Allelopathy and Application of Natural Phytochemicals as Pesticides: A Review in Present Scenario

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Received: June 14, 2018
Accepted: June 22, 2018

ABSTRACT
Biocides using in agriculture and in social life are basically synthetic chemical compounds which have a strong adverse effect upon environment. The concept of allelopathy is very noble which can be used in development of biocides. Allelopathy is a natural process where on plant interacts with other plant by chemical means other than competition. Plant possesses a huge number of water soluble organic compounds which have the ability to suppress the growth of other plant. Terpenoids, alkaloids, flavonoids derivatives, sesquiterpenoid lactone, saponins are some common natural phytochemicals present in plants. Plants contain a virtually untapped reservoir of biocides that can be used directly or as templates for nature friendly biocides. Phytochemicals are mainly the secondary metabolites of plants may be considered as source materials for formulating pesticides with the help of advances of chemical technology. Government should have a clear motto in this regard.

Keywords: Allelopathy, pesticide, phytochemicals, biocide.

Pesticides are pest controlling substances. Pesticide is an umbrella term which includes herbicides, insecticides, nematicides, molluscicide, avicide, rodenticide, fungicide, antimicrobial agents. Herbicide is used in higher extent than other pesticides of which a large amount, approximately 80-85% is used to protect crop plants, which in general, protect plants from weeds, fungi, or insects. Pesticides have been used for crop protection from very early period. With the evolution of agricultural technology and industry the nature of pesticide has been changed from natural products to chemical one. At the time of onset of agriculture, plant materials were used to control pest or insect attack. The chemical compound mainly the secondary metabolites present within the plant part e.g. leaf, bark, root etc. were the basic active principle which interferes chemically with herbs, weeds or insects. This interference of a compound needs no special condition rather it works well in natural atmosphere.

The phenomenon of allelopathy, where a plant species interferes chemically with other plants under natural conditions other than nutritional ones have been known for over 2000 years. Theophrastus (372 to 285 BC), a disciple of Aristotle, reported an example of the inhibitory effect of ‘pigweed’ on alfalfa (Jelenic, 1987). According to Rice (1984), the soil sickness problem in agriculture might be due to exudes of crop plants. Schreiner and Reed (1907, 1908) isolated soil organic acids released by plant roots that inhibited the overall growth of some crop plants.

In 1937, Hans Molisch studied the effect of ethylene on plant and first coined the term ‘Allelopathy’, from two Greek words “allelon” means ‘of each other’ and “pathos” mean ‘to suffer’. At that time he considered the allelopathy as harmful biochemical interaction between organisms. However, the term is today generally accepted to cover both inhibitory and stimulatory effects of one plant on another plant (Rice 1984). Evenari (1961) defined allelopathy as the ‘effect of one plant upon another occurring under natural conditions and exerted by some chemical means other than nutritional ones’. Tinnin and Muller (1971) described allelopathy as the form of interference which is basically different from competition and acts through depletion of resources. Allelopathy is also an expression of the ecological phenomenon which are normal constituents of the environment of the terrestrial plants (Dutta and Sinha-Roy, 1974).

Allelopathy is a subject of current fascination and controversy among plant ecologists. In recent years plant ecologists have focused primarily on the harmful interactions, and most workers now use the term in the sense implied by E. L. Rice - that is, to mean any direct or indirect effect (commonly negative) of one plant on another through the production of chemical compounds that escape into the environment (Rice,1974). The concept of plants waging chemical warfare is attractive in view of evolutionary considerations and, in part, as a rationale for the great diversity and quantity of secondary metabolites produced by plants.

Considerable evidences have been added during last six decades demonstrating the presence of inhibitory compounds in a wide variety of plant extracts and volatiles. The compound mentioned is simple...
water soluble organic acids, straight-chain alcohols, aliphatic aldehydes and ketones, simple unsaturated lactones, long chain fatty acids, napthoquinones, terpenoids and steroids, simple phenols, benzoic acids and derivatives, coumarins, flavonoids, tannins, alkaloids and cyanohydrins etc. (Bandopadhyay, 1983). Whittaker and Fenny (1971) coined ‘allelochemicals’ and stated that “allelochemicals are chemicals agents that are of major significance in adaptation of species and organization of communities”. Evolving from allelochemics Chou and Waller (1983) used “Allelochemicals” to describe all biochemical interactions between organism both inter and intraspecifically. Yang and Tang (1988) showed references of 267 plants containing pesticide activity, many of them also exhibiting allelopathic potential through literature review in between 25 to 220 A.D. in China.

Primary allelopathy is often ecologically significant in interactions between parasitic plants and their hosts (Rice, 1984). Possibly there are no known examples of primary allelopathy in which phytotoxins affect through soil-root interface. However, a bibenzyl Batatasin-III in northern crowberry [Empetrum nigrum sp. hermaphroditum (Hagerup) Bacher] fulfils several properties of a primarily allelopathic chemical. First, it accumulates into specific glands on leaf surface; if the primary function of the compound were protection from sunlight or low temperatures, it should be spread evenly in the leaf instead of accumulating in specific glands. Second, it is leached by water from these glands; if the primary function were herbivore avoidance, natural selection should favour individuals whose batatasin-III concentration does not fall rapidly during the period of active growth (Nilsson et al. 1998). Surplus production of batatasin-III is also an unlikely explanation since E. nigrum is capable of accumulating high concentrations of other toxic compounds in old stem tissues (Monni et al. 2000), and concentration of batatasin-III is highest in green leaves. If nutrient immobilization were the primary reason for production of batatasin-III, natural selection should have favoured the release of a compound with a lower pKa-value than 10 of batatasin-III since compounds with low pKa-values have. Unlike the northern subspecies, E. nigrum ssp. nigrum does not dominate groundvegetation anywhere in boreal forests (Tybirk et al. 2000). Due to these reasons, batatasin-III is a candidate for a primarily allelopathic compound. This, of course, does their highest activity in acidic conditions when the risk of leaching of inorganic ions is high (Northup et al. 1995; Lehman and Blum, 1999; Wallstedt et al. 2002).

The sesquiterpenoid lactone, artemisinin from the plant Artemisia annua L., was found to inhibit plant growth. Other compounds, such as 2,4-dihydroxy-1,4-benzoaxazin-3-one are also active as plant growth inhibitor. Plants produce many photodynamic compounds, such as hypericin, that are strongly phytotoxic. These compounds are unlikely to be developed as pesticides because, in the presence of light, they are toxic to all living organisms. However, any plant can be caused to generate phototoxic levels of photodynamic porphyrin compounds by treating the plant with both d-aminolevulinic acid, a natural porphyrin precursor, and 2,2'-dipyridyl, a synthetic compound. Thus, a natural product, not the synthetic herbicides is the acutely toxic compound in these cases.

A problem with plant-produced phytotoxins as potential herbicides is that in the native state, they are generally only weakly active compared to commercial herbicides. This is not unexpected, because production of highly phytotoxic compounds would lead to strong autotoxicity unless the producing plant develops metabolic or physical mechanisms to cope with its own phytotoxins. Some of the more potent allelochemicals are toxic to the producing species and this autotoxicity has been implicated in vegetation shifts. Microbial conversion of relatively non-phytotoxic compounds in the soil to highly phytotoxic derivatives has been documented.

Plant products have been successfully exploited as insecticides, insect repellents, and insect antifeedants. Probably the most successful use of a plant product as an insecticide is that of the pyrethroids. The insecticidal properties of the several Chrysanthemum species were known for centuries in Asia. After elucidation of the chemical structures of the six terpenoid esters (pyrethrins) responsible for the insecticidal activity of these plants. Synthetic pyrethroids have better photostability and are generally more active than their natural counterparts.

Another plant terpenoid, camphene, was a very successful herbicide in its polyhalogenated form sold as Toxaphrene. This product was the leading insecticide in the United States before it was removed from the market. Although this product was a mixture of over two hundred chlorinated forms of camphene, certain specific compounds in the mixture were found to be much more active than the mixture on a unit weight basis. Many other terpenoids have been demonstrated to have insecticidal or other insect-inhibiting
activities. For instance, azadirachtin and other terpenoids of the limonoid group from the families Meliaceae and Rutaceae are potent growth inhibitors of several insect species.

Phystostigmine, an alkaloid from Physostigma venenosum was the compound upon which carbamate insecticides were designed. Furo-quinoline and beta-carboline alkaloids such as dictamine and harmaline, respectively, are potent photosensitizing compounds that are highly toxic to insect larvae in sun light. The relative high cost toxicity to mammals, and limited efficacy have limited the use of natural alkaloid insecticides.

Preparations of roots from the genera Derris, Lonchocarpus, and Tephrosia, containing rotenone, were commercial insecticides in the 1930s. Rotenone is a flavonoid derivative that strongly inhibits mitochondrial respiration. No other phenolic compound has been used commercially as an insecticide, although the content of certain phenolic compounds in plant tissues have been correlated with host plant resistance to insects and many have been demonstrated to be strong insect growth inhibitors and antifeedants.

As in plants, delta-aminolevulinic acid (ALA), in combination with 2,2'-dipyridyl, can cause accumulation of toxic levels of photodynamic porphyrin compounds. Larvae of several insect species, when fed these compounds and exposed to light were rapidly killed. Protoporphyrin IX the same compound caused to accumulate in plants by certain photobleaching herbicides is the prophyrin responsible for the toxicity of these compounds to insects. Other photodynamic compounds from plants such as polyacetylenes are acutely toxic to insects; however, their general toxicity would probably preclude them from commercial use. Plants produce many compounds that are insect repellents or act to alter insect feeding behavior, growth and development ecdysis (molting), and behavior during mating and oviposition. Most insect repellents are volatile terpenoids such as terpenen-4-ol. Other terpenoids can act as attractants. In some cases, the same terpenoid can repel certain undesirable insects while attracting more beneficial insects. For instance, geraniol will repel houseflies while attracting honey bees. Compounds from many different chemical classes have been reported to act as insect antifeedants. Thus, polygodial a sesquiterpenoid from Polygonum hydropiper, is a potent inhibitor of aphid feeding. Several plant-derived steroids that are close analogues of the insect molting hormone, ecystosterone, prevent insect molting. Other chemically unrelated terpenoids inhibit molting by unknown mechanisms.

Several plant-derived compounds have been demonstrated to be strong elicitors of phytoalexins. For instance, certain oligosaccharide components of cell walls from stressed or dying higher plant cells will act as elicitors. Further knowledge of plant-derived phytoalexin elicitors could lead to their use as fungicides. Several isoflavonoid compounds, such as glyceollin, phaseolin, and pisatin in soybean, garden bean, and pea, respectively have been implicated in protection of these crops from pathogens. Many other confirmed or suspected phytoalexins have been identified. Some of these compounds have demonstrated utility against fungi under field conditions. Wyerone, an acetylenic acid derivative produced by legumes as a phytoalexin has a wide fungicidal spectrum against plant pathogens and has been successfully tested against fungal infection of crop plants. Despite a repertoire of many antifungal and antibacterial compounds, plant products have not been used to any significant extent in the development of antimicrobial pesticides. Many plant species are known to be highly resistant to nematodes. The most well-documented of these include marigolds (Tagetes spp.), rattlebox (Crotalaria spectabilis), chrysanthemums (Chrysanthemum spp.), castor bean (Ricinus communis), margosa (Azadiracta indica), and many members of the family Asteraceae. The active principle(s) for this nematicidal activity has not been discovered in all of these examples and no plant-derived products are sold commercially for control of nematodes. In the case of the Asteraceae, the photodynamic compound alpha-terthienyl has been shown to account for the strong nematicidal activity of the roots.

The plant-derived saponins are generally highly toxic to snails. Cyanogenic glucosides are responsible for resistance of certain legumes to snails and slugs. No plant-derived natural products are commercial products are available for control of snails and slugs.

Plants contain a virtually untapped reservoir of pesticides that can be used directly or as templates for synthetic pesticides. Numerous factors have increased the interest of the pesticide industry and the pesticide market in this source of natural products as pesticides. These include diminishing returns with traditional pesticide discovery methods, increased environmental and toxicological concerns with synthetic pesticides, and the high level of reliance of modern agriculture on pesticides. Despite the relatively small
amount of previous effort in development of plant-derived compounds as pesticides, they have made a large impact in the area of insecticides.

The number of options that must be considered in discovery and development of a natural product as a pesticide is larger than for a synthetic pesticide. Furthermore, the molecular complexity limited environmental stability, and low activities of many biocides from plants, compared to synthetic pesticides, are discouraging. However, advances in chemical and biotechnology are increasing the speed and ease with which man can discover and develop secondary compounds of plants as pesticides. These advances, combined with increasing need and environmental pressure, are greatly increasing the interest in plant products as pesticides.

A few highly phytotoxic plant-produced compounds have been discovered. However, none have been developed as herbicides. Various funding agencies should look upon the matter and take some measures to initiate projects to develop pesticides from plant products. Government should take matters seriously and may construct a board regarding this which will dedicate to development of nature friendly biocides. Biocides might be purely plant product or combined with synthetic herbicides or as a hybrid one.

Acknowledgements: This review work would have not been possible to complete without the encouragement of my respected teacher Prof. Aloke Bhattacharjee. I express my sincere thank to him. I also thank T.D.B College authority for providing me library and INFLIBNET access.

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