RESIDUAL ANALYSIS OF SOME ORGANIC INSECTICIDES.

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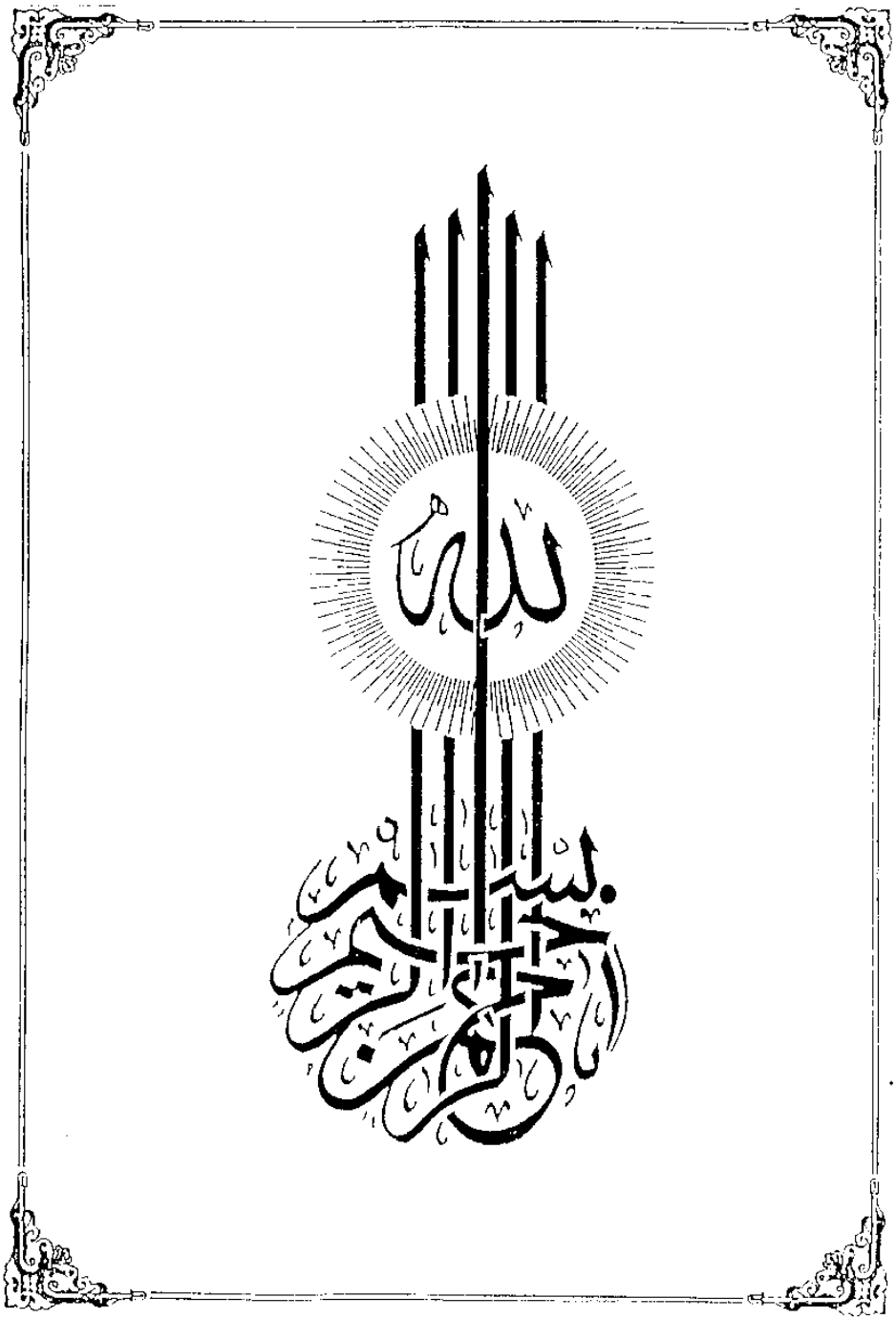

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INTRODUCTION

As plants are the vital source of food to man, it was of utmost importance to protect such resources from the attack of pests. Since chemical control of pests is so successful, there has been an explosive expansion in the development of synthetic organic insecticides. The most widely used insecticides, the chlorinated hydrocarbons were generally prefered in the past because they have long residual effect. However, some of these compounds such as DDT and Dieldrine persist amazingly long in soils, water, plants, and animal bodies[1-7]. On the contrary, organophosphorus, and carbamate insecticides are generally unstable, and short-life in the environment as well as biological systems. They are commonly degraded into nontoxic and water soluble metabolites. The rapid decomposition of these compounds and their transformed metabolites has led to their disappearance from the ecosystem.

Also, the introduction of granular formulation of insecticides has opened up new possibilities of application for the control of various pests. Granular systemic insecticides also help and contribute in minimizing toxic hazards to mammals and birds during treatment[8]. When the product is applied to the growing plant the prim objective should be to obtain data on the residue remaining in or on the crops at the time of harvest. If significant residues are expected at harvest time it will be necessary to obtain information on

the effect of storage and processing on the residue subsequent to harvesting, as this will provide a basis for ascertaining the likely in take by consumers. However, the presence of such residues within the crops, in the water, or in the soil is a source of undesired and serious pollution in the environment.

Synthetic pyrethroids are recently introduced in the Egyptian market (Firstly at 1978). This novel group of insecticides is possessed an excellent efficient and performance against a wide range of pests infesting field crops and vegetables.

Synthetic as well as natural pyrethroids are non-polar compounds and have very small solubility in water. Although they have no systemic or translaminar properties; unlike the organochlorine compounds, they are unstable and non- persistent. New pyrethroids combine the most valuable properties as agricultural insecticides. The insecticidal activity of pyrethroids is up to four or five times higher than that of the other classes to most insect species. Relative safety as insect by the ratio of toxicatur to rat and insect prove the superiority of pyrethroids. They are both very active against insects and relatively non-toxic to mammales. Pyrethroids play an increasingly important role in insect control in agriculture, public health and veterinary fields.

As an insecticide residues usually occur in very low concentration, a delicate and accurate methods of extraction, clean-up, identification, and determination are of utmost importance. These four main steps in residue analysis were extensively studied during the course of the present investigation. The aim was to find out satisfactory and reproducible methodology for each of the tested compounds.

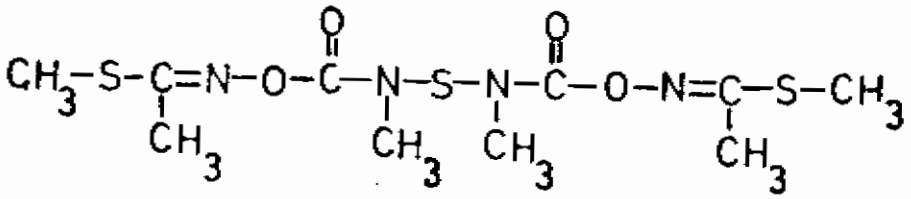
Many attempts were carried out in order to find out suitable conditions for thin-layer chromatography and ultraviolet spectrophotometry detection of insecticide residues as well as their transformed products in the contaminated samples. Recovery of the fortified samples was done with water, soil, and plants under laboratory conditions. The fate of the considered insecticides i.e. THIODICARB " Carbamate " ; PYRIDAPHENIHION " Organophosphorus ", and FLUCYTHRINATE "Synthetic pyrethroids" in the above mentioned media was investigated.

COMPOUNDS STUDIED

1- THIODICARB :

- Larvin, UC 51762.

Dimethyl N N̄ [thiobis [(methylimino) Carbonyloxy]] bis [ethanoimidothioate] .



White to light tan crystalline powder, melting point at 173 - 174°C.; vapor pressure, 4.3×10^{-5} mm Hg at 20°C. Solubilities at 25°C. "weight %": acetone (0.8), dichloromethane (11.1), methanol (1.0), xylene (0.3), water (35 ppm).

Toxicity :

Acute oral LD50 rat (H2O), 66 mg/kg.

acute dermal LD50 rabbit > 2000 mg/kg.

Use :

Broad-spectrum control of insects in many vegetables, soybeans, cotton, and other field crops, certain fruit crops, and ornamentals.

2 - **PYRIDAPHENTHION** :

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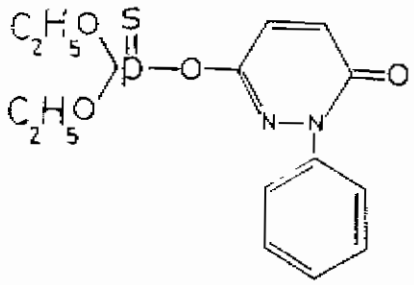
O, O-Diethyl-O-(3-oxy-2-phenyl-2H- pyridazin-6-yl) phosphorothioate.



Yellow crystalline powder melting at 25-56 ^{o}C. ; insoluble in water, soluble in most organic solvents.

Toxicity :

Acute oral LD50 (rat), 850 mg/kg;
dermal LD50 (rat), 2100 mg/kg.

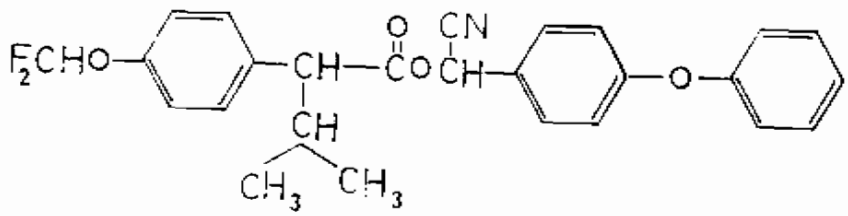
Use :

For controlling shewing and sucking insects on rice, orchard fruits, vegetables, cereals. Also, fly and mosquito control on farms and in public health programs.

3 - **FLUCYTHRINATE :**

Cybolt, OMS 2007 (WHO); Al_3-29391 (USDA); AC222, 705; C1222, 205.

(RS) -∝-cyano-m-phenoxybenzyl (S)-2- [P-(difluoromethoxy) - phenyl] -3-methylbuterate.



Viscous, dark amber liquid, boiling point at 108 °C. at 0.35 mm Hg.

Solubility in water 6 ppm at 21 °C.

Soluble in organic solvents, such as acetone, xylene, and 2-propanol.

Toxicity :

Acute oral LD50 for rat 347 mg/kg (male) and 260 mg/kg (female). For rabbit, dermal LD50>2022 mg/kg.

Use :

Used for control of insects in cotton and a wide range of other crops.

PART II

THE ANALYTICAL PART :

* Thin-layer Chromatography

* Ultraviolet Absorption Spectrophotometry

THIN-LAYER CHROMATOGRAPHY

Thin-layer chromatography is an efficient technique for the analysis of insecticides.[9-27] It may be used as a screening procedure followed by confirmation and quantitation using gas chromatography[27-50] or ultraviolet spectrophotometry[51-57]. Extraction, clean-up, and concentration steps normally preceed thin-layer chromatography.

Careful reviewing of the literature revealed that the use of thin-layer chromatography as a technique for the residue analysis of the studied insecticides is lacked, this may be attributed to the fact that these insecticides are recently introduced in the market . Thus, the behavior of these studied insecticides on chromatoplates covered with different types of adsorbents and by using different solvent systems was investigated in details to reach sample and rapid method for residues analysis of these insecticides.

EXPERIMENTAL

A - **Insecticide Studies :**

1- THIODICARB.

2- PYRIDAPHENTHION.

3- FLUCYTHRINATE.

B - **Adsorbents :**

10 x 20 cm glass plates coated with :

1- Silica gel G "type 60".

2- Aluminium oxide incorporating 15% calcium sulfate.

C - Solvents :

On Silica gel G.

Hexane.

Chloroform.

Diethylether.

Acetone.

Hexane: Chloroform (1:1).

Hexane: Diethylether (7:3).

Hexane: Diethylether (65:35).

Hexane: Acetone (4:1).

Hexane : Acetone (7:3).

On Aluminium Oxide :

Hexane.

Chloroform.

Diethylether.

Ethylacetate.

Hexane: Chloroform (1:4).

Hexane : Diethylether (7:3).

Hexane: Ethylacetate (9:1).

Hexane: Acetone (9:1).

D - Spot Location :

One percent iodine solution in methanol was used to detect separated spots.

RESULTS AND DISCUSSION

Data concerning the Rf "relative flow" values of the separated parent insecticides on the two selected adsorbents "silica gel G and aluminium oxide" and different solvents are tabulated in Tables (1 and 2). The solvent selection was made up of a "back-ground solvent" hexane and an eluting component which increase solvent polarity. Data obtained proved the increase in Rf values by increasing the polarity of the used solvent system. Chromatograms indicated the suitability of the solvent systems; chloroform; hexane: acetone (4:1); hexane: diethylether (7:3) and hexane: chloroform (1:1) in resolution of the three studied insecticides on silica gel G. The best resolution of the same compounds on aluminium oxide was achieved by using the solvent systems of hexane: acetone (9:1); hexane: diethylether (7:3) and hexane: chloroform (1:4), respectively. Table (2).