MS) Analysis of this pesticide product reveals that there are many chemical constituents and pesticide active ingredient is present in the sample.

The product is labeled with a trade name FIACO but there is no pesticide active ingredient on the product label which means that the product is not registered with National Agency for Food and Drug Administration and Control (NAFDAC). This is because the label on the product does not indicate active ingredient (chemical component) and his concentration, storage conditions, NAFDAC registration number, risk, disposal, use et c. Even though the product label does not suggest Dichlorvos as the active ingredient in the product, the 50.96% Dichlorvos suggests so.

Table 3.1: Identified Compounds in the product (FIACO)

Peak No	RT Time	Area %	Formula	Compound Name	Molecular Structure
1	3.555	5.48	C_7H_8	Toluene	
2	7.111	5.88	C_9H_{12}	(1-methylethyl)-Benzene(Cumene)	
3	7.653	8.99	C_9H_{12}	1,2,3-Trimethyl- Benzene	
4	8.975	6.09	$C_{10}H_{22}$	Decane	
5	10.172	6.25	$C_{11}H_{24}$	Undecane	
6	11.085	50.96	$C_4H_7Cl_2O_4P$	Dichlorvos	
7	11.399	8.02	$C_{12}H_{26}$	Dodecane	
8	12.868	3.20	$C_{16}H_{30}Br_2O_2$	11, 12-Dibromo-tetradecan-1-ol acetate	
9	14.438	50.2	$C_{15}H_{32}$	Pentadecane	

Eighty percent (80%) of the compounds identified are aliphatic and aromatic hydrocarbons which are main constituents of Kerosene Oil ($C_{10}H_{22}$-$C_{12}H_{26}$) and Fuel oil $C_{13}H_{28}$-$C_{15}H_{22}$) and when present in the environment at a substantial amount has no or little environmental impact. These chemicals are not likely to persist in the environment, as they will largely partition to the air where they will degrade via photo-oxidation. Half-lives in air (during daytime) are calculated to be 9.2 hours for n-decane, 10.2 for n-undecane, and 11.5 hours for n-dodecane (VCCEP, 2004). As these chemicals have shown ability to biodegrade, the small portion that partitions to soil or sediment should not persist. Being insoluble in water and less dense than water, any releases to water of these n-alkanes should separate and volatilize to the air

4. CONCLUSION

The analysis has demonstrated the presence of many other compounds that are not pesticide active ingredients in the analyzed product and research has shown that the constituents identified alongside with the active ingredient has no or little environmental impact at substantial amount. The product is not registered with NAFDAC even though the pesticide active ingredients identified from the analysis is not a banned or restricted pesticide as listed in Nigeria NESREA regulations of National Environmental (Sanitation and waste control) regulations of 2009 and such unregistered product should not be allowed in our market since its chemical constituents is unknown.

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