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Review on Generation types of botanical pesticides and its mode of action

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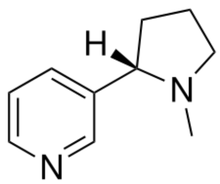
Abstract
An eco-friendly alternative to chemical pesticides is biopesticides, which encompasses a broad array of microbial pesticides, bio-chemicals derived from micro-organisms and other natural sources and processes involving the genetic incorporation of DNA into agricultural commodities that confer protection against pest damage. Main aspects of botanical pesticides, search and exploitation of new botanicals as pesticides including isolation, identification and evaluation of the active components and another use of botanicals in agriculture in different forms like direct spray applications of various plant materials, soil amendments for different plant parts, intercropping of biologically active plants with main crop, use of botanical based synthetic pesticidal formulations and also use of botanicals as synergists/ binders for synthetic pesticides.

Keywords: eco-friendly, pesticidal, formulations, biologically

Introduction
Use of botanicals is now emerging as one of the important means to be used in protection of crop produce and the environment from pesticidal pollution, which is a global problem. Botanical pesticides are naturally occurring chemicals extracted from plants. It is important alternatives to minimize or replace the use of synthetic pesticides as they possess an array of properties including toxicity to the pest, repellency, antifeedance, insect growth regulatory activities against pests of agricultural importance. In fact botanical pesticides are use in Indian agriculture for over a century to minimize losses caused by pests and diseases. Protection against pests is a priority and due to the adverse impact of chemical insecticides, use of biopesticides is increasing. Therefore, there is a need to develop biopesticides which are effective, biodegradable and do not leave any harmful effect on environment. The botanical pesticides could be divided into first and second generation pesticides. The first generation botanical pesticides includes Nicotine, Rotenone, Sabadilla, Ryania, Pyrethrum and Plant essential oils and the second generation botanical pesticides includes Synthetic Pyrethroids and *Azadiractin.*

First generation botanical pesticides
a) Nicotine
Nicotine, an alkaloid obtained from the foliage of tobacco plants (*Nicotiana tabacum*) and related species, as an insecticide. Nicotine and two closely related alkaloids, nornicotine and anabasine are synaptic poisons that mimics the neurotransmitter acetylcholine. Nicotine constitutes 2-8% of dried tobacco leaves. Insecticidal formulations generally contain nicotine in the form of 40% nicotine sulfate and are currently imported in small quantities from India. Furthermore, alkaloids of *Haloxylon salicornicum* and *Stemona japonica* are known be strong against at nicotinic acetylcholine receptors (El- Shazly *et al.* 2005) [26].



Structure ($C_{10}H_{14}N_2$)

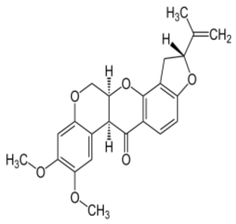
Tobacco (*Nicotiana tabacum)*

Fig 1

Mode of action
Nicotine is an extremely fast-acting nerve toxin. It competes with acetylcholine, the major neurotransmitter, by bonding to acetylcholine receptors at nerve synapses and causing uncontrolled nerve firing. This disruption of normal nerve impulse activity results in rapid failure of those body systems that depend on nervous input for proper functioning. In insects, the action of nicotine is fairly selective and only certain types of insects are affected.

b) Rotenone
Rotenone is one of several isoflavonoids that occurs in the roots or rhizomes of the tropical legumes *Derris*, *Lonchocarpus* and *Tephrosia*. Currently the main commercial source of rotenone is Peruvian *Lonchocarpus*, which often is referred to as cube root. Extraction of the root with organic solvent yields resins containing as much as 45% total rotenoids; the major constituents are rotenone (44%) and deguelin (22%) (Cabizza *et al.* 2004) [12]. Rotenone is commonly sold as a dust containing 1% to 5% active ingredients. The resin is used to make liquid concentrates or to impregnate inert dusts or other carriers used in organic agriculture can contain as much as 8% rotenone and 15% total rotenoids. Most rotenone products are made from the complex resin rather than purified rotenone itself. Alternatively, cube roots may be dried, powdered and mixed

directly with an inert carrier to form an insecticidal dust.



Structure ($C_{23}H_{22}O_6$)

Tephrosia

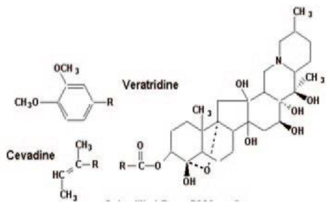
Fig 2

Mode of action

Rotenone is a broad spectrum cytotoxin, as it inhibits the electron transport chain in mitochondria and prevents energy production (Hollingworth *et al.* 1994) [36]. It is a respiratory enzyme inhibitor acting between NAD+ (a coenzyme involved in oxidation and reduction in metabolic pathways) and coenzyme Q (a respiratory enzyme responsible for carrying electrons in some electron transport chains) resulting in failure of the respiratory functions. In insects rotenone exerts its toxic effects primarily on nerve and muscle cells, causing rapid cessation of feeding. Death occurs several hours to a few days after exposure.

c) Sabadilla

Sabadilla is a botanical pesticide derived from the ripe seeds of sabadilla lily (*Schoenocaulon officinale)*. When sabadilla seeds are aged, heated or treated with alkali, several insecticidal alkaloids are formed or activated. The alkaloids in sabadilla are known collectively as veratrine or as the veratrine alkaloids. They constitute 3-6% of aged, ripe sabadilla seeds. Of these alkaloids, cevadine and veratridine are the most active insecticidal property. Sabadilla is considered among the least toxic of botanical insecticides. The alkaloids are remarkably similar to that of the pyrethrins, despite their lack of structural similarity.



Structure ($C_{36}H_{51}NO_{11}$)

Schoenocaulon officinale

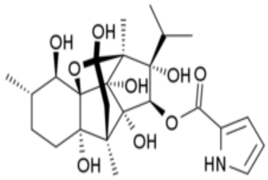
Fig 3

Mode of action

In insects, sabadilla's toxic alkaloids affect nerve cell membrane action, causing loss of nerve cell membrane action, causing loss of nerve function, paralysis and death. It kills insects of some species immediately, while others may survive in a state of paralysis for several days before dying. It acts as a contact and stomach poison and has been effective against caterpillars, leaf hoppers, thrips, stink bugs and squash bugs.

d) Ryania

Another botanical in declining use is ryania, comes from the woody stems of *Ryania speciosa* (Flacourtiaceae). Powdered Ryania stem wood is combined with carriers to produce a dust or is extracted to produce a liquid concentrate. The most active compound in ryania is the alkaloid ryanodine, which constitutes approximately 0.2% of the dry weight of stem wood.



Structure ($C_{25}H_{35}NO_9$)

Ryania speciosa

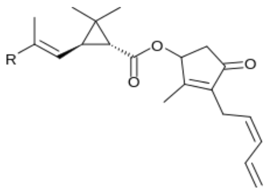
Fig 4

Mode of action

Ryania is a slow acting stomach poison. Although it does not produce rapid knockdown paralysis, it does cause insects to stop feeding soon after ingesting it. Little has been published concerning its exact mode of action in insect systems.

e) Pyrethrum

Pyrethrum is the most widely and heavily used botanical insecticide worldwide and it is well known as fast knockdown household aerosols. It refers to the oleoresin extracted from the dried flowers of the pyrethrum is daisy, *Chrysanthemum cinerariaefolium* (Asteraceae). The term "pyrethrum" is the name for the crude flower dust itself and the active ingredient is "pyrethrins" refers to the six related insecticidal compounds that occur naturally in the crude material, the pyrethrum flowers. The flowers are ground to a powder and then extracted with hexane or a similar nonpolar solvent, removal of the solvent yields an Orange-coloured liquid that contains the active principle (Glynne-Jones, 2001) [33]. Technical grade pyrethrum, the resin used in formulating commercial insecticides, typically contains from 20% to 25% pyrethrins (Isman, 2006) [41].



Pyrethrin ($C_{21}H_{28}O_3$)

Chrysanthemum cinerariaefolium

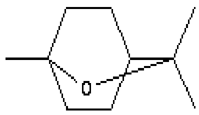
Fig 5

Mode of action

Pyrethrins exert their toxic effects by disrupting the sodium and potassium ion exchange process in insect nerve fibers and interrupting the normal transmission of nerve impulses. Pyrethrins insecticides are extremely fast acting and cause an immediate "knockdown" paralysis in insects. Despite their rapid toxic action, however, many insects are able to metabolize (break down) pyrethrins quickly. After a brief period of paralysis, these insects may recover rather than die. To prevent insects from metabolizing pyrethrins and recovering from poisoning, most products containing pyrethrins also contain the synergist, piperonyl butoxide (PBO). Without PBO, the effectiveness of pyrethrins is greatly reduced.

f) Plant essential oils

Essential oils are complex mixtures of volatile organic compounds produced as secondary metabolites in plants. They are produced commercially from several botanical sources, many of which are members of the mint family (Lamiaceae). The oils are generally composed of complex mixtures of monoterpenes, biogenetically related phenols and sesquiterpenes. Examples include 1,8-cineole, the major constituent of oils from rosemary (*Rosmarinus officinale*) and eucalyptus (*Eucalyptus globus*), eugenol from clove oil (*Syzygium aromaticum*); thymol from garden thyme (*Thymus vulgaris*); and menthol from various species of mint (*Mentha* species) (Isman 1999) [41].



1,8-cineole ($C_{10}H_{18}O$)

Mint

Fig 6

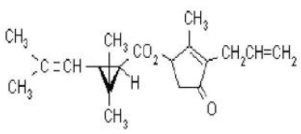
Mode of action

Essential oils interfere with basic metabolic, biochemical, physiological and behavioral functions of insects. Insects inhale, ingest or skin absorb essential oils. The rapid action against some pests is indicative of a neurotoxic mode of action and there is evidence for interference with the neuromodulator octopamine (Kostyukovsky *et al.* 2002) [51] by some oils and with GABA-gated chloride channels by others (El-Hosary, 2011) [24]. Some essential oils have larvicidal effect and the capacity to delayed development and suppress the emergence of adult insects (Khater, 2011) [50]. However, as broad-spectrum insecticides, both pollinators and natural enemies are vulnerable to poisoning by products based on essential oils.

Second generation botanical pesticides

a) Synthetic Pyrethroids

Pyrethroids are synthetic materials designed to imitate natural pyrethrum. Allethrin is the first pyrethroid synthesized (active ingredient of Raid) and found naturally in the Chrysanthemum flower. The widely used pyrethoids seem to present no problem to birds or other wildlife. Bees, important non-target arthropods, are only affected if sprayed directly. Otherwise, the pyrethroids effectively repel them from foraging in fields that have been sprayed.



Allethrin ($C_{19}H_{26}O_3$)

Chrysanthemum flower

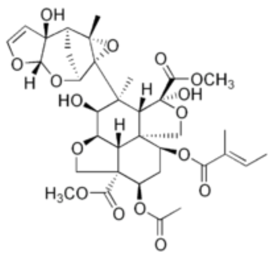
Fig 7

Mode of action

Synthetic pyrethroids are generally recognized as neurotoxicants that act directly on excitable membranes. These compounds induce intense repetitive activity in sense organs and in myelinated nerve fibers. Pyrethroids are also known to cause prolongation of the sodium current together with repetitive activity in nerve fibres of invertebrates (Henk *et al*. 1982) [34]. It has been suggested that the sodium channel in the nerve membrane is the major target site of pyrethroids. These compounds modify sodium channel gating in a strikingly similar way and reduce selectively the rate of closing of the activation gate (Narahashi, 1976) [61].

b) Neem products (*Azadiractin*)

Neem is a botanical pesticide derived from the seeds of the neem tree, a native of India (Schmutterer, 2002) [73]. All parts of the neem tree possess insecticidal activity but seed kernel is the most effective. Neem seeds typically contain 0.2% to 0.6% azadirachtin by weight, so solvent partitions or other chemical processes are required to concentrate this active ingredient to the level of 10% to 50% seen in the technical grade material used to produce commercial products. It has a multitude of pesticidal active ingredients which are together called “triterpene” more specifically “limnoids”. The four best limnoids compounds are: *Azadirachtin*, Salannin, Meliantriol and Nimbin. *Azadirachtin* ($C_{35}H_{44}O_{16}$) itself is a group of compounds such as *Azadirachtin* A, B, C, D, E, F, G etc. Of these, *azadirachtin-A* (Aza A) is the most plentiful and biologically active one which has shown repellent, antifeedent and insecticidal activity against a number of insect pests and it is generally *Aza* A that is used for commercial insecticides (Isman *et al*. 1996) [41].



Azadirachtin ($C_{35}H_{44}O_{16}$)

Neem

Fig 8

Mode of action

In insects, neem is most active as a feeding deterrent, but in various forms it also serves as a repellent, growth regulator, oviposition (egg deposition) suppressant, sterilant or toxin. As a repellent, neem prevents insects from initiating feeding. As a feeding deterrent, it causes insects to stop feeding. As a feeding, either immediately after the first “taste” (due to the presence of deterrent taste factors) or at some point soon after ingesting the food (due to secondary hormonal or physiological effects of the deterrent substance). As a growth regulator, neem is thought to disrupt normal development interfering with chitin synthesis. In addition, azadirachtin is a potent antifeedant to many insects. On the other hand, azadirachtin has systemic action in certain crop plants greatly enhancing its efficacy and field persistence. They have been shown to control gypsy moths, leafminers, sweet potato whiteflies, western flower thrips, loopers, caterpillars and mealybugs.

Table 1: Botanical pesticides used to control different insect pests

Botanical pesticides	Source	Mode of action	Insect pests	References
Nicotine	Tobacco plants	Mimics the neurotransmitter acetylcholine	Aphids, thrips, caterpillars	Casanova *et al*. (2002) [16]
Rotenone	Roots	Disrupts energy metabolism in mitochondria in nerve axons	Bugs, aphids, potato beetles, spider mites, carpenter ants	Cabizza *et al*. (2004) [12]
Ryania	Woody stem	Activates Ca ion release channels & causes paralysis in muscles	Codling moths, potato aphids, onion thrips, corn earworms, silkworms	Isman (2006) [41]
Sabadilla	Seeds	Causing loss of nerve function, paralysis and death.	Grasshoppers, codling moths, armyworms, aphids, cabbage loopers, squash bugs	Bloomquist (2003) [5]
Pyrethrum	Flowers	Interfere with Na & K ion movement in nerve axons	Caterpillars, aphids, leafhoppers, spider mites, bugs, cabbage worms, beetles	Glynne-Jones (2001) [33]
Essential oils	Mint family	Neuro toxic and interference with the neuromodulator octopamine	Caterpillars, cabbage worms, aphids, white flies land snails	Abdelgaleil (2010) [1]
Neem products	Neem plants	Repellent, Growth regulator, oviposition (egg deposition) suppressant, sterilant, or toxin.	Armyworms, cutworms, stem borers, bollworms, leaf miners, caterpillars, aphids, whiteflies, leafhoppers, psyllids, scales, mites and thrips	Dimetry *et al*. (2010) [21]
Synthetic pyrethroids	Flowers	Neurotoxicants	Caterpillars, aphids, thrips	Sallam *et al*. (2009) [70]

Table 2: Mechanism of action of pesticides of plant origin (modified from Rattan 2010)

System	Mechanism of action	Compound	Plant source	References
Cholinergic system	Inhibition of acetyl choline estrase (AChE)	Essential oils	*Azadirachtina indica*, *Mentha* spp., *Lavendula* spp.	Keane and Ryan (1999) [44]
	Cholinergic acetylcholine nicotinic receptor agonist/antagonist	Nicotine	*Nicotiana* spp., *Haloxylon salicornicum*, *Stemona Japonicum*	Kukel and Jennings (1994) [55]
GABA system	GABA-gated chloride channel	Thymol, Silphinenes	*Thymus vulgaris*	Bloomquist *et al*. (2008) [7]
Mitochondrial system	Sodium and potassium ion exchange disruption	Pyrethrin	*Crysanthemum cinerariaefolium*	Casida (1973) [19]
	Inhibitor of cellular Respiration (mitochondrial complex electron transport inhibitor (METI))	Rotenone	*Lonchocarpus* spp.	Khambay *et al*. (2003) [47]
	Affect calcium channels	Ryanodine	*Ryania* spp.	Copping and Menn (2000) [20]
Octopaminergic system	Affect nerve cell membrane action	Sabadilla	*Schoenocaulon officinale*	Bloomquist, 2003) [5]
	Octopaminergic receptors	Essential oils	*Cedrus* spp., *Pinus* spp., *Citronella* spp., *Eucalyptus* spp.	Enan (2005a)
	Block octopamine receptors by working through tyramine receptors cascade	Thymol	*Thymus vulgaris*	Enan (2005b)
Miscellaneous	Hormonal balance disruption	*Azadirachtin*	*Azadiractina indica*	Copping and Menn (2000) [20]

Potential New Botanicals

Annonaceous Acetogenins

Botanical pesticides have been traditionally prepared from the seeds of tropical *Annona* species, members of the custard apple family (Annonaceae). The major acetogenin obtained from seeds of *A. squamosa* is annonin or squamocin and a similar compound asimicin (Johnson *et al.* 2000). These compounds are slow acting stomach poisons particularly effective against chewing insects such as lepidopterans and the Colorado potato beetle (*Leptinotarsa decemlineata*). The acetogenins have a mode of action identical to that of rotenone, i.e., they block energy production in mitochondria (Londershausen *et al*. 1991) [59].

Sucrose Esters

Sugar esters naturally occurring in the foliage of wild tobacco (*Nicotiana gossei*) were pesticidal to certain soft-bodied insects and mites. Although patented (Pittarelli *et al*. 1993) [65], extraction of these substances on a commercial scale from plant biomass proved impractical, leading to the development of sucrose esters manufactured from sugar and fatty acids obtained from vegetable oils. It is contact pesticide that kills small insects and mites through suffocation (by blocking the spiracles) or disruption of cuticular waxes and membranes in the integument as recorded by Buta *et al*. (1993) [11], leading to desiccation.

Flavonoids

Castor oil due to its purgative properties used in Ayurvedic medicine (Liu, 2006) [58]. They have antimicrobial activity against *Bacillus firmus*, *Pseudomonas putida* and excellent insecticidal activity against *Callosobruchus chinensis*.

Limonoids

It is the first report on antifungal effects of these compounds. Chemical investigations of diethyl ether extract of the stem bark of *Khaya ivorensis* (african mahogany) afforded ten limonoids of angolensates, limonoids and mexicanolides.

Parthenin

The aerial parts of *Parthenium hysterophorus* plant contain eleven sesquiterpene lactone among which parthenin is the most important (Rajendran *et al.*, 2005) [67]. It has herbicidal activity and shows insect growth regulatory activity against the cotton stainer, fifth instar larvae of *S. litura* and cabbage leaf webber. Nematicidal activity against *Meloidogyne incognita*, antifeedant activity against 6th instar larvae of *Spodoptera litura*, *Tribolium castaneum*, termite.

Ginger rhizomes *(Zingiber officinale Rosae)*

Compounds exhibited moderate IGR activity and antifeedant activity against *Spilosoma obliqua* and antifungal activity against *Rhizoctonia solani*. 6-dehydroshogalol showed maximum IGR activity and dehydrozingerone showed maximum antifungal activity.

Conclusion

The use of bio-pesticides has emerged as promising alternative to chemical pesticides. Biopesticides clearly have a potential role to play in development of future integrated pest management strategies. Hopefully, more rational approach will be gradually adopted towards biopesticides in the near future and short-term profits from chemical pesticides will not determine the fate of biopesticides. Major emphasis over the last 10 years has been given to identify active principles of new molecules as compare to synthesis of analogue. Hence, the future emphasis should be on development of molecules which are ecofriendly, effective, low dose, selective and target specific, exploitation of the unexplored wealth of botanicals and biopesticides for plant protection-a distinct order of tomorrow, research on botanicals continues to be the area of maximum interest and with lot of still unexplored potential. In India also, there has been a distinct trend in the decreased use of conventional chemical insecticides with a concomitant but gradual increase in consumption of biopesticides. Already developing resistance to even newly introduced agrochemicals leading to synthetic chemicals being registered at a slower rate than in the past. This situation has helped to reopen the market for a new generation of biopesticides. With fast paced changes in development of effective delivery systems and possibility of identifying newer potential biomolecules, a relook at the utility of biopesticides may be worthwhile in future.

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