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Families of Common Synthetic Agrochemicals Designed to Target Insect Pests or Vectors in Landscapes and Households

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Abstract The global usage of agrochemicals is expanding in scale and intensity, thus, objective of completing this article is to know the properties of chemical families used to manage insect pests and vectors concerning health and environmental risks. Insecticides are grouped into families according to chemical structure and knowing about the chemical family allows an applicator to make or inform choices on protective option. Organochlorines or chlorinated hydrocarbons represent one of the first groups of pesticides synthesized; all targets the nervous system, and the properties of persistence and bioaccumulation leads eventually to the withdrawal of registration and use of organochlorine insecticides. Organophosphates act by inhibiting the cholinesterase enzyme that is enzyme used in nerve function. A number of insecticides in this family are used to control a wide range of landscape insect pests and these products tend to have a short persistence in the soil. The carbamate group includes insecticides, most of which have a short persistence in the environment. Like organophosphates, carbamate insecticides inhibit cholinesterase and have moderate to high toxicity. Pyrethroids are synthetically produced molecules that are chemically similar to pyrethrins and are not persistent. At rates applied for insect's control, they break down quickly in sunlight and are rarely present after just a few days. Recently, due to various problems like insect pests resistance in existing insecticides, some new insecticides have been developed like neonicotinoids, fermentation products, avermectins, spinosad, pyrroles and phenyl-pyrazole shaving novel mode of actions. Novel chemistry insecticides are also able to give higher productivity, sustainability, safety, biodegradability and phytosanitary measures, and require in very little amount, have very less residue problem, target specific pest and cause no harm to non-target organisms. The type of surface, training, equipment, runoff, drift, habits of the pest and safety are all considered when a manufacturer designs an insecticide formulation.

Keywords Insecticide, Organochlorine, Organophosphat, Pyrethroid, Carbamate

1. Introduction

There are some 10,000 species of organisms and of them more than 1 million species of insects are crop-eating, and of these, approximately 700 species worldwide cause most of the damage to man's crops, in the field and in storage. Insecticides are manmade agents of chemical origin that control insect pests. Pest control may result from killing the insect or otherwise preventing it from engaging in behaviors deemed destructive, or may be all materials that are used to prevent, destroy, repel, attract or reduce harmful organisms. Insecticides are designed to control insects, and acaracides control ticks and mites. In public health applications they are most commonly used to control mosquitoes, flies, ticks, mites, lice and fleas. Since insecticides and acaracides are often the same pesticides, they are not discussed separately here. Insecticides can be grouped in a number of ways; by mode of action, by target pest or by chemical family. Insecticides are often complex chemical formulations and they are built around a number of core chemical structures or building blocks. Chemists have grouped these core structures into chemical families andInsecticides in the same chemical family often have similar properties (e.g., poisoning symptoms, persistence in the environment). Knowing the chemical family provides an idea of the health and environmental risks. This helps to make sound decisions and choose the least hazardous insecticide. Knowing the family also helps to choose the proper personal protective equipment and identify safeguards needed to protect the environment [1-3].

Insecticides in the same family are likely to control pests in anequivalent way. Repeated use of insecticides that control pests in the same way increases the risk of pesticide resistance. For example, repeated use of an insecticide in one chemical family can speed insect resistance to other insecticides in the same family. Using pesticides from more than one chemical family reduces risk of pesticide's resistance development and this extends the useful life of each product. When insecticides are used in an Integrated Pest Management (IPM) program, care is taken to alternate pesticides of different chemical families. Insecticide applicators must know to which chemical family a given pesticide belongs to. Synthetic insecticides are manufactured in a laboratory and marketed or sold by a chemical company. Insecticides can be grouped in a number of different ways based on their active ingredients and how they work such as synthetic pesticides, organic pesticides, inorganic pesticides and biorational. Synthetic pesticides are further grouped into comparable chemical classes such as organochlorines, organophosphates, pyrethroids, and carbamates. Synthetic insecticides have been widely used since the end of World War II. During the last 60 years new synthetic insecticides have become more pest specific, exhibit lower toxicity and are less environmentally damaging. While synthetic insecticides have contributed to an abundant and cheap food supply they still present a certain amount of risk to human and environmental health [4-6].

Natural toxins are a source of new chemical classes of pesticides, as well as environmentally and toxicologically safer molecules than many of the currently used pesticides. Furthermore, they often have molecular target sites that are not exploited by currently marketed pesticides. There are highly successful products based on natural compounds in the major pesticide classes [7-9]. Therefore, this article looks at how a number of chemical families of insecticides are used in the landscapes and households.

2. Classification of Insecticide Families by Chemistry

Insecticides are commonly classified by their chemical basis, so, the following classification is manly recognized:-

2.1. Older Insecticides

Old insecticides and products are mainly pre 1995 era, and can pose a risk to people, pets and the environment for many years. While these synthetic insecticides have contributed to an abundant and cheap food supply they still present a certain amount of risk to human and ecological health.

2.1.1.Organochlorines or Chlorinated Hydrocarbons

The organochlorines are insecticides that contain carbon (therefore known as organo), hydrogen and chlorine. They are also known by other names such as chlorinated hydrocarbons, chlorinated organics, chlorinated insecticides and chlorinated synthetics. The organochlorines are now primarily of historic interest, since few of these survive in today's arsenal. Organochlorines represent the one of the first group of pesticides synthesized, and include the well-known first synthetic organochlorine insecticide, dichlorodiphenyl-trichloroethane (DDT) discovered, which remained very effective and used extensively to control head and body lice, human disease vectors and agricultural pests. Then Benzene hexachloride (BHC) and chlordane have been discovered, and toxaphene and heptachlor originated slightly later on. Shortly thereafter, two cyclodiene organochlorines, aldrin and dieldrin, have been introduced, followed by endrin, endosulfan and isobenzan. All these insecticides act by blocking an insect's nervous system, causing malfunction, tremors and finally death. All organochlorines are relatively insoluble, persist in soils and aquatic sediments, can bio-concentrate in the tissues of invertebrates and vertebrates from their food, move up in trophic chains and affect top predators. These properties of persistence and bioaccumulation led eventually to the withdrawal of registration and use of organochlorine insecticides, in industrialized nations, although they continued to be used in developing countries. Few of these are still used legally for vector control in some areas of the world particularly where malaria occurs. Most of other organochlorines used for arthropods control, including chlordane, dieldrin and lindane, have met similar fates. Because these insecticides persist in the environment and increase in the fatty tissues of animals, so, many insect populations have developed resistance to these insecticides. The oldest classification of the organochlorines is theinsecticides groups Diphenyl Aliphatics, Hexchlorocyclohexane, Cyclodienes and Polychloro terpenes [10-11].

2.1.2.Organophosphates

Organophosphateis the term that includes all insecticides containing phosphorus. Other names used, but no longer in vogue, areorganic phosphates, phosphorus insecticides, nerve gas relatives andphosphoric acid esters.All organophosphates are derived from one of the phosphorus acids, and as a class are generally the most toxic of all insecticides to vertebrates. Because of the similarity of these chemical structures to the nerve gases, their modes of action are also similar. Initially, their insecticidal discovery is made in search of substitutes for nicotine, which is heavily used as an insecticide but in short supply. The organophosphate*s* have two distinctive features i.e., they are generally more toxic to vertebrates than other classes of insecticides, and most are chemically unstable or non-persistent. It is this latter characteristic that brought them into agricultural use as substitutes for the persistent organochlorines. Because of the relatively high toxicity of the organophosphate, many of these have been voluntarily canceled and others lost their uses. Although a few organophosphate formulations remain available for vector control, their use has dramatically decreased because of resistance to them, the potential for non-target effects and the development of alternative products. Thus, those developed as insecticides, such as tetraethyl pyrophosphate and parathion, have high mammalian toxicities [12-13].

The organophosphates work by inhibiting certain important enzymes of the nervous system, namely cholinesterase. The enzyme is said to be phosphorylated when it becomes attached to the phosphorous moiety of the insecticide, a binding that is irreversible. This inhibition results in the accumulation of acetylcholine at the neuron/ neuron and neuron/ muscle (neuromuscular) junctions or synapses, causing rapid twitching of voluntary muscles and finally paralysis. In insects, as in mammals, these act by inhibiting the enzyme cholinesterase that breaks down the neurotransmitter acetylcholine at the nerve synapse, blocking impulses and causing hyperactivity and tetanic paralysis of the insect, and then death. Some are systemic in plants and animals, but most are not persistent and do not bio-accumulate in animals or have significant environmental impacts. They are generally more toxic to vertebrates than the chlorinated hydrocarbons, but they tend to be less persistent in the environment. All members of this group contain phosphorous in their molecules having varying combinations of oxygen, carbon, sulfur and nitrogen attached, resulting in six different subclasses i.e., phosphates, phospho-nates, phosphorothioates, phosphorodithioates, phosphorothiolates and phosphoramidates. These subclasses are easily identified by their chemical names. These are generally divided into three groups i.e., aliphatic, phenyl and heterocyclic derivatives. Products currently labeled for vector control include naled, malathion and some formulations of dursban. Organophosphates are considered by most people to pose a greater human health risk for pesticide applicators than other families of pesticides. Common examples include phorate, diazinon and dimethoate. The scores of other organophosphates including demeton, methyl schradan, phorate, diazinon, disulfoton, trichlorophon, chlorpyrifos and mevinphos have been registered [14-15].

2.1.3. Carbamates

The carbamate insecticides are chemically similar in structure to organophosphates, but derivatives of carbamic acid (as the organophosphate*s* are derivatives of phosphoric acid). Like organophosphates, their mode of action is that of inhibiting the vital enzyme cholinesterase and these behave in almost identical manner in biological systems, but with two main differences. Some carbamates are potent inhibitors of aliesterase (miscellaneous aliphatic esterases whose exact functions are not known), and their selectivity is sometimes more pronounced against the cholinesterase of different species. Secondly, the cholinesterase inhibition by carbamates is reversible. When cholinesterase is inhibited by a carbamate, it is said to be carbamylated, as when an organophosphate results in the enzyme is being phosphorylated. In insects, the effects of organophosphates and carbamates are primarily those of poisoning of the central nervous system, since the insect neuromuscular junction is not cholinergic, as in mammals. The only cholinergic synapses known in insects are in the central nervous system. The chemical neuromuscular junction transmitter in insects is thought to be glutamic acid. The oldest groups of the carbamate insecticides are Formamidines, Dinitrophenols and Organotins. Carbaryl, the first carbamate insecticide, acts on nervous transmissions in insects and also through effects on cholinesterase by blocking acetylcholine receptors. Other carbamate insecticides include aldicarb, methiocarb, methomyl, carbofuran, bendiocarb and oxamyl. In general, they are broad-spectrum insecticides, of moderate toxicity and persistence, they rarely bio-accumulate or cause major environmental impacts. Insecticides in this group used for vector control are carbaryl for dusting rodent burrows to control fleas, propoxur for use against insect pests, and certain brands of bee and wasp control sprays. Carbamates also pose a relatively high risk for human poisoning and most have a short persistence in the environment. Carbamates have been initially used against insects that developed resistance to chlorinated hydrocarbons and organophosphates. However, some pest insects have now developed resistance to these carbamates [16-18].

2.1.4. Pyrethroids

Pyrethroids are synthetically produced molecules that are chemically similar to pyrethrins. Pyrethrum is a natural organic insecticide that is derived from plants in the genus Chrysanthemum.There are about 30 species in the genus, most of which use the generic name as their common name. The insecticide is produced by grinding of the flowers, thus releasing the active components of the insecticide called pyrethrins. The main active constituents are pyrethrin I and pyrethrin II plus smaller amounts of the related cinerins and jasmolins. Insecticides containing pyrethrins are neurotoxic to nearly all insects. They are harmful to fish, but are far less toxic to mammals and birds than many synthetic insecticides, and non-persistent or breaking down easily on exposure to light. They are considered to be amongst the safest insecticides for use around foodstuffs. Pyrethrins and pyrethroids are now among the most common public health pesticides used, especially for the control of adult mosquitoes. Their use now far outstrips that of conventional synthetic pesticides such as organochlorines, organophosphates and carbamate. Pyrethrin containing insecticides are used widely for vectors control. They are broadly labeled, and can be used in both rural and urban areas in a variety of habitats. Pyrethrins are usually mixed with piperonylbutoxide, which act as a synergist. Synergists are materials that are not necessarily pesticidal by themselves, but have the effect of increasing the toxicity of insecticides with which they are mixed. Without piperonylbutoxide, insects treated with the same dose of pyrethrins would be knocked down, but would eventually recover. Pyrethrins are highly toxic to fish and their direct application to water is restricted [19-20].

Synthetic pyrethroid insecticides are with structures based on the natural compound pyrethrum and chemists have made these compounds more stable and more persistent than natural pyrethrum. A synergist, like piperonylbutoxide, is usually added to the synthetic pyrethroid to further increase its effectiveness. One characteristic of using synthetic pyrethroids is that insects become more excited and active. This impacts their use for structural pests such as brown recluse spiders and cockroaches. Mostly, the mode of action of pyrethroids is the same as that of pyrethrins. Several generations of pyrethroids have been produced, with the latest formulations being effective at extremely small doses. Some of these new compounds may not break down as readily as do pyrethrins, and in some cases pyrethroid synergists may not markedly improve their effectiveness. Pyrethroids are not persistent, at rates applied for vector control; they break down quickly in sunlight, and are rarely present after just a few days. Like the botanical pyrethrum, synthetic pyrethroids have fast knockdown activity against flying insects and low mammalian toxicity. Pyrethroids are very toxic against fish so precautions must be taken to cover fish tanks and disconnect filters, at the very least. Exposure to synthetic pyrethroids may trigger asthmatic attacks in persons who have respiratory problems. They have very low mammalian toxicities and potent insecticidal action, are photostable with low volatilities and persistence. They are broad-spectrum insecticides and may kill some natural enemies of pests. They do not bio-accumulate and have few effects on mammals, but are very toxic to aquatic invertebrates and fish. There may be limit in their uses in sensitive areas; however, tetramethrin, resmethrin, fenvalerate, permethrin, lambda-cyalothrin and deltamethrin, all are used extensively in agriculture [21-22].

2.2. Newer Insecticides

During the last many years new synthetic pesticides have become more pest specific, exhibit lower toxicity and are less environmentally damaging. New insecticide classes and active ingredients have been introduced since about 1995. The results demonstrate that most of the newer compounds are more selective in action than older insecticides.

2.2.1. Novel Chemistries

Conventional insecticide formulations are endangering to human health and polluting environment. In recent years, new classes of insecticides have been marketed, none of which are persistent or bio-accumulate. Newly developed modern formulations like water emulsifiable gel, floating granules, drift less dust, macro and micro encapsulated suspension, hollow fibers, monolithic matrix, laminated structures etc., can avoid these problems. The prime motto for these developments is to give protection to the crops along with safety to the natural enemies of different pests as and a whole safety to environment. These further include juvenile hormone mimics, synthetic versions of insect juvenile hormones that act by preventing immature stages of the insects from molting into an adult, avermectins and natural products produced by soil microorganisms that are insecticidal at very low concentrations. The *Bacillus thuringiensis* toxins are proteins produced by a bacterium that is pathogenic to insects. When activated in the insect gut, they destroy the selective permeability of the gut wall. The first strains have been toxic only to Lepidoptera, but strains toxic to flies and beetles have since been developed. The *B. thuringiensis* has also been incorporated into plants genetically. The focus of the insecticide discovery and development efforts at various companies, however, has changed over the past decade. The evolution of following materials continued with new chemical families discovered that offer reduced persistence and environmental concerns along with attractive and valued benefits to producers and end-users [23-28].

2.2.1.1. Fermentation Products

Fermentation products cannot be readily synthesized directly, but these are produced by bacteria in fermentation vats. Such products and their acceptance by both consumers and farmers will continue to drive users towards even better unmodified natural product insecticides. Fermentation-derived natural products include avermectin (abamectin) and spinosad that affect receptors in the central nervous system of Lepidoptera, Diptera, Thysanoptera and some Coleoptera.

I. Avermectin

It is produced by the soil bacterium, *Streptomyces avermitilis*, interferes with interneuron function and mainly used as anti-helminth in livestock. In insects, avermectins binds into multiple sites of Cl^- channel resulting loss of cell function and nerve impulse. Then the insects are paralyzed and stop feeding.

II. Spinosad

Spinosad from *Saccharopolyspora spinose* is a neurotoxin that acts as an acetylcholine agonist like nicotine, but through another unknown mechanism. Spinosad acts by disrupting binding of acetylcholine in nicotinic acetylcholine receptors at the postsynaptic cell. No its phytotoxic activity yet is reported, and has quick degradation by microbes, wide safety to mammals, birds and beneficial organisms.

2.2.1.2. Neonicotinoids

Neonicotinoids displace radio labeled alphabungraotoxin that is a special legend of the nicotinicacetylcholine receptors from its bindingsites. Neonicotinoids act directly on the nAchR causing its toxic effect on insects. The presence of an electron donating groups which makes H-bonding to the receptor apart from the positively charged center interacts with the anionic site of thereceptor. The partially positively center in neonicotinoids must be the center to interact with theanionic center.

2.2.1.3. Phenyl-Pyrazoles

These are designed as non-systemic contact and stomach miticides, and these interfere with exchange of chloride ions by neurons. Pyrazoles block the gamma-aminobutyric acid regulated chloride channel in neurons. The pyrazoles consist of tebufenpyrad and fenpyroximate, are used for the control of soil and foliar insects.

2.2.1.4. Pyrroles

The pyrroles are compounds that act as metabolic toxins and work by uncoupling oxidative phosphorylation in the mitochondria. They have trans-laminar activity, and are toxic both by contact and ingestion to chewing and sucking arthropods.

2.2.1.5. Pyridazinones

It is a selective contact insecticide and miticide, and provides exceptionally long residual control, and rapid knockdown at a broad range of temperature. The mode of action of pyrroles, pyrazoles andpyridazinonesis that these inhibit mitochondrial electron transport, leading to thedisruption of adenosine triphosphate (ATP) formation, which is thecrucial energy molecule. They disrupt theproton gradient across mitochondrial membranes and thus impair the ability of mitochondria to produce ATP,leading to cell destruction and ultimately death of the organism.

2.2.2. Testing and Reclassification of Insecticides

New insecticides require extensive laboratory and field testing's and may take further few years to reach at swing in market. A pesticide company has to identify their uses, test effectiveness, and provide data on chemical structure, production, formulation, fate, persistence and environmental impacts [29]. The product is tested in the laboratory, greenhouse and field under different environmental conditions. After several years of testing, the company submits a registration data package studies on acute, chronic, reproductive, and developmental toxicity to mammals, birds and fish, the pesticide's environmental fate, rates of degradation, translocations to other sites, and ecological studies on its harmful effects on non-target plants and animals. After its review by scientists, government grants registration of the product for certain uses, with agreed label data and directions for use. A review of insecticide may be called for when new evidence indicates possible unreasonable risks to human health or the environment, including toxicity or ill health to humans or animals, hazards to non-target organisms, and risks to endangered species and suggests that the risks may outweigh the benefits of continued registration. After review, the government may take no action, alter the insecticide label to minimize risk, reclassify the approved uses or eliminate specific uses, or cancel or suspend the insecticide's registration entirely [30-31].

3. Conclusion

This article represents only a small fraction of such compounds that have been patented for pesticide uses, and a minute fraction of the toxins that have been reported to have potential utility as pesticides. From this exceeding arguments it can be conclude that in case of insecticides, the mode of actions are sought by the way so that it does not harm the mammals or non-target organisms, like beesand soil microbes. The development of pest resistance can be delayed or avoided by rotating pest control chemicals that work through different modes of action. In fact, insecticides must not have strong toxicity toward non-target organisms, especially animals and humans. Yet, to be efficient, they must be highly toxic toward their intended target pests. The mechanism of this type of selectivity is often the targeting of a molecular target site that is found only in the pest, or if in other organisms, is particularly vulnerable in the pest e.g., an enzyme form that is significantly different from that of other organisms. Natural toxins are a source of new chemical classes of pesticides, as well as environmentally and toxicologically safer molecules than many of the currently used pesticides. Besides, they often have molecular target sites that are not exploited by currently marketed insecticides. Due to various problems like insect pest resistance in existing insecticides, researchers have to develop new insecticides having novel mode of action and also that are able to give higher productivity and sustainability, safety and phytosanitary measures, ecologically require in very little amount, biodegradable, very less residue problem, target specific and cause no harm to non-target organisms. It is expected that many more natural toxins-based insecticides would become available in coming some years.

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