

Phytochemicals taken from plants with potential in management of *Spodoptera frugiperda* (Lepidoptera: Noctuidae)

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ABSTRACT

In agriculture, there is a constant search for natural products with biological activities that minimize the environmental impact of various pesticides used such as insecticides. The chemical constituents present in plants have these activities and show promise in fighting pests in agriculture. An approach to the selection of new insecticides that fulfill the requirements of safety, efficacy and selectivity, can be through the study of defense mechanisms of plants. Recent studies have shown the potential insecticide substances and extracts isolated from plants against various insect pests that cause serious damage to crops or stored grain. These active ingredients are distributed by different plant organs and involved in secondary metabolism, are divided into three major groups: terpenes, phenols and nitrogenous compounds. Thus, this review aims to give an overview of the active ingredients obtained from plant extracts with potential insecticidal to *Spodoptera frugiperda* J.E. Smith (Lepidoptera: Noctuidae).

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INTRODUCTION

Since an ancient time in history the use of plant extracts is present not only because of his food character, but also to its herbal, cosmetic and agrochemical properties (Júnior and Bolzani, 2006). Biodiversity Brazilian genetics is very complicated, with more than 55,000 species cataloged from a total estimated between 350,000 to 550,000, which popularly have several biological activities (Simões and Schenkel, 2001). A Country like Brazil, with many climatic and geographical peculiarities, is home to a very big diversity of insects and plants. Besides the native species and the portion cultivated for commercial purposes, both for domestic consumption and for export, many plant species have been introduced by settlers and immigrants, being responsible for the introduction of exotic predators phytophagous. For many decades, Brazil has had its economy based on primary production sector and even today occupies a prominent position in the global supply of cereals, fruits and other products of plants and therefore pest control native or exotic is one challenge that remains and has

gotten worse year after year (Roel, 2001). In agriculture, there is a constant search for natural products with biological activities that minimize the environmental impact of various pesticides used such as insecticides. The chemical constituents present in plants have these activities and show promise in fighting pests in agriculture (Brito *et al.*, 2006). An approach to the selection of new insecticides that fulfill the requirements of safety, efficacy and selectivity, can be through the study of defense mechanisms of plants. Plant extracts have been used by man since the ancient world, a practice that continues today. Commercially, however, only few of these plants, including those that contain pyrethrins, rotenoids and alkaloids are used as a source of insecticides (Marangoni *et al.*, 2012). Recent studies have shown the potential insecticide substances and extracts isolated from plants against various insect pests that cause serious damage to crops or stored grain (Matos *et al.*, 2009; Lima *et al.*, 2009; Nebo *et al.*, 2010; Lima *et al.*, 2010). These active ingredients are distributed by different plant organs and involved in secondary metabolism (Oliveira *et al.*, 2006). Thus, this review aims to

give an overview of the active ingredients obtained from plant extracts with potential insecticidal to lepidopteran *Spodoptera frugiperda*.

PLANT SECONDARY METABOLITES

We give the name metabolism to the whole of chemical reactions that are continually taking place in each cell. Chemical compounds are formed, degraded or transformed by the action of enzymes, supplying the body with energy and compounds. The presence of specific enzymes ensures a certain direction to these reactions, establishing what is called the metabolic pathways (Lenhinger *et al.*, 2002). Plants have two types of metabolism: at first a metabolism which synthesizes the major macromolecules (proteins, carbohydrates, lipids and nucleic acids, which are the same in a plant or animal organism) and the secondary, which produces multiple compounds that are not considered essential, however guarantee the survival advantage to the plant (Simões *et al.*, 2004). These reactions aim, at first, the use of nutrients to satisfy the fundamental requirements of the cell (primary metabolism) (Simões *et al.*, 2007).

Plants, microorganisms and, in less extent, animals, have a whole arsenal metabolic able to produce, process and accumulate a lot of other substances not necessarily linked directly to maintaining the life of the organism producer (secondary metabolism) (Panizzi and Parra, 1990; Simões *et al.*, 2007; Taiz and Zeiger, 2013).

Secondary metabolites have their source from the metabolism of glucose via two intermediaries' main shikimic acid and ethyl acetate. They produce large molecules with functional groups such as fatty acids, esters, hydrocarbons, alcohols, aldehydes, ketones, acetylenic compounds, alkaloids, phenols and coumarins (Santos, 2001). Secondary metabolites are dissimilar from primary metabolites, because besides not being directly linked to the function of sustaining life, they have restricted distribution within and between plants (Taiz and Zeiger, 2013, Gonzaga *et al.*, 2008).

These metabolites have already been considered as plant excretion products. Currently it is known that many of these substances are directly involved in

the mechanisms that allow the adaptation of the producer in the environment where they live. Already they have been recognized several adaptive functions of these metabolites as defense against herbivores and microorganisms, UV protection, attraction of pollinators and attraction of seed dispersers animals, besides, functions allelopathic (Simões *et al.*, 2007; Schoonhoven *et al.*, 1997; Panda and Khush, 1995; Panizzi and Parra, 1990). The formation and storage of secondary metabolites are restricted to certain stages of plant development, organ and tissue-specific or specialized cells (Panda and Khush, 1995).

With regard to defense against herbivores, plants have developed two types of defenses, direct and indirect. In the direct defense, there are involved substances such as silica, secondary metabolites, enzymes and proteins, and organs such as trichomes and thorns that directly affect the performance of the insect. In the indirect defense, there are involved substances emitted by the plant itself that attract parasites and predators of phytophagous insect. Volatile terpenes and phenylpropanoids synthesized by plant species can have, depending the insect in case, attractive properties (supply, pollination) and / or deterrents and insecticides (Simas *et al.*, 2004). It can affect herbivores in several ways, such as deterrence, indigestible, inhibitors of oviposition and mortality of young adults (Gutiérrez and Villegas, 2008).

Some authors associate the fact that plants produce many different secondary metabolites to the fact that they do not have the ability to move on, being an easy target for herbivores (Panda and Khush, 1995, Schoonhoven *et al.*, 1997, Simões *et al.*, 2007, Taiz and Zeiger, 2013). The ability of competition and survival of plants is therefore deeply affected by the ecological functions of these metabolites (Taiz and Zeiger, 2013). The secondary metabolites that exhibit biological activity are known as active ingredients and have aroused interest for a promising market for the discovery of therapeutic activities. Secondary metabolites are divided into three major groups: terpenes, phenols and nitrogenous compounds (Schoonhoven *et al.*, 1997, Taiz and Zeiger, 2013).

Terpenes

Terpenes cover a wide variety of substances of plant origin and its ecological importance as defensive plants are well established. According to Garcia and Carril (2009), terpenoids constitute the largest group of secondary metabolites, with more than 40,000 different molecules (Figure 1), which function in plant is to protect or to attract beneficial organisms (Tholl and Lee, 2011) generally insoluble in water and connected to defense against herbivore due to the fact of conferring bitter or having the same molecular structure of the molting hormone of insects, to interrupt that process function, or by making complex sterol precursors of animal hormones (Ziger and Taiz, 2013).

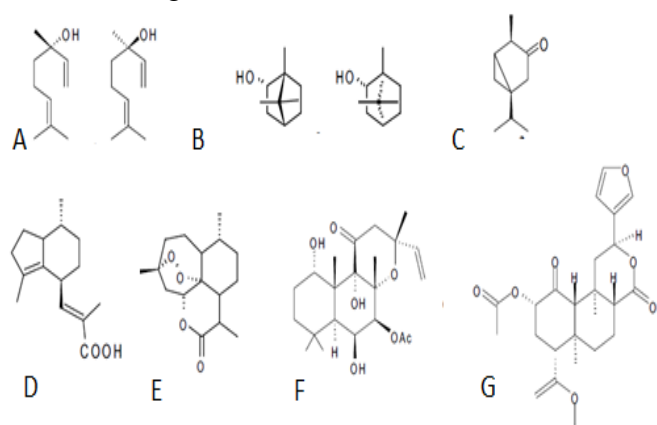


Figure 1. Chemical structure terpenoids (A) Linalool, (B) Borneol, (C) α -thujone, (D) valerenic acid, (E) artemisiana, (F) Forskolol, (G) A. Salvinorin. Adapted from Passos *et al.* (2009).

Several monoterpenes were isolated and evaluated for toxicity to different insects. These studies involved α -pinene, β -pinene, 3-carene, limonene, myrcene, α -terpinene and camphene (Junior, 2003). On the lower level, the relatively simple structure of monoterpenes such as limonene, myrcene and the epoxy-pulegone, they functions to the plants that produce them. Apparently its insecticidal activity was due to inhibition of acetylcholinesterase in insects, which is the case of epoxy-pulegone, which causes effects such as retardation or growth inhibitor, reduction of reproductive capacity, appetite suppressants and may lead the predatory insects to death by starvation or direct toxicity (Marangoni *et al.*, 2012).

Phenolic Compounds

Among the products of secondary metabolism of plants, phenolic or polyphenols are present themselves as one of the most numerous groups of substances, with more than 8,000 phenolic structures known and widely distributed throughout the plant kingdom (Harborne, 1993). They are a class of very diversify natural products, presenting like common characteristic the presence of at least one aromatic ring, wherein at least one hydrogen is substituted by one free hydroxyl group or other derivative function as ester or heteroside (Carvalho *et al.*, 2007). They can to be from simple molecules, such as phenolic acids, to highly polymerized compounds such as tannins. They appear primarily in the conjugated form with one or more sugar residues linked to hydroxyl groups, although there have direct connections from a sugar unit with an aromatic carbon (Bravo, 1998).

The phenolic compounds are chemically a heterogeneous group, with some soluble in water and others not; in general molecules are very unstable, easily oxidized, and susceptible to degradation. While some phenolic compounds have attractive function to pollinators or to fruit dispersers, other have refuse function to herbivores. They also act as protection against UV radiation or to have allelochemistry function in competing adjacent plants (Ziger and Taiz, 2013).

Several groups of plant secondary metabolites are classified like phenolic compounds such as phenolic acids, coumarins, xanthenes, flavonoids, anthocyanins, tannins and lignans polymers (Bruneton, 2001; Carvalho *et al.* 2007). Flavonoids and phenolic compounds act in plants like antioxidants, antimicrobials, photoreceptors, visual appeal and as a repellent. Many studies suggest that these compounds exhibit several biological activities. The ability of polyphenolic compounds to act as antioxidants *in vitro* has been the subject of several studies in the last years (Pieta, 2000). Flavonoids (Figure 2) represent one of the most important and diverse groups among the products of plant origin and are widely distributed in the plant kingdom. The biochemical activities of flavonoids and their metabolites depend on their chemical structure, which can vary with substitutions

including hydrogenation, hydroxylation, methylation, malonilation, sulfatation and glycosylation. Flavonoids and isoflavones commonly occur as esters, ethers or derivatives of glycosides or yet mixture of them (Birto *et al.*, 2001).

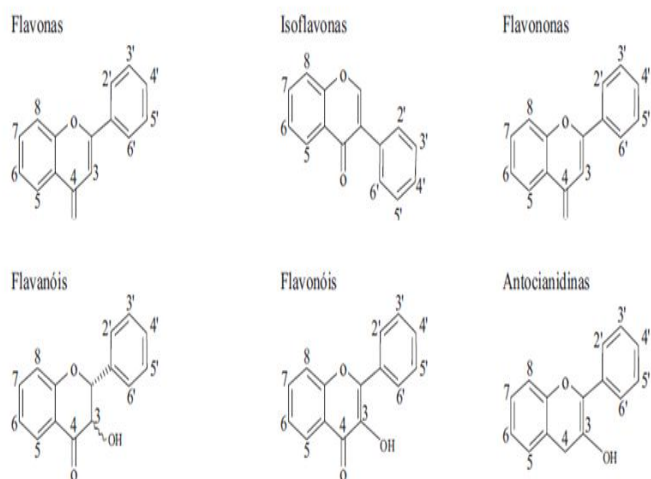


Figure 2.The main Flavonoids found in the plant kingdom. Adapted from Silva and Jorge (2011).

Nitrogen compounds

Nitrogenous compounds are well known in plant defense against herbivory, mainly alkaloids and cyanogenic glycosides. These compounds have toxic or medicinal action for humans (Ziger and Taiz, 2013). Alkaloids constitute a wide group of secondary metabolites with structural diversity (Figure 3) and be defined as "cyclic organic compounds of natural origin containing one nitrogen in a negative oxidation state with limited distribution among organisms" as methylxanthine, theophylline, theobromine, codeine, thebaine, papaverine and narcotine caffeine (Pelletier, 1983).

Among the most important natural alkaloid used to control pests are nicotine and nor-nicotine. The use of these alkaloids began in the sixteenth century and reached 2,500 tons in the middle of the nineteenth century. Since then, the annual production has been declining and currently covers about 1,250 tons of nicotine sulphate and 150 tons of nicotine, because of their high cost of production, bad odor, extreme toxicity to mammals and limited insecticidal activity (Viegas Jr., 2003).

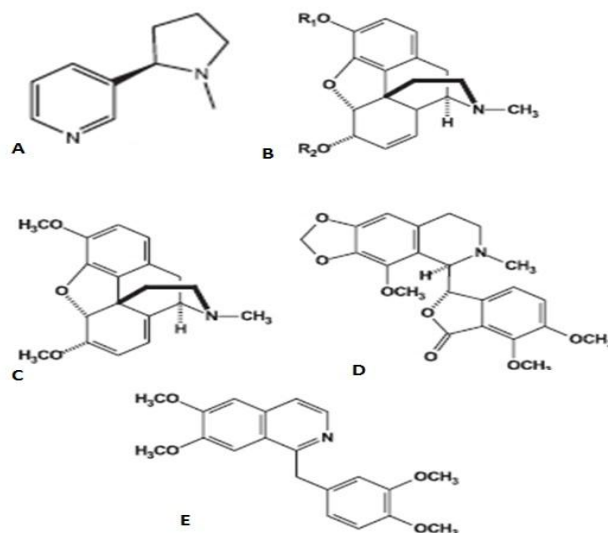


Figure 3.Chemical structure of alkaloids. (A) nicotine, (B) codeine; (C) thebaine; (D) narcotine; (E) Papaverine. Adapted from Viegas Jr. (2006).

Management of *Spodoptera frugiperda*

The fall armyworm corn, *Spodoptera frugiperda* (J.E. Smith, 1797) (Lepidoptera: Noctuidae) is a polyphagous insect widely distributed in tropical and subtropical regions of the Americas, being found from southern Canada to southern South America (Uruguay and Argentina) (Ashley *et al.*, 1989; Sarmiento *et al.*, 2002; Alves *et al.*, 2012). It is frequently observed attacking crops of maize, rice, cotton, sorghum and soybean, where causes significant feed more than 80 species of plants, distributed over 20 families (Cruz, 1995; Barros *et al.*, 2010), predominantly in grasses (Sarmiento *et al.*, 2002). Crop rotation is favoring the movement of *S. frugiperda* between crops due to being considered a minor pest, previously, in some cultures (Barros *et al.*, 2010). The larvae feed on the leaves, leaf area and reducing the photosynthetic capacity of the plant and, consequently, the production of crop (Sarmiento *et al.*, 2002).

The rice (*Oryza sativa* L.), a plant belonging to the family Poaceae, is considered the most important cereal in the world, since this is a staple food for a third of world population. It presents an enormous economic importance for the Country, since in Brazil are planted annually 2,454,700 hectares, which about 1,053,0000 are in the state of Rio Grande do Sul State, which has an area of 43% of all acreage in Brazil, participated with 32% of this reduction, the remaining balance due to the

reduction of other states (Conab, 2012). In rice, *Spodoptera frugiperda* (Smith) considered plague of early stage because it attacks seedlings at the beginning of their development, feeding the leaves and cut the new stems, close to the ground (Sosbai, 2005), causing loss of 14 to 24% of the grains. Depending on the population level, the destruction of the crop can be full (Busato *et al.*, 2006).

The area planted with maize [*Zea mays* L. (Poaceae)], first harvest in the period 2011/12 was set at 7,52 million hectares, and Rio Grande do Sul responsible for 1,153,70000 hectares (Conab, 2012). The economic importance of maize is characterized by various forms of use, which varies from the feed to the high-technology industry. In fact, the use of maize grain as animal consumption of most of the cereal, i.e. about 70% of the world. In the United States, about 50% is used for this purpose, while in Brazil ranges from 60 to 80%, depending on the source of the estimate and from year to year (Embrapa, 2011). In corn, the attack of *S. frugiperda* can occur from the seedling stage until tasseling and the formation of spikes. In the later attacks can be found between individuals and thatched cob, which pierce the female inflorescence destroying grains (Oliveira *et al.*, 2007). There have been losses of 20% to 100% in the production of this crop, only caused by this insect (Rossi *et al.*, 2012). Associated with the occurrence of pests there are still risks of environmental impact rising from the growing irrational use of chemical insecticides applied to control. The market for agrochemicals in Brazil, driven by sales of insecticides, the Brazilian market of agrochemicals increased 14.4%, or 1,2 billion, and reached a record of US\$ 9,71 billion (about R\$ 19,5 billion) in 2012. Altogether we sold 823,220 tons of chemicals to control pests and weeds in crops, an increase of 12.6% (FNP, 2013).

With this, Brazil maintains its position as the second largest world market for pesticides. The country lags behind the United States, where sales totaled US\$ 12.9 billion (about US\$ 26 billion) last year, according to the U.S. Department of Agriculture (USD) (FNP, 2013). Chemical insecticides are widely used for the control of pests and are used improperly, leading to the development of resistant populations of the insect, the emergence of new

pests or other upwelling (Mária and Rosilda, 2010). The phytotoxicity of chemical insecticides on other non-target organisms, besides the increase in the cost of pesticides, the cost for the development of chemical pesticides is high and has increased over the years due to the need for new molecules and formulations more appropriate, what has led to an increased interest in research of alternative insecticides (Raguraman and Singh, 1999; Almeida and Batista Filho, 2001). Among these alternatives, we highlight the use of allelochemicals extracted from plants (Jacobson, 1989).

Extracts on the management of *S. frugiperda*

The use of plant extracts in the control of pests is growing positively in light of the requirement of consumers in having the product available free of pesticides, awareness is contributing to the continuity of local biodiversity and enabling a better quality of life for the farmers (Veiga, 2003). Many studies have demonstrated the effect of the use of plant extracts, which are a source of secondary metabolic compounds such as natural insecticides in the management of *S. frugiperda* (Table 1). The deleterious effects on insects may be toxicity, growth inhibition, reduced fecundity, fertility and repellency.

Encouraging research on interactions plants / insects in recent decades reveals the potential use of plant metabolites or allelochemicals as agents for this purpose (Pavela, 2004). Phytochemicals taken from plants with potential for insect control can be used as an alternative to synthetic chemicals or added to other insecticides in pest control programs. On demand for the development of new active agents based on natural products, efforts are made to select, isolate, and develop phytochemicals with pesticidal activity (Mulla and Tianyun, 1999). Several strategies are able to determine the activity of natural products against insects. In general, the use of substances extracted from plants, as insecticides, has numerous advantages compared to synthetic materials: natural insecticides are obtained from renewable resources and are rapidly degradable; development of insect resistance to these substances, comprising the association of several active principles is slow, these pesticides are easy to access and obtain and leave no residues in food, in addition to having low production cost (Roel, 2001).

Table 1. Deleterious effects on *Spodoptera frugiperda* after ingestion of different plant extracts.

| Plant | Action | Reference |
|--|---|--------------------------------------|
| <i>Anadenanthera macrocarpa</i> (Berth.) Brenan (Fabaceae) | Reduction of larval and larval viability (%) increase in the number of eggs/egg mass was higher in treatments plus extract. | De Moura <i>et al.</i> (2012) |
| <i>Artemisia verlotorum</i> Lamotte (Asteraceae), <i>Malva sylvestris</i> L. (Malvaceae), <i>Petiveria alliacea</i> L. (Phytolaccaceae) and <i>Zingiber officinale</i> (Zingiberaceae) | >80% Mortality | Tagliari <i>et al.</i> (2010) |
| <i>Trichilia pallida</i> Swartz (Meliaceae) | 100% Mortality | Roel <i>et al.</i> (2000) |
| <i>Cabralea canjerana</i> (vell.) Mart. (Meliaceae), <i>Trichilia pálida</i> Swartz (Meliaceae), <i>Cedrela fissilis</i> (vell.) (Meliaceae) and <i>Melia azedarach</i> L. (Meliaceae) | 100% Mortality | Hernandez and Vendramim (1996) |
| <i>C. canjerana</i> (vell.) Mart. (Meliaceae) and <i>Swietenia macrophylla</i> King (Meliaceae) | Reduction in weight of larvae. | Hernandez and Vendramim 1997 |
| <i>Azadirachta indica</i> A. Juss (Meliaceae) | 100% Mortality | Hernandez and Vendramim 1997 |
| <i>Melia azedarach</i> L. (Meliaceae) | 100% Mortality | Brito <i>et al.</i> (2004) |
| <i>Trichilia pallens</i> C.DC. (Meliaceae) | 98,7% Mortality | Borgoni and Vendramim (2005) |
| <i>Cara paguianensis</i> Aubl. (Meliaceae) | Stretching larval, pupal weight reduction in mortality of 50%. | Sarria <i>et al.</i> (2007) |
| <i>Lupinus estipula</i> J. Agardh (Fabaceae) | 83% Mortality | Bermúdez-Torres <i>et al.</i> (2009) |
| Saponina - <i>Passiflora alata</i> Curtis (Passifloraceae). | Prolongation of the larval period. | D’ Incao <i>et al.</i> (2012) |
| <i>Copaifera langsdorffii</i> Desf. (Fabaceae) | 60% Mortality | Alves <i>et al.</i> (2012) |
| <i>Ricinus communis</i> L. (Euphorbiaceae) | 89.9% Mortality | Rossi <i>et al.</i> (2012) |
| <i>Azadirachta indica</i> (Meliaceae) and <i>Trichilia pallida</i> (Meliaceae). | Mortality, weight and length of the tracks and head capsules were significantly affected. | Conceschi <i>et al.</i> (2012) |
| <i>Malva silvestris</i> (Malvaceae), <i>Canavalia ensiformes</i> (Phaseaceae), <i>Cordia verbenacea</i> (Boraginaceae), <i>Curcuma zedoaria</i> | Prolongation of larval and pupal stages, reduction in size and weight of pupae, negative effects on oviposition and fertility and abnormalities in the formation. | Knaak <i>et al.</i> (2012) |

Phytochemicals for *Spodoptera*

| | | |
|---|--|-------------------------------|
| (Zingiberaceae), <i>Cymbopogon citratus</i> (Poaceae), <i>Symphitum officinalis</i> (Boraginaceae), <i>Ruta graveolens</i> (Rutaceae), <i>Baccharis genistelloides</i> (Asteraceae), <i>Zingiber officinale</i> (Zingiberaceae), <i>Artemisia verlotorum</i> (Asteraceae) and <i>Melissa officinalis</i> (Lamiaceae). | | |
| <i>Cedrela fissilis</i> and <i>Cipadessa fruticosa</i> (Meliaceae) | Elongation of the larval stage, followed by a decrease in pupal weight, larval mortality of 63.3%. | Matos <i>et al.</i> (2010) |
| <i>Azadirachta indica</i> A. Juss. (Meliaceae) | All concentrations tested negatively affect larval development. | Viena <i>et al.</i> (2007) |
| <i>Ochroma pyramidalis</i> (Bombacaceae), <i>Schinus terebinthifolius</i> (Anacardiaceae), <i>Enterolobium contortisiliquum</i> (Fabaceae) and <i>Peltophorum dubium</i> (Fabaceae) | Reduction in weight of larvae and pupae, decreased survival during the larval and pupal stages, extending the duration of the immature stages. | Tirelli <i>et al.</i> (2010) |
| <i>Azadirachta indica</i> A. Juss. (Meliaceae). | CL ₅₀ = 2,67 mg mL ⁻¹ | Teixeira <i>et al.</i> (2003) |

The toxicity of a chemical in insects does not necessarily qualify it as an insecticide. Several properties must be associated to activity, such as effectiveness at low concentrations, lack of toxicity against mammals and higher animals, absence of phytotoxicity, to be easily obtained, easy handling and application, and economic feasibility not be accumulated in the adipose tissue of human and animal household. It is evident that the characteristics listed refer to that insecticide considered ideal, which is rarely the case. Within the classification of insecticides are also included substances that repel and attract insects (Mariconi, 1984; Addor, 1994).

However, Isman (1997) reported some barriers to the commercialization of phytochemicals. Among these, we have (1) the scarcity of botanical resources, necessitating the production of botanical insecticides on a large scale for the market, unless the plant in question is extremely abundant in nature

or have already been produced for other purposes; (2) standardization of extracts and quality control, based on the active ingredients, and (3) difficulties in recording these phytochemicals. This can prevent many botanical pesticides reaching the commercial sphere in countries where they have demand for these products.

PERSPECTIVES

The pest control, using plants with insecticidal activity, is a promising, feasible and environmentally friendly and as we can see, has increased importance and attention of the various segments of science, for its various effects on insects. But there are other plants that have not yet been studied their activities insecticides, opening the door for several other researches. New substances are therefore required for effective pest control, offering greater safety, selectivity, biodegradability, economic feasibility, applicability in integrated pest management of insect control and low environmental impact.

The use of botanical insecticides as a strategy within the Pest Management is promising, to be extended the research on plant extracts, in field trials and studies of quality control to enable greater adoption of these natural products for farmers and technicians. Currently, there is a promising market for biopesticides and natural insecticides. The production of natural chemicals represents 7.5% of the market for chemicals, pharmaceuticals, veterinary and plant protection. In this sense, to isolate, characterize and synthesize or finally biosynthesize compounds of interest in insect control becomes a constant challenge.

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