Current Status of Botanical Pesticides for Crop Protection

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The problems caused by synthetic pesticides have led the need for effective biodegradable pesticides with greater selectivity. Botanical pesticides are generally recognized as safe in agriculture systems. Thus, they have been regarded as attractive alternatives to synthetic chemical pesticides for the pest management. Both lower efficacy and higher costs of production make botanicals more expensive to use than conventional pesticides. Moreover, only a small portion of plant-derived metabolites among a number of bioactive metabolites are in use because commercialization of botanicals is inhibited by several problems such as toxicity, or high production cost. However, with the growing acceptance of botanical pesticides as an efficient crop protection alternative resulting in increasing demand, plant-based pesticides will play a significant role in achieving sustainable agriculture in future.

Keywords: Botanical pesticides, Plant-derived metabolites, Sustainable agriculture, Synthetic pesticides

Introduction

The agents that cause disease in plants are known to include pathogenic microorganisms such as viruses, bacteria, fungi, protozoa and nematodes. Plants also suffer from competition with weeds and are often damaged by attacks of insects. It is conservatively estimated that diseases, insects and weeds together annually interfere with the production of, or destroy, between 31 and 42% of all crops produced worldwide. Out of 36.5% average of total losses, 14% are caused by diseases, 10.2% by insects, and 12.2% by weeds. Oerke and Dehne (2004) reported that the actual losses were estimated at 26–30% for sugar beet, barley, soybean, wheat and cotton, and 35%, 39% and 40% for maize, potatoes and rice, respectively, for the period 1996–1998. The total annual worldwide crop loss from plant diseases is about $ 220 billion (2002 prices) (Agrios, 2005).

After World War II, the agrochemical industry with discoveries of the major classes of synthetic pesticides (organochlorines, organophosphates and carbamates) provided agriculture with a vast array of crop protection chemicals such as fungicides, insecticides, nematicides, and herbicides (Jespers and De Waard, 1993). Crop growers have mainly used such synthetic agrochemicals to control plant diseases. However, overuse of these synthetic pesticides has led to resistance in plant pathogens and other numerous problems unforeseen at the time of introduction such as acute and chronic pollution, negative effects on wildlife (fish, birds), disruption of biological control and pollination, and groundwater contamination.

Governments responded to these problems with regulatory action, banning or restricting the most damaging products and creating policies to make more stringent pesticide registration procedures and replace such chemicals and to pose fewer or lesser risk to human health and the environment (Gonzalez-Coloma et al., 2010; Isman, 2006).

New pesticides including botanical pesticides are being discovered and developed to replace the active compounds that are lost due to the new registration requirements. Botanical products have long been considered as crop protectants. A lot of plant derived-compounds with pesticidal activities such as essential oil, terpenoids, lipids, sterols, alkalooids, flavanones and polyketides have been discovered and registered as biopesticides (Copping and Duke, 2007; Copping and Menn, 2000). Phytochemicals have been interested in controlling plant diseases because they are specific to target species, have often unique modes of action and little toxicity to human and are rapidly degraded into non-toxic substances under environmental conditions.
Some of them possess modes of action different from introduced chemicals and are, therefore, lack cross-resistance (Vidhyasekaran, 2004). Thus, botanical pesticides have been long recommended as attractive alternatives to synthetic chemical insecticides for pest management. The number of scientific literature documenting pesticidal activity of plant metabolites continues to increase, yet only a minority of botanical pesticides are currently used in agriculture over the world. In this paper, we reviewed only a minority of botanical pesticides are currently used to synthetic chemical insecticides for pest management. Resistance (Vidhyasekaran, 2004). Thus, botanical pesticides introduced chemicals and are, therefore, lack cross-resistance. Some of them possess modes of action different from introduced chemicals for pest management.

**Botanical fungicides**

Numerous phytochemicals have the potentials to control fungal diseases of crops (Copping and Duke, 2007; Engelmeier and Hadacek, 2006; Isman, 2000b). Jojoba (Simmondsia californica) oil, rosemary (Rosmarinus officinalis) oil, thyme (Thymus vulgaris) oil, clarified hydrophobic extract of neem (Azadirachta indica) oil, and cottonseed (Gossypium hirsutum) oil with garlic (Allium sativum) extract are several botanical extracts and essential oils marketed as botanical fungicides for organic farmers (Dayan et al., 2009).

Cinnamaldehyde (Fig. 1) is used in mushrooms, row crops, horticultural crops, turf and pine forests to control diseases such as dry bubble (Verticillium fungicola), and pitch canker disease (Fusarium moniliforme var. subglutinans) (Copping and Duke, 2007). Its mode of action is apparently through inhibition of synthesis of the fungal cell wall component chitin (Bang et al., 2000). Thymol and carvacrol (Fig. 1) from essential oil of Thymbra spicata show strong antifungal activity against F. moniliforme, Rhizoctonia solani, Sclerotinia sclerotiorum. They efficiently inhibited all of the fungi with concentrations ranging from 50–100 μg/ml (Muller-Riebau et al., 1995). β-Thujaplicin and γ-thujaplicin (Fig. 1) are monoterpenes from Calocedrus macrolepis var. formosanum heartwood, exhibiting a broad antifungal spectrum against white rot fungi and brown rot fungi (Yen et al., 2008). The MIC values of β-thujaplicin and γ-thujaplicin were in the range of 5.0–50 μg/ml. β-Caryophyllene oxide and α-terpineol (Fig. 1) of Hypericum hyssopifolium and H. heterophyllum were strongly inhibitory to the growth of Fusarium species and R. solani at 1,000 μg/ml (Cakir et al., 2004). T-muurolol and α-cadinol (Fig. 1) exhibited activity against R. solani and F. oxysporum with the highest antifungal indexes ranging from 60% to 85% (Chang et al., 2008). Asaraldehyde and α-asarone (Fig. 1) derived from Acorus gramineus rhizome and R. solani were active against Phytophthora infestans and R. solani with control values of 50–100% at 1,000 μg/ml (Lee, 2007).

Singh et al. (2008) reported that securine and alloscurine (Fig. 1) isolated from Phylloctenium amarum completely inhibit spore germination of Alternaria spp., Heterosporium spp. and Curvularia spp. at 200 μg/ml. Nor-securine (Fig. 1) was fungicidal to H. frumentacei at 1,000 μg/ml (Sahni et al., 2005). Alkaloids neo-overatelines A and B (MICs about 200 μg/ml), veramitine, stenophylline B, stenophylline B-3-β-D-glucopyranoside, veramiline-3-β-D-glucopyranoside, jervine, and jervine-3-β-D-glucopyranoside (Fig. 1) isolated from rhizomes of Veratrnum taliense exhibited strong antifungal activity to Phytophthora capsici and Rhizoctonia cerealis (Zhou et al., 2003).

Emodin, physoin, and rhein (Fig. 1) isolated from Cassia tora showed fungicidal activities against Botrytis cinerea, Blumeria graminis f. sp. hordei, P. infestans, and R. solani with IC50 values in a range of 46–375 μg/ml. Aloe-emodin had an apparent IC50 value of 177 and 275 μg/ml against R. solani and B. cinerea, respectively (Kim et al., 2004a, b). Chrysophanol, paeonin (physcion), and nepodin (Fig. 1) isolated from roots of Rumex crispus showed activity against B. graminis f. sp. hordei and synergistic activity against fungus Sphaerotheca fuliginea. They controlled B. graminis f. sp. hordei with IC50 values of 4.7, 0.48 and 20 μg/ml, respectively (Choi et al., 2004; Yang et al., 2007). Dehydro-α-lapachone (Fig. 1) from stems of Catalpa ovata completely inhibited the mycelial growth of B. cinerea. Colletotrichum spp., Magnaporthe oryzae and Pythium ultimum over a range of 0.4–33.3 μg/ml (Cho et al., 2006b). Cho et al. (2006a, c) also demonstrated an antifungal activity of curcumin, demethoxycurcumin and bisdemethoxycurcumin (Fig. 1) against red pepper anthracnose in a range of 0.4–100 μg/ml. Curcumin was fungicidal to P. infestans, Puccinia recondita, and R. solani with 100%, 100%, and 63% control values at a concentration of 500 μg/ml (Kim et al., 2003).

Lignans erythro-austrobailignan-6, meso-dihydrouguaretic acid and nectandin-B (Fig. 1) from Myristica fragrans efficiently suppressed A. alternata, B. cinerea, Colletotrichum cocccodes, Colletotrichum gloeosporioides, F. oxysporum, R. solani and M. oryzae with IC50 from 24 to 100 μg/ml (Cho et al., 2007). Four neolignans from Magnolia obovata such as magnolol, honokiol, 4-methoxyhonokiol and bisdemethoxycurcumin (Fig. 1) against red pepper anthracnose in a range of 0.4–100 μg/ml. Curcumin was fungicidal to P. infestans, P. recondita, and R. solani with 100%, 100%, and 63% control values at a concentration of 500 μg/ml (Kim et al., 2003).

Saponinoids including spirostanol saponins dioscin, prosapogenin of dioscin and gracillin (Fig. 1) isolated from Dioscorea colletti var. hypoglaucua rhizomes induced
Fig. 1. Phytochemicals with antifungal activity against phytopathogenic fungi.
morphological deformation of mycelia and conidia of *M. oryzae* with MMDC (minimum morphological deformation concentration) 2.3, 5.5 and 9.0 µM, respectively (Hu et al., 2003). Hederagenin aglycone (Fig. 1) was reported to be active against *Rhizoctonia bataticola* (ED$_{50}$ 1636.0 µg/ml) and *Sclerotium rolfsii* (ED$_{50}$ 412.5 µg/ml) (Saha et al., 2010; Saniewska et al., 2006). Quinonoid triterpenes pristimerin and celastrol (Fig. 1) from the roots of *Celastrus hypoleucus*, inhibited the mycelial growth of *Glomerella cingulata*, *B. cinerea*, *R. solani* and *M. oryzae* (Luo et al., 2005).

In the case of commercialized phytochemicals L-glutamic acid and γ-aminobutyric acid, they are introduced as active ingredients of AuxiGro used as a fungicide and plant growth regulator for fungal managements of fruits and vegetables, tree nuts, peanuts, grains, turf grasses and for preventing powdery mildew on grapes. They are not toxic to mammals or other organisms tested and they are not likely to be toxic to plants (Copping and Duke, 2007).

Fig. 2. Phytochemicals with insecticidal activity against insects.
Botanical insecticides

Botanical insecticides from phytochemical resources being used currently include azadirachtin, nicotine, pyrethrins, rotenone, and numerous essential oils. Neem seeds (Azadirachta indica) contain 0.2 to 0.6% azadirachtin (Fig. 2) and numerous minor azadirachtin analogs (Isman, 2006). Azadirachtin has two effects on phytophagous insects; it disrupts insect molting by blocking the synthesis and release of ecdysteroids hormones, and is a potent antifeedant to many insects (Gonzalez-Coloma et al., 2010). Azadirachtin is effective against whitefly, thrips, leaf miners, caterpillars, aphids, jassids, beetles and mealybugs (Copping and Duke, 2007). Lepidoptera were extremely sensitive to the chemical and show effective antifeedances from below 1 to 50 g/ml, depending on species (Mordue and Nisbet, 2000). Azadirachtin is sold with a wide range of trade names such as Azatin, Align, Bio-neem, Bollwhip, Neem, Neemazad, Neemix, and so on (Copping and Duke, 2007).

Seeds of chinaberry tree (Melia azedarach), the most closely related genus of neem, contain a number of remarkable insecticidal triterpenoids (meliatoxins) such as 1-cinnamoylmelianolone (Fig. 2) (Isman, 2000a). The meliatoxins are abundant in chinaberry tree at Asia and toxic to mammals. However, the seeds of M. azadarach growing in Argentina lacked meliatoxins, but produced a notably triterpene mieliartenin that is a strong feeding deterrent to insects (Isman, 2006).

Nicotine (Fig. 2) is the main bioactive component of the tobacco plants Nicotiana tabacum (Copping and Duke, 2007). Nicotine is a nonsystemic insecticide that binds to the cholinergic acetylcholine nicotinic receptor. Nicotin and its semi-synthetic derivatives are used for the control of a wide range of insects, including aphids, thrips and whitefly, on protected ornamentals and field-grown crops, including orchard fruit, vines, vegetables and ornamentals (Addor, 1995; Copping and Duke, 2007).

Pyrethrins I (Fig. 2) and II are most abundant in pyrethrum of Tanacetum cinerariaefolium and account for most of the insecticidal activity (Isman, 2006; Gonzalez-Coloma et al., 2010). Pyrethrins block voltage-gate sodium channels in nerve axons, resulting in a neurotoxic action. Technical grade pyrethrum (20 to 25% pyrethrins) controls a wide range of insects and mites on fruit, vegetables, field crops, ornamentals, glasshouse crops and house plants (Copping and Duke, 2007).

Rotenone (Fig. 2) has been used for more than 150 years and is found in Derris, Lonchocarpus and Tephrosia species. It is used to control a wide range of arthropod pests, including aphids, thrips, suckers, moths, beetles and spider mites in fruit and vegetable cultivation. Rotenone is mitochondrial poison, which blocks the electron transport chain and prevents energy production. It is considered as a stomach poison because it must be ingested to be effective (Isman, 2006).

Karanjin (Fig. 2) is a furanoflavonol, a type of flavonoid. It is obtained from the seeds of the karanjin tree (Millettia pinnata = Derris indica), a tree growing wild in south India. Karanjin is an acaricide and insecticide. It suppresses the effects of ecdysteroids and thereby acts as an insect growth regulator (IGR) and antifeedant. It also inhibits cytochrome P-450 in susceptible insects and mites (Gonzalez-Coloma et al., 2010).

Plant essential oils disrupt the endocrinologic balance of insects. They may be neurotoxic or may act as insect growth regulators, disrupting the normal process of morphogenesis. Several volatile substances of essential oils such as linalool (Fig. 2) have been shown as inhibitors of acetylcholinesterase (AChE) against different insect species. Thujone, thymol, menthol and borneol (Fig. 2) have been classified as a neurotoxic insecticide, which acts on GABA receptors (Rameshwar Singh, 2010). Camphor and eucalyptol (Fig. 2) are used for control the honeybee parasite varroa (Varroa jacobson and V. destructor). trans-Anethole, estragole, eugenol (Fig. 2) and carvacrol showed topical activity to insects (Addor, 1995). Eugenol is effective on arthropod, armyworms, thrips, aphids and mites (Isman, 2000b). Cinnamaldehyde is toxic to corn rootworm and other pest of animals (Copping and Duke, 2007; Gonzalez-Coloma et al., 2010). Two asarones, a-asarone and cis-asarone (Fig. 2), caused high mortalities for Sitophilus oryzae, Callosobruchus chinensis and Lasioderma serricorne adults (Park et al., 2003).

Ryanodine (Fig. 2) and related alkaloids are poisonous alkaloids found in the stem of Caribbean shrub Rynia speciosa. It controls codling moth (Cydia pomonella), citrus thrips in maize, apples, pears and citrus. It has extremely high affinity to the open-form ryanodine receptor, a group of calcium channels found in skeletal and heart muscle cells. It affects muscles by binding to the calcium channels in the sarcoplasmic reticulum and cause rapidly death. The effect of the nanomolar-level binding is that ryanodine causes release of calcium from calcium stores in the sarcoplasmic reticulum leading to massive muscular contractions (Copping and Duke, 2007; Isman, 2006).

Piperidine, dihydrodipiperidine (Fig. 2) of black pepper Piper nigrum was active to adzuki bean weevil (Callosobruchus chinensis). Piperidine and dihydrodipiperidine
caused LD50 values 0.56 and 0.23 µg/insect, respectively (Isman, 2006).

Sabadilla is a botanical insecticide from the seeds of the South American lily (*Schoenocaulon officinale*). The plant contains a (2:1) mixture of cevadine and veratridine (Fig. 2), which account for the insecticidal activity of the plant (Isman, 2006). They act on the voltage-sensitive sodium channels of nerve, heart, and skeletal muscle cell membranes (Gonzalez-Coloma *et al*., 2010). The compounds were effective against thrips (*Frankliniella* spp. and *Thrips* spp.) in citrus and avocados (Copping and Duke, 2007).

Another aphidicide, 1,5-diphenyl-2-penten-1-one and 1,5-diphenyl-1-pentanone (Fig. 2) isolated from the roots of *Stellara chamaejasme* caused aphicial activity against *A. gossypii* and *Schizaphis graminum* (Ping *et al*., 2001). *ar*-Turmerone (Fig. 2) caused 100 and 64% mortality for *Nilaparvata lugens* female adults at 1000 and 500 µg/ml, respectively (Lee *et al*., 2001). 5-Hydroxy-1,4-naphthoquinone (Juglone, Fig. 2) isolated from *Diospyros kaki* roots was effectively active against *N. lugens* and *Laodelphax striatellus* (Jeon *et al*., 2011).

**Botanical nematicides**

Phytochemicals with nematicidal activities have been also known as botanical nematicides. Most of secondary metabolites are responsible for the nematicidal activities.
The volatile constituents of plant essential oils are promising remarkable nematicides (Choi et al., 2007a, b; Kim et al., 2008; Kong et al., 2006, 2007a, b; Park et al., 2007). Monoterpenes presented in Fig. 3 such as citronellol (Fig. 3), geraniol, menthol, thymol, citral and cimtonellal (Fig. 3) have shown noteworthy nematicidal activity against J2s pine wood nematode (PWN; Bursaphelenchus xylophilus) (Choi et al., 2007a; Kim et al., 2008; Park et al., 2007). Bornyl, carveol (Fig. 3), citral, geraniol and α-terpineol are potential nematicides.
against root knot nematode (RKN); the effects of soil treatment on galling of tomato caused by *Meloidogyne incognita* are significant (Echeverrigaray et al., 2010; Oka et al., 2000). The EC_{50} values at 96 h after treatment against *M. incognita* of benzaldehyde, γ-eudesmol (Fig. 3) and estragole are 9, 50 and 180 µg/ml, respectively. The synergistic nematicidal interactions of terpene pairs trans-anethole/geraniol, trans-anethole/eugenol, carvacrol/eugenol and geraniol/carvacrol were the most potent (Ntalli et al., 2011).

Salicylic acid (Fig. 3) and cinnamaldehyde were effective against RKN and provided control of galling on tomato plants (Chitwood, 2002). Eugenol (LD_{50} 0.48 µg/ml), methyl eugenol (LD_{50} 0.517 µg/ml), isoeugenol (LD_{50} 0.2 µg/ml) and methyl isoeugenol (LD_{50} 0.21 µg/ml) affected on PWN (Park et al., 2007). *cis*-Asarone, trans-cinnamyl alcohol, trans-2-decen-1-ol, trans-2-decanal (Fig. 3), decanal, undecanone and benzaldehyde caused mortalities (77–100%) for PWN (Kim et al., 2008).

Sesquiterpenes α-humulene (Fig. 3) (Suga et al., 1993) from barks of *Pinus* species and 4,5-epoxy-1(10)-E,11(13)-germacadien-12,6-olide from *Magnolia grandiflora* (Hong et al., 2007) were active against PWN. Thoden et al. (2009a, b) reported nematicidal activity of pyrrolizidine alkaloids heliotrine, lasiocarpine, senecionine, monocrotaline and monocrotaline N-oxide (Fig. 3) against RKNs *M. hapla* and *M. incognita*. Quinolizidine alkaloids from *Sophora flavescens* and *S. alopecuroides* including N-methylcytisine, cytisine (sopherine), matrine, aloperine and sophocarpine (Fig. 3) were significantly nematicidal PWN (Chitwood, 2002; Matsuda et al., 1989, 1991; Zhao, 1999). Among of those alkaloids, aloperine are the most effective alkaloid (Zhao, 1999). Colchicine (Fig. 3) isolated from *Gliricidia sepium* superb seeds, at concentration of 1% and 2%, showed nematotoxicity of 32% and 85% to J2s of *M. incognita*, respectively (Nidiry et al., 1993). Serpentine (Fig. 3) from *Catharanthus roseus* induced death and inhibited hatching of *M. incognita* (Chandravada et al., 1993).

Saponins from top and root tissues of *Medicago sativa* showed 86–91% mortality against *M. incognita* (D’Addabbo et al., 2010). *Furostanol glycosides and glycoalkaloids such as deltonine, deltoside, protodioscin, α-chaconine, α-solasonine, α-solamargine, α-ecdysone and matrine (Fig. 3) reduced moderately the number and size of root knots on tomato (Udalova et al., 2004). Two prenylated flavanones of *Phyllanthus niruri* have been evaluated their efficacy against *M. incognita*, and *Rotylenchulus reniformis*. The nematicidal activity against *M. incognita* of 8-(3-methyl-but-2-enyl)-2-phenyl chroman-4-one (LD_{50} 70.9 µg/ml) and 2-(4-hydroxyphenyl)-8-(3-methyl-but-2-enyl)-chroman-4-one (LD_{50} 14.5 µg/ml) (Fig. 3) was dose-dependent (Shakil et al., 2008).

Miscellaneous compounds such as fatty acid derivatives, polyynes, dithiins, and furans are considered to possess the nematicidal activity (Ghisalberti, 2002). Three diarylnonanoids malabaricones A, B and C (Fig. 3) from *Myristica malabarica* caused mortalities from 31-75% for PWN (Choi et al., 2008). Methyl pelargonate (Fig. 3) was active to *M. incognita* on soybean at concentrations less than 1.6 µg/ml (Davis et al., 1997).

Two polyynes pentayne and 9, 10-epoxy-heptadec-l-ene-4, 6-diy-n-8-ol (Fig. 3) from the roots of *Cirsium japonicum* inhibited reproduction of PWN. 1-Phenylhepta-1, 3, 5-triyne and 2-phenyl-5-(1-propynyl)-thiophene (Fig. 3) from *Coreopsis lanceolata* and *cis*-dehydromatricaria ester from *Solidago altissima* also inhibited the propagation of PWN at a dose of 110 µg/ball (Kawazu et al., 1980).

Thiarubrine C (Fig. 3) from the roots of *Rudbeckia hirta* was toxic to *M. incognita* and *Pratylenchus penetrans* at LC_{50} of 12.4 µg/ml and 23.5 µg/ml, respectively. Thiarubrine C was also effective in reducing plant infection when mixed with soil 24 hours prior to or at planting, unlike other related compounds such as α-terthieryl (Sánchez Deviála et al., 1998).

Marigold (*Tagetes* spp.) was reported to contain nematicidal principles such as α-terthiophene, bithienyl-butenin, acetoxybutinylbithiophene and hydroxybutinyl-bithiophene (Fig. 3) (Chitwood, 2002; Ploegn, 1999). Allicin (Fig. 3) from garlic *Allium sativum* caused inhibition on hatching of *M. incognita* at concentrations less than 0.5 µg/ml (Gupta and Sharma, 1993).

**Conclusions**

Sustainable agricultural development is consistently considered for most of countries to sustain the growing population. Currently, integrated crop management is playing an important role in organic farming. Biopesticides are key components of integrated crop disease management. Moreover, interest in phytochemical based-pesticides for crop protection is increasing because in public perception they are regarded as environmentally safe and less toxic to humans than synthetic chemicals. Additionally, it has been suggested that botanical extracts are more complex in comparison to synthetic pesticides and therefore, they may delay the development of resistance of phytopathogens.

Many natural product based-pesticides have been discovered up to now. Nevertheless, only about 30 different biopesticides are registered and currently marketed (Copping and Duke, 2007; Copping and
Menn, 2000). This is mainly due to high cost, low activity, or phytotoxic effects to crops. These factors have hindered commercialization of botanical pesticides. Despite this situation, however, efforts related to botanical pesticides have increased to develop commercial products that would abate the negative effects of inappropriate and intensive use of synthetic agrochemicals. With the growing acceptance of botanical pesticides as next generation of pest control products, the major companies as well as small companies will include botanical pesticides in their portfolio. Botanical pesticides can play an important role in the production of organic food and postharvest disease protection of food as well as in achieving sustainable agriculture.

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