Potentially Phytotoxic of Chemical Compounds Present in Essential Oil for Invasive Plants Control: A Mini-Review

Mozaniel Santana de Oliveira,
Wanessa Almeida da Costa,
Priscila Nascimento Bezerra,
Antonio Pedro da Silva Souza Filho and
Raul Nunes de Carvalho Junior

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Abstract

The control of invasive plants is still carried out with the use of synthetic chemical agents that may present high toxicity and, consequently, be harmful to humans and animals. In Brazil, especially in the Amazon, small producers use this kind of technique in a rustic way, with brushcutters or fire. In this sense, the search for natural agents with bioherbicide potential becomes necessary. Examples of these agents are the essential oils that over the years have been shown to be a viable alternative to weed control. Thus, this review aims to show the potentially phytotoxic activity of allelochemicals present in essential oils of different aromatic plants.

Keywords: natural products, essential oils, allelochemicals, allelopathy

1. Introduction

The performance of agricultural activity in tropical regions, both in fertile and in low fertility soils, has been limited by the occurrence of a series of extremely aggressive and diverse plants, called weeds. The main consequence of crop infestation by these plants is increasing costs to maintain the crops and reduction of productivity and its consequent competitive capacity. These plants may also represent an additional problem for farmers either because they are often toxic to different animals or because they are permanent sources for the spread of diseases to crop plants [1]. In this context, weed management and control become crucial both from the point of view of crop productivity and the profitability of the farming system.

In modern agriculture, where high yields are expected, in the face of increasing demands for food – due to the increasing world population – the control of these plants has been made, basically, by the use of chemical herbicides. However, such a procedure may not be sustainable over time, especially because it conflicts with the interests of modern society, which is increasingly concerned with the quality of food and with the preservation of natural resources. At the same time, the reduction in the efficiency of the current products available in the market has been observed as a consequence of the appearance of resistant plants [2, 3], leading to an increase in the use of herbicides or the contractions employed, which only increases the problem. All these factors point to the need of science to make available new and revolutionary methods of weed control.

A viable alternative to this challenge are the numerous chemically diverse compounds produced by plants that may offer new chemical structures capable of efficiently replace those already available in the market. In this line, crude extracts and isolated or associated chemical substances can be an excellent strategy to partially or totally replace the use of herbicides.

Over the last decades, different chemical compounds with bioherbicidal properties have been isolated and identified in different plants [4–7]. Among the many chemical classes with potential use in weed management, the secondary metabolites present in essential oils can be highlighted, since the different chemical classes of volatile compounds are notable for the wide potential of use in different activities of interest for humanity and specifically in the management of weeds.

2. Allelopathy history

Allelopathy is the chemical interaction between plants and other living organisms [8]. There are two types of interactions between plants: a phytotoxic one, which inhibits the germination of seeds and the development of the radicle and hypocotyl [9], and a stimulatory effect, which favors the development of the plant [10]. The chemical substances responsible for the allelopathic effect are called allelochemicals [11].

The allelopathy is a relatively new science, having its basic concepts established over the last 8 decades. However, chemical interactions among plants are not exactly new, since reports on the subject are found in old references. [12–16]. In the 1800s, several phenomena were attributed to the chemical interaction among plants [17]. In the early 1900’s, [18] reported the presence of toxic compounds produced by plants that could be extracted from the soil. The first reports proving the interference promoted by chemical compounds were developed in the 1960’s [19], showing that the volatile compounds were affecting the dynamics among plants.

3. Control of invasive plants

Currently, the chemical control method is the most used to inhibit the growth of invasive plants, which includes the use of synthetic herbicides, in large quantities, mainly by large producers, as reported by some authors [20, 21]. The use of synthetic and toxic chemical herbicides in management areas promotes the death of weeds in a selective way and, consequently, it ends the competition among the plants, helping to increase the production of green mass in the pasture [22]. The increasing use of agrochemicals may represent an unsustainable practice because these pesticides can pollute the environment and promote the contamination of various animal species. Also, new insecticide-resistant insects are appearing and invasive plants that are tolerant to modern herbicides are becoming more frequent [23].

Weed resistance to herbicides may be related to an evolutionary process; however, some developments of resistant weed biotypes are imposed by agriculture through selection pressure caused by the intensive use of herbicides. Weed resistance to herbicides may result from biochemical, physiological, morphological or phenological changes of certain invasive plant biotypes. Many cases of resistance to herbicides result from either the alteration of the site of action of the herbicide or the increase of its metabolism, or the departmentalization and compartmentalization of the herbicide in the plant [24, 25]. This way, allelopathy can be a natural alternative for the control of invasive plants.

4. Volatile allelochemicals

Weeds promote two basic types of interference in agricultural crops: allelospoly and allelopathy. Allelospoly is the type of interference promoted by competition for essential factors to the species survival, such as water, nutrients and physical space. Allelopathy involves the production of allelochemicals and subsequent release into the environment [26]. Almost all allelochemicals exist in conjugated, non-toxic forms. The toxic fragment can be released after exposure to stress or after tissue death [27].

The use of allelopathy for weed control may be an ecologically viable alternative [28]. Thus, the use of essential oils with phytotoxic potential is becoming widespread, since the allelochemicals present in these oils generally have low cytotoxicity. For example, [29] evaluated the effect of *Carum carvis* essential oils rich in carvone (71.08%) and limonene (25.42%), and verified that this oil has a strong phytotoxic activity on seed germination and radicle elongation of *Linum usitatissimum*, *Phalaris canariensis* and *Triticum aestivum*.

Another example is the eucalypt essential oil that has a rich chemical composition in 1,8-cineole (58.3%), α-pinene (17.3%) and α-thujene (15.5%), which significantly inhibited seed germination of *Sinapis arvensis*, *Diplotaxis harra* and *Trifolium campestre*, in different intensities according to the recipient species, demonstrating that each species has a different specificity. In addition, the application of post-emergence oil causes inhibition of chlorophyll production, leading to injuries such as chlorosis, necrosis and even complete wilting of plants [30].

Plant species such as *Origanum onites L.* and *Rosmarinus officinalis L.* also show strong allelopathic activity on species of *Poaceae* and invasive plants, by suppressing germination rate and elongation of radicle and hypocotyl [31]. The phytotoxic effects related to these two species of aromatic plants may be related to their rich chemical composition in the oxygenated monoterpenes 1,8-cineole, linalool, camphor and carvacrol and the monoterpene hydrocarbon p-cymene [32–35], however, compounds found in lower concentrations as methyl phenylpropanoids have also demonstrated good allelopathic activity [36].

In the case of essential oils for the control of invasive plants, it is usually analyzed the effects of individual form, attributing the phytotoxic activity to only one component [37, 38]. However, the effects of volatile oils can also be related to the mixture of compounds, such as *Artemisia scoparia* oil which has a mixture of compounds such as monoterpene hydrocarbons, oxygenated monoterpenes, sesquiterpene hydrocarbons, oxygenated sesquiterpenes, aliphatic compounds and other aromatic compounds [39]. The chemical composition of the essential oils depends on the biosynthetic path of the different classes of compounds, as can be observed in **Figure 1**, which brings the biosynthesis of some classes of volatile compounds.

Compounds such as eucalyptol, β-phellandrene, hexyl butanoate, *p*-cymene, α-ionone, (z)-3-octen-1-ol, theaspirane a, vitispirane, dihydro-(−)-neoclovene, β-caryophyllene, (e)-2-octen-1-ol, a-terpineol, dehydro-ar-ionene, methyl salicylate, (z)-b-damascenone, (z)-dehydro-ar-ionene,

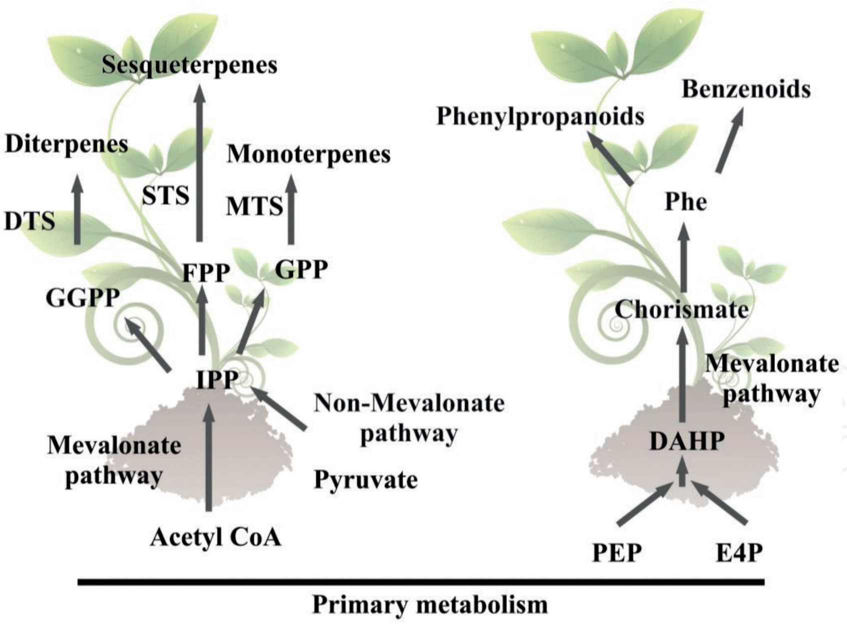

Figure 1. Biosynthesis of plant volatiles. Overview of biosynthetic pathways leading to the emission of plant volatile organic compounds. The plant precursors originate from primary metabolism. Abbreviations: DTS: Diterpene synthase; FPP: farnesyldiphosphate; GGPP: geranylgeranyldiphosphate; GLVs: green-leaf volatiles; GPP: geranyldiphosphate; IPP: isopentenyl pyrophosphate; MTS: Monoterpene synthase; STS: Sesquiterpene synthase; DAHP: 3-deoxy-D-arabinoheptulosonate-7 phosphate; E4P: erythrose 4-phosphate; PEP: phosphoenolpyruvate; Phe: phenylalanine. This flowchart was adapted from [40] and [41].

10-(tetrahydro-pyran-2-yloxy)-tricyclo[4.2.1(2,5)]decan-9-ol, (−)-caryophyllene oxide, dihydro-β-ionone, viridiflorol, cubenol, caryophyllene, α-bisabolol oxide-b, tetracosane and *n*-hexadecane can be found in *Anisomeles indica* essential oil and also present good phytotoxic activity against invasive plants [42]. As well as *P. heyneanus Benth* essential oils, rich in patchouli alcohol, α-bulnesene, α-guaiene, seichelene and α-patchulene, and *P. hispidinervium* C. DC oils, rich in safrole, terpinolene, (E)-β-ocimene, δ-3-carene and pentadecane [43].

4.1. Monoterpenes

The monoterpenes have presented good phytotoxic activity, and reports of the use of these compounds to control plants refer to the 1960s [44]. This activity depends on the structural

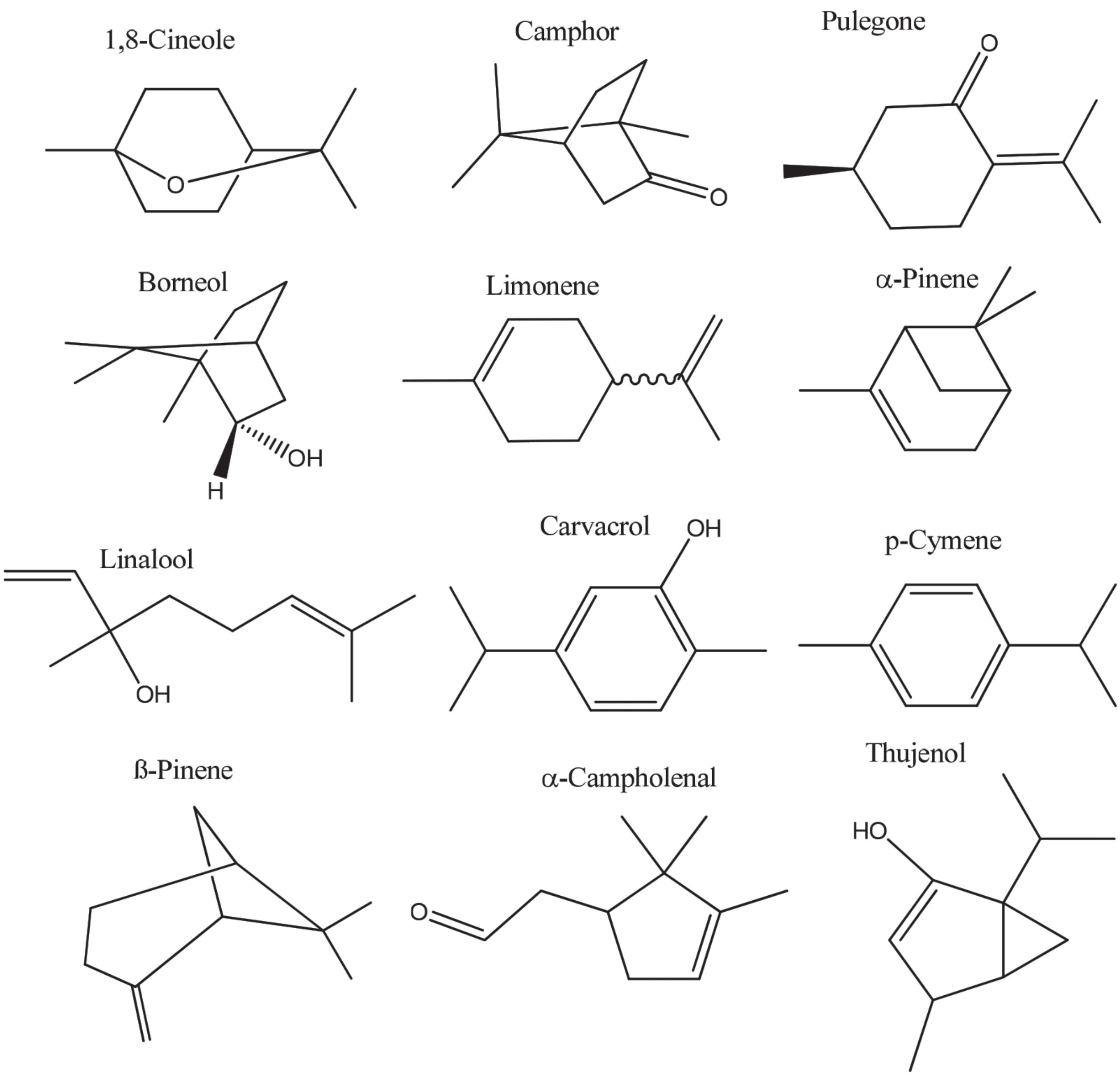

Figure 2. Chemical structures of oxygenated and non-oxygenated monoterpenes with bioherbicidal action.

characteristics of the molecules; for example, oxygenated monoterpenes exhibit different effects on germination and seedling development, and also alter cellular respiration, which impairs energetic metabolism [33, 34]. However, these phytotoxic effects promoted by a chemical species depend on its concentration, for example, *Lactuca sativa* essential oil composed essentially of α-pinene (16.00%), 1,8-cineole (66.93%) and pimonene (10.04%) presents different rates of germination inhibition [45].

In general, oxygenated monoterpenes have the highest phytotoxic effects over non-oxygenated [46]. However, there are non-oxygenated volatile molecules such as limonene which also have good phytotoxic activity [47]. Some monoterpenes had high inhibitory activity on germination and radicle elongation, and this may be related to the anatomical and physiological changes in the host plants, as well as to the reduction in some organelles such as mitochondria, and accumulation of lipid globules in the cytoplasm [48]. In **Figure 2**, the chemical structures of some monoterpenes with phytotoxic activity can be observed.

4.2. Sesquiterpenes

Bioassays have demonstrated that the sesquiterpenic allelochemicals β-cariofilene, β-copaene, spathulenol, germacrene B, bicyclogermacrene, globulol, viridiflorol, a-guaiene, and g-elemene have presented phytotoxity against various invasive plants and, in some cases, promote inhibition of other plants development, when they are close to species that produce these secondary metabolites [49–51]. Authors compared the effects of essential oils rich in sesquiterpenes and others rich in monoterpenes and found that the effects presented by sesquiterpenes, in some cases, may be smaller in relation to the affections exhibited by monoterpenes [52]. **Figure 3** shows the chemical structures of oxygenated and non-oxygenated sesquiterpenes with phytotoxic action.

However, this depends largely on the presence of oxygenated and non-oxygenated, cyclic or acyclic molecules, because depending on the molecular conformation the allelopathic effect may be higher or lower [53, 54]. This justifies the results obtained by other authors [55], who analyzed the effects of fractions of essential oils of *E. adenophorum,* of the inflorescence region, rich in sesquiterpenes, and its root rich in monterpenes. When the oils were tested at the same concentration (1 μL/mL), they inhibited germination and seedling elongation at the same ratio.

4.3. Phenylpropanoids

Phenylpropanoids are a class of secondary metabolites that are also naturally present in plants, and have exhibited strong phytotoxic activity against invasive plants. In 2016, [9] demonstrated that eugenol is the main active ingredient of clove essential oil and is also the agent possibly promoting phytotoxic activity against the invasive plants *Mimosa pudica* and *Senna obtusifolia*. Other authors also report the potentially allelopathic activity

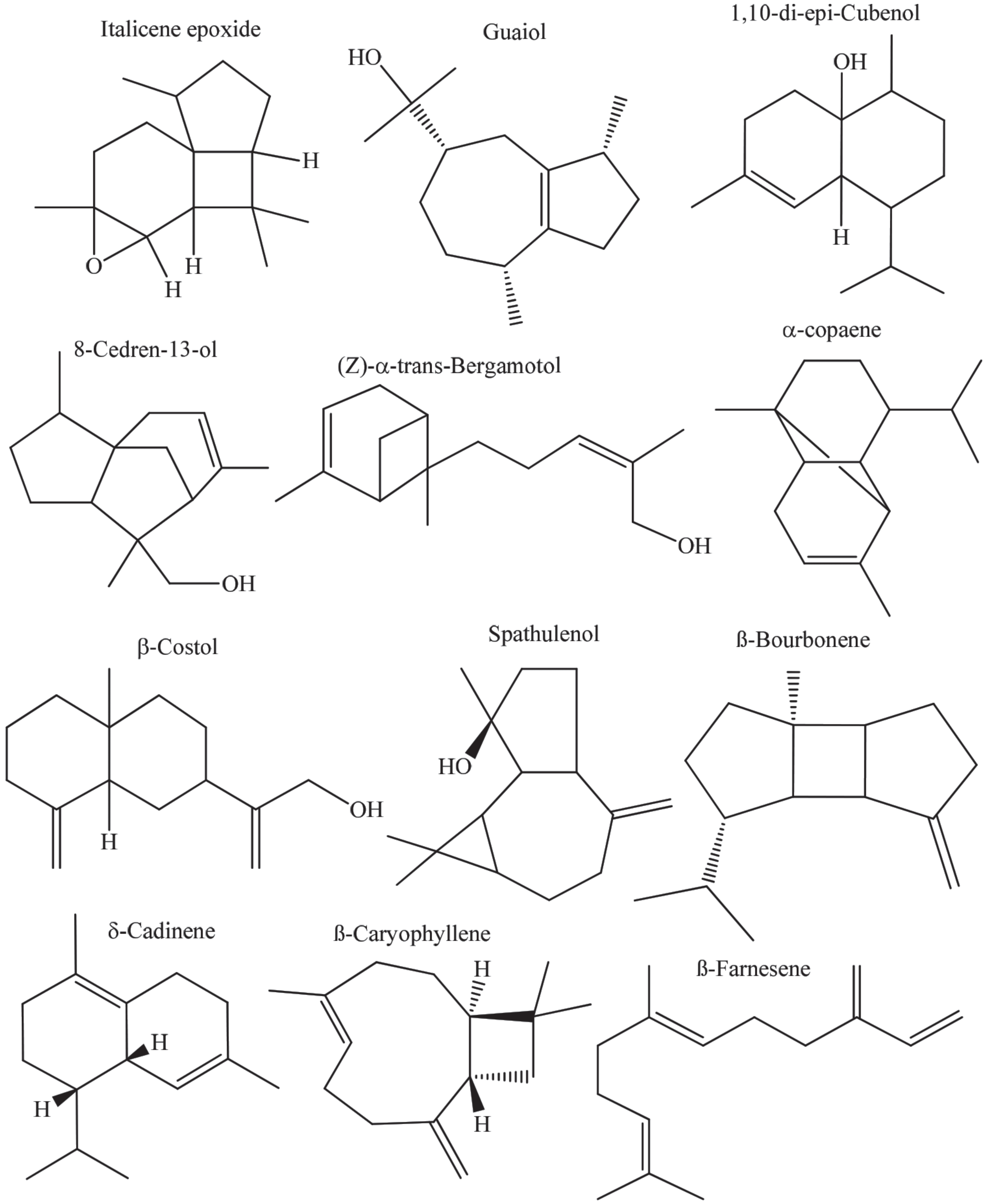

Figure 3. Chemical structures of oxygenated and non-oxygenated sesquiterpenes with bioherbicidal action.

of clove essential oil *Syzygium aromaticum* [56–58]. In addition to eugenol, other phenylpropanoids present in essential oils with phytotoxic activity are eugenyl acetate, safrole, methyl eugenol, anethole, myristicin, estragole, anethole and trans-anethole [36, 59–64]. **Figure 4**

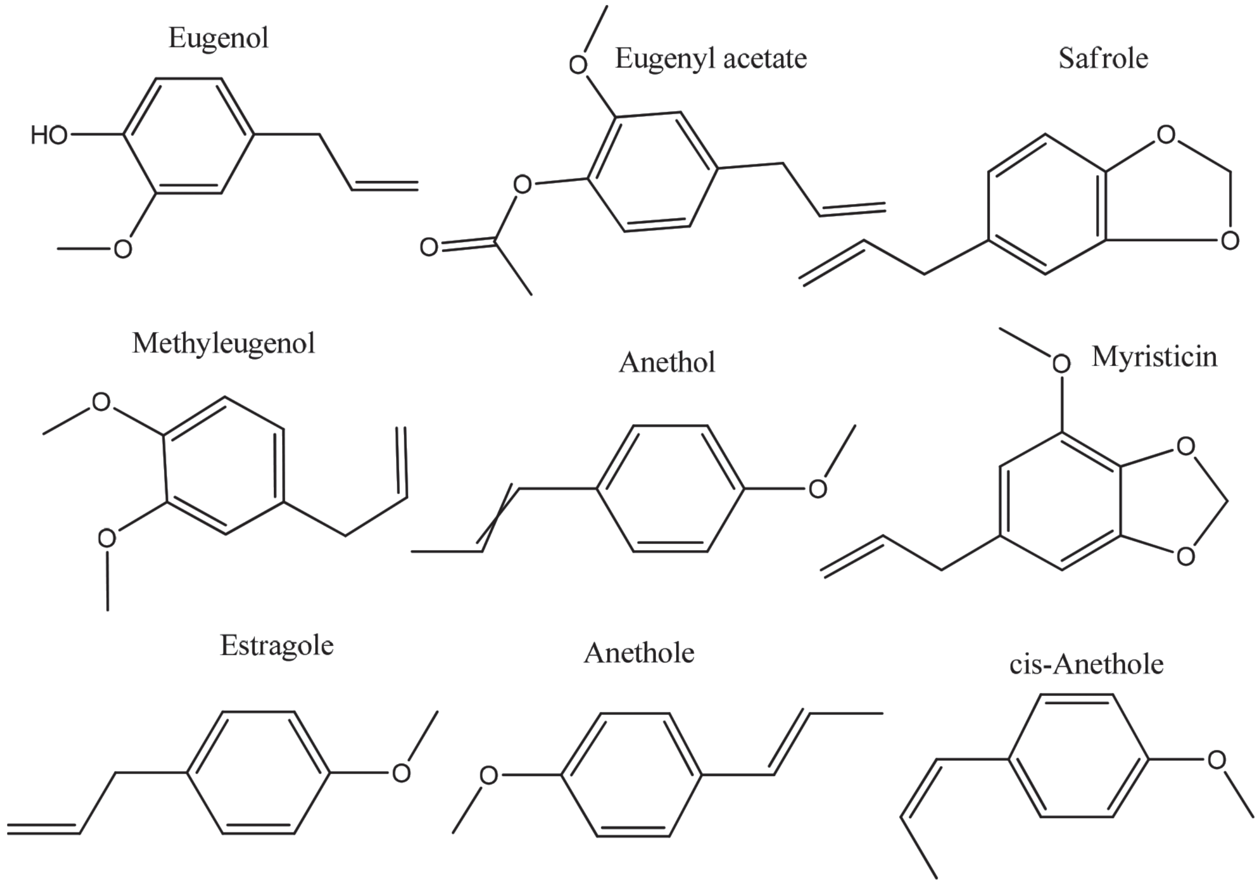

Figure 4. Chemical structures of phenylpropanoids with bioherbicidal action.

shows the chemical structures of the phenylpropanoids with potential use for control of invasive plants.

5. Conclusion

For essential oils to have good phytotoxic activity, some factors such as chemical composition, concentration and host plants may be taken into account. Among the monoterpene allelochemicals we can highlight the 1,8 cineole, among the sesquiterpenes or β-caryophyllene and among phenylpropanoids, eugenol. On the other hand, one of the difficulties that can appear for the use in large scale of essential oils is the volatility of their components.

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Author details

Mozaniel Santana de Oliveira[1]*, Wanessa Almeida da Costa[2], Priscila Nascimento Bezerra[1], Antonio Pedro da Silva Souza Filho[3] and Raul Nunes de Carvalho Junior[1,2]*

*Address all correspondence to: mozaniel.oliveira@yahoo.com.br and raulncj@ufpa.br

1 LABEX/FEA (Faculty of Food Engineering), Program of Post-Graduation in Food Science and Technology, Federal University of Para, Belém, Pará, Brazil

2 Program of Post-Graduation in Natural Resources Engineering, Federal University of Para, Belém, Pará, Brazil

3 Laboratory of Agro-industry, Embrapa Eastern Amazon, Belém, Pará, Brazil

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