

## **Role of Botanicals in Plant Protection**

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### **SUMMARY**

Indiscriminate use of pesticides has generated problems, like pest resistance, resurgence of pests, ecotoxicity and elimination of natural enemies. These glitches attract the attention of scientific world to develop an eco-friendly and human safe alternative method of pest control. In this regard use of phytochemicals (botanicals), bio-pesticides and biocontrol agents (natural enemies) offer a good alternative to manage the different pests and diseases in an eco-friendly manner. Over the last four decades, many useful phytochemicals have been identified and isolated with specific and general application to pest control. Of the known about 4,00,000 plant species, only about 3,000 plant species have been screened to possess pesticidal potential. Till now, more than 500 pesticidal compounds have been identified from various plant species and few have achieved the commercial status worldwide. Present day bio-pesticide market in the world includes pyrethrins, rotenone, nicotine, ryanodine, sabadilla and azadirachtins *etc.* Constituents of secondary plant metabolism may have applications in weed and pest management, if developed for use as pesticides themselves, or they can be used as model compounds for the development of chemically synthesized derivatives. The main chemical classes of constituents of secondary plant metabolism that have been used in crop protection focusing on the most recent advances in the chemicals disclosed, their mode of action, role in controlling pests and pathogens as well as their fate in the ecosystem are briefly discussed.

### **INTRODUCTION**

Future agricultural and rural development is influenced by the rapidly increasing food demand. Achieving food sufficiency in a sustainable manner is a major challenge for farmers, agro-industries, researchers and governments (Schillhorn van Veen, 1999). The intensification of agriculture to fulfil food needs has increased the number of insect pest species attacking different crops and as a result the annual production losses of the standing crops. In the past, synthetic pesticides have played a major role in crop protection programmes and have immensely benefited mankind. Nevertheless, their indiscriminate use has resulted in the development of resistance by pests (insects, weeds *etc.*), resurgence and outbreak of new pests, toxicity to non-target organisms and hazardous effects on the environment endangering the sustainability of ecosystems (Jeyasankar and Jesudasan, 2005; Jena and Sahoo, 2022). Due to environmental side effects and health concerns, many synthetic pesticides have been banned. All these facts necessitate the urge for new and alternative pest control methods (Chitwood, 2002). An interesting way of searching for biorational pesticides is screening naturally occurring compounds in plants (Isman, 2006; 2008). Plants, as long-lived stationary organisms, must resist attackers over their lifetime, so they produce and exude constituents of the secondary metabolism playing an important role in their defence mechanisms. In fact, the phytochemicals' research has its roots in allelochemistry, involving the complex chemical mediated interactions between a plant and other organisms in its environment (Chitwood, 2002). Botanicals and plant allelochemicals are clearly defined as semiochemicals by Organization for Economic Cooperation and Development (OECD). This definition includes all chemicals involved in species communication (pheromones, but also plant extracts, plant volatiles, and natural oils) and exhibiting pest control activities. The concept of biocontrol agents (BCAs) has recently been preferred to that of biopesticides (Regnault-Roger & Philogène, 2008). Botanicals are environmentally friendly, pose less risk to humans and animals, have a selective mode of action, avoid the emergence of resistant races of pest species, and as a result they can be safely used in Integrated Pest Management (IPM) (Isman, 2006).

### **Kinds of Botanicals**

#### **1. Essential Oils (EOs)**

Essential oils (EOs) are volatile, natural, complex compounds characterized by a string odour and are formed as constituents of secondary metabolism by aromatic plants belonging to a number of botanical families, like Myrtaceae, Lauraceae, Lamiaceae and Asteraceae. These chemical volatiles have functions in chemical defence, acting as insecticides, acaricides, avoiding bacterial or fungal phytopathogen colonization, attracting

natural enemies of herbivores. Usually, they are obtained by hydro-distillation and they comprise terpenes and terpenoids and other aromatic and aliphatic constituents. The biological activity of EOs and their components on pest insects comprise behaviour and feeding deterrence effects, fumigant toxicity, knockdown activity and lethal toxicity *via* contact. While these substances are generally active against a broad spectrum of pests, interspecific toxicity of individual oils and compounds is highly idiosyncratic. Perhaps the most attractive aspect of using EOs and their constituents in pest management is their favourable mammalian toxicity and their nonpersistence in the environment.

## 2. Triterpenoids (Intact and degraded tetranortriterpenoids as well as triterpenoid saponins)

Limonoid triterpenes are known to possess insecticidal and antifungal properties. Limonoids are metabolically altered triterpenes and have a prototypical structure either containing or deriving from a precursor with a 4,4,8-trimethyl-17-furanylsteroid skeleton. Limonoids are confined to plant families of the order Rutales and more abundantly in the families Meliaceae and Rutaceae, and less frequently in Cneoraceae and *Harrisonia spp.* of Simaroubaceae. Of the 300 limonoids known today, about one third is obtained from Meliaceae species (*Azadirachta indica* and *Melia azedarach*), also known as meliacins.

The technical grade material of azadirachtin of the Indian Neem tree is used for the production of a wide range of commercial formulations exhibiting good efficacy against more than 400 insect species, mites and nematodes. Neem is a mixture of more than 100 limonoid compounds, including azadirachtin, salannin, and nimbin and their analogues provoking repellence, feeding deterrence and insect growth inhibition. Similar to *A. indica*, *M. azedarach* extracts possesses insecticidal, acaricidal and fungicidal properties and some of the limonoids isolated are 21-acetoxymelianol, meliantriol, melianone, melianol, meliacin (1-cinnamoyl melianone), meliacarpin and meliartenin, azedarachin B. Limonoids do not have direct negative effects on beneficial insects, a fact that indicates their potential to be combined in biological pest control programmes. Azadirachtin is the mostly ever studied tetranortriterpenoid and its mode of action lays on (i) deterrent effects on chemoreceptors resulting in antifeedancy (ii) effects on ecdysteroid and juvenile hormone titres through a blockage of morphogenetic peptide hormone release (e.g. PTH, allatotropins) and (iii) direct effects on tissues resulting in an overall loss of fitness of the insect. Within the azadirachtin molecule, the decalin fragment is responsible for the insect growth regulation and development effects observed, while the hydroxyl-furan fragment causes the antifeedant effects more widely observed among target species. Azadirachtin provokes a rapid increase in the mitotic index of insect cells, induces the appearance of many aberrant mitotic figures and prevents to some extent the polymerisation *in vitro* of mammalian tubulin. Additionally, it has no effects on skin sensitization, eye irritation, and is not mutagenic. Under field conditions azadirachtin and other neem constituents, e.g., salannin, nimbin, deacetylnimbin, and deacetylsalannin, are not persistent. Sunlight photodegradation is the main factor influencing the rate of its disappearance after greenhouse treatment while tomato epicuticular waxes double the photodegradation rate of a commercial formulation.

Besides limonoids, also the quassinoids and saponins fall in the category of triterpenoids. Quassinoids, the bitter principles of the Simaroubaceae family (*Quassia amara*, *Cassia camara* and *Picrasma exelca*), are a group of structurally complex and highly oxygenated degraded triterpenes. They are divided into five groups according to their basic skeleton, C-18, C-19, C-20, C-22 and C-25. These show promising biological activities phytotoxic, antifeedant, insecticidal properties and act against insects, nematodes and weeds. In nematodes, quassinoids acts as noncompetitive antagonists of the ionotropic GABA receptors. The plant-derived saponins are triterpene glycosides obtained from the soap bark (or soapbark) tree, *Quillaja saponaria* (Quillajaceae) as well as various other plant species of the families Alliaceae, Asteraceae, Polygalaceae and Agavaceae. Their side chains of hydrophilic carbohydrates provide them with surfactant properties, but they possess also significant antifeedant, fungicidal and nematicidal properties. Saponins disrupt also membranes.

## 3. Glucosinolates and Isothiocyanates (*Brassicaceae*)

Glucosinolates (GLSs) are sulphur and nitrogen containing constituents of secondary metabolism produced by “mustards” (*Brassica* and *Sinapis spp.*) as well as other genus of the Capparales order. Glucosinolates are an important and unique class of secondary plant products containing b-D-thioglucose and sulphonated oxime moieties. These include thioglucosides, characterized by side chain with varying aliphatic, aromatic and heteroaromatic carbon skeletons. Glucosinolates get inverted into various degradation products (isothiocyanates,

thiocyanates, indoles *etc.*), when vegetables containing them are cut or chewed, because during this process they come in contact with the enzyme myrosinase that hydrolyses them. By incorporating glucosinolate-containing plant material in soil their bioactive hydrolysis products, named isothiocyanates (ITCs) are released. These products can be used to control soil pests and weeds - a practice known as biofumigation. This practise is considered an ecological substitution of the soil fumigation with toxic fumigants such as Methyl Bromide (MeBr), used in the past to suppress soil fungus, bacteria, nematodes and weeds, since it is considered fully biodegradable and less toxic.

ITCs trigger the plant's defence mechanism, produce toxins that kill the target organisms, and produce defensive barriers around the roots of the host plant thus preventing the harmful fungi to enter the host. In fungus, ITCs inhibit the oxygen uptake through the un-coupler action of oxidative phosphorylation in mitochondria, they inhibit the coupling between the electron transport and phosphorylation reactions and eventually hinder the ATP synthesis. In bacteria, ITCs inactivate various intracellular enzymes by oxidative breakdown of -S-S- bridges and they obstruct ATP synthesis in cells through un-coupler action of oxidative phosphorylation in mitochondria. In insects, ITCs inactivate the thiol group of essential enzymes, alkylate the nucleophilic groups of biopolymers like DNA and act as un-couplers accelerating the respiration, which needs more ATP as source of energy, while at the same time ATP production is blocked. This causes exhaustion of stored energy sources which finally leads to death of the pest. In weeds, they inhibit seed germination by interfering with protein synthesis and formation of phosphorylated sugars, or inhibit plant enzyme activity. The ITCs' sorption, degradation or loss from soil mechanisms is fundamental for developing effective, but environmentally benign bio-fumigation strategies. Effective bio-fumigation relies on maximum hydrolysis of the glucosinolates in the plant tissue to generate high isothiocyanate concentrations in the soil after incorporation.

#### 4. Cyanogenic glucosides

Cyanogenic glucosides constitute a limited number of amino acid derived constituents of secondary plant metabolism known to be present in more than 2500 plant species. This group of compounds is considered to play an important role in plant defence against herbivores due to their bitter taste and release of toxic hydrogen cyanide. Upon tissue disruption (e.g. chewing insects) the cyanogenic glucosides are released from the vacuoles and hydrolyzed by specific  $\beta$ -glucosidases to yield glucose, a ketone or an aldehyde and toxic HCN. This process is known as cyanogenesis and serves to facilitate a rapid HCN release that suppress insects, fungus, nematodes and weeds. Cyanogenic glycosides, through the action of cyanide, prevent oxygen utilization by the inhibition of cytochrome oxidase.

#### 5. Alkaloids

Alkaloids are constituents of secondary plant metabolism containing nitrogen atoms derived from various botanical families and abundantly from Solacaneae family. Nicotine is undoubtedly the oldest alkaloid used in agriculture as well as the one of the first molecules used as insecticide. It is an acetylcholine mimic binding to postsynaptic receptors and interfering with the transmission of signals in nerves, leading to a continuous firing of the neuroreceptor. This overstimulation leads to depression in the central nervous system. It acts predominately through the vapour phase and to a less degree through stomach and contact. Nicotine's high toxicity to humans limited its use as a pesticide. Biotransformations of nicotine, involving activation reactions and detoxification mechanisms, have led to neonicotinoids, representing the current major class of insecticides of outstanding potency, systemic action and low toxicity to mammals.

Other alkaloids falling in the same category are veratrine and cevatrine, the major components of *Sabadilla* (*Schoenocaulon officinale* (Grey)) seeds, which are mainly used to control thrips, but recently resistance issues have broken up. *Sabadilla* alkaloids possess, like pyrethrins, a neurotoxic activity by slowing the shutting of  $\text{Na}^+$  channels and disturbing membrane depolarization. They cause paralysis before death. They are contact and nonsystemic insecticides, readily degraded in air and sunlight and are not considered hazardous to non-target organisms. Ryanodine and its derivative, the dehydro-ryanodine, are extracted from *Ryania speciosa* (Liliaceae) naturalizing the Amazonian basin. Ryanodine acts against insects by interfering with the nerve impulse at the  $\text{Ca}^{2+}$  channel level and provoking a sustained contraction of the muscles and paralysis. The toxicity of *Ryania* extracts towards mammals and fish has precluded its continuing use. Finally, 2,5-dihydroxymethyl-3,4-dihydropyrrolidine (DMDP) is a sugar analogue, pyrrolidine alkaloid contained in the genera *Lonocarpus* and

*Derris*, exhibiting nematicidal activity. It is downwardly mobile in plant phloem, applications on plant foliar decrease galling in roots.

## 6. Phenolics – Flavonoids

Phenolics are toxic to insects, fungi, bacteria, nematodes and weeds. Flavonoids, a major class of phenolic compounds, are distributed widely in vascular plants and Bryophytes, and Nearly 5,000 kinds have been reported to possess feeding attractant and deterrent properties. Rotenone, a flavonoid, present in plants of the genus *Derris* or *Lonchocarpus* (Leguminosae) is, with the alkaloid nicotine, one of the oldest insecticides used all over the world. The principal commercial product of the botanical insecticide rotenone comes from Cube resin, a root extract of *Lonchocarpus utilis* and *Lonchocarpus urucu*. Although rotenone is the primary major constituent in insecticides containing these preparations, a second isoflavone, deguelin, also possesses similar biological properties. Rotenone inhibits cellular respiration and energetic metabolism at the level of the mitochondrial respiratory chain. It is easily biodegradable and its half-life under field conditions is 5 to 7 hour. Initially it has been characterised moderately toxic to mammals, but it eventually links to Parkinson's disease and recently rotenone has not been included in Annex I of Council Directive 91/414 EEC

## 7. Polyacetylenes & Polythienyls

They are substances present in *Tagetes* species, commonly “marigolds”, of the botanical family Asteraceae. Polyacetylenes and Polythienyls possess insecticidal and nematicidal properties.

## 8. Pyrethrum

Pyrethrum is a powder obtained by crushing dried flowers of daisies belonging to the family of Asteraceae such as *Chrysanthemum. spp.*, *Pyrethrum. spp.*, and *Tanacetum spp.* Pyrethrum is a mixture of six esters, pyrethrins I and II, (the most abundant), cinerin I and II, and jasmoline I and II. Pyrethrins control a wide range of insects and mites binding to Na<sup>+</sup> channels and prolonging their opening. The insect presents hyperactivity followed by convulsions and finally it dies. The rapid action of pyrethrins is called knockdown effect. Pyrethrins have a relatively low toxicity toward mammals but toxicity is mentioned for nontargeted species, especially fish and bees. However, their great instability to light, air, and moisture reduce considerably the risks related to its use. Currently, pyrethrum is limited and costs have risen in recent years, making it inaccessible to less affluent societies.

## 9. Organic Acids

Vegetable oils contain large and heterogeneous quantities of fatty acids, saturated or unsaturated, with medium to long esterified carbon chains, and esters of fatty acids with high molecular weight. They develop toxicity by inhalation and contact suffocating the insect by forming an impermeable film upon the cuticle. Some compounds penetrate through the cuticle, disrupt cellular membrane, and uncouple oxidative phosphorylation. Some fatty acids, such as oleic (C<sub>18</sub>), have their own insecticidal activities, whereas undecylenic (C<sub>11</sub>) acid has a lower toxicity, but increases the activity of other insecticidal compounds by potentiation.

## 10. Others

The Constituents of secondary plant metabolism produced by many species in the genus *Piper* are called piperamides and they are characterised by insecticidal activity. Piperamides provoke contact toxicity, repellent and antifeedant activities and in a biochemical level act as neurotoxins. They quickly degrade under full sunlight. Capsaicin is obtained from the genus *Capsicum* such as chili peppers (*Capsicum frutescens* (Mill)) and is characterised by nematicidal, insecticidal and insect repellent properties.

## CONCLUSION

Botanicals have long been touted as attractive alternatives to synthetic chemical pesticides for pest management because botanicals reputedly pose little threat to the environment and to human health. Only a handful of botanicals are currently used in agriculture in the industrialized world, and there are few prospects for commercial development of new botanical products. Several factors appear to limit the success of botanicals, most notably regulatory barriers and the availability of competing products (newer synthetics, fermentation

products, microbials) that are cost-effective and relatively safe compared with their predecessors. Botanical pesticides presently play only a minor role in crop protection. The regulation of natural products as crop protection agents may have to undergo the same procedure as for a conventional chemical product. There is the requirement of concerted efforts that are hoped to remove limitations in bio-pesticides raw material availability, potency variations, standardization of extraction methods, quality control, shelf life and improved bio-efficacy.

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