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Natural Compounds as Active Ingredients for Potential New Bioherbicides: Towards Sustainable Weed Control

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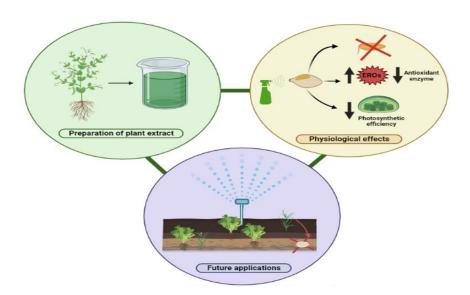
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Abstract

Plants have a great diversity of species and metabolic complexity. In the environment, they can interact between species by releasing chemical compounds, known as allelochemicals. This has aroused interest in the agricultural area due to the demand for environmentally friendly products, which cause less risk to human health and to the surroundings of cultivated areas. In this review we report results of plant extracts rich in allelochemicals that have herbicidal potential, since they alter the physiological responses of plants, being the percentage of germination, antioxidant activity and effect on the photosynthetic apparatus. This evidence strengthens the improvement of natural compounds as herbicidal active principles, as substitutes for chemical pesticides. Since the application of bioherbicides in agricultural crops are the subject of research and future applications in the field.

Key Words: allelochemicals; plant extracts; germination; natural compounds; bioherbicides

Graphic summary



1. Introduction

Associated with increase in urban population, we have a need to increase the food production (Satterthwaite et al., 2010). New technologies are developed for increase the food quality and food production; however, a concern raises about the environmental impact of these technologies to natural ecosystems. Nowadays, the production challenge based on sustainable principle depends on the collaborative efforts for understand the functioning of ecological production systems, aiming to maintenance of the relationship among production, organisms and natural environment (Mensah and Casadevall 2019).

Currently, pesticides are the major inputs used for food production in agricultural activity, these compounds have important bioactivity (Ngegba et al., 2022), specially, biocidal activity against living organisms that cause damages to cultivated plant species. Among the pesticides (agrochemicals), herbicides are the most used class of active compounds, based on synthetically formulated product. Herbicides are used to inhibits growth and development of weeds, causing weed organism death or controlling their development (Holt et al., 2013). Thus, decrease the competition of crop plants with alien weed species. Additionally, as example of commercial formulations used as herbicide we have glyphosate, 2,4-D, paraquat, atrazine, trifluralin and others, with distinct modes of action.

Since its discovery, herbicides represent a great leap in agricultural activity, increase significantly the plant productivity (Holt et al., 2013). According to their mode of action, herbicides could be classified in two basic categories: post-emergent those whose effective activity occurs on developed plants and pre-emergent herbicides showed its activity as inhibit seed germination (Holt et al., 2013; Sherwani et al., 2014).

Associated with the increased use of conventional pesticides in agriculture and their recognized risks to human health and the environment, alternative inputs that allow and increase food production to ensure food security are desirable (FAO 2017).

Environmentally friendly products for weed control, has a grow demand in the last decades. Bioherbicidesor biopesticides are products based on natural substances as an active ingredient, among their sources we have plants or plant compounds, they stand out due to the high production of biomolecules that inhibit/reduce seed germination and development of weed plants. Additionally, studies with focus on increasing and diversifying its applicationhas increased greatly in recent years (Hasan et al., 2021). Bioherbicides have some advantages over synthetic herbicides, such as their

specific performance based on plant allelopathic responses, less resistance, and environmentally friendly behavior (Archana et al., 2022).

In this context, essential oils (EOs) produced by diverse plant tissues and species, may present a great bioherbicide action depending on the plant species source, usually aromatic plants (i.e., rosemary (Salvia rosmarinus), lemongrass (Cymbopogon citratus), eucalyptus (Eucalyptus spp.) present secondary metabolites associated with plant resistance or defense mechanism to pest and predators (Ootani et al., 2013; Lima 2020). These metabolites present a great potential to act as novel natural herbicides. Thus, considering the relevance of design novel ecofriendly agrochemical inputs, the present study shows environmentally sustainable alternatives in potential pre-emergent bioherbicides for control seed germination are presented.

2. Allelopathic behavior

The term plant allelopathy refers to the interaction between plants that receive or release compounds (called allelochemicals) that influence plant growth, being stimulus or inhibition responses (Hickman et al., 2021). Exploring the mode of action of allelopathic plant compounds and their application in agriculture can help in the implementation of sustainable systems. This application can be carried out by extracting allelochemicals from plants and applied to the target species, being great substitutes for synthetic pesticides. Seed germination inhibition responses, low plant growth and lower residue levels are found after use (Polechonska et al., 2020).

The allelochemical compounds of plants that influence the reduction of plant parameters gain prominence in the economic sector and are soon called botanical bioherbicides (Scavoand Mauromicale 2021). Bioherbicides have some advantages over synthetic herbicides, such as specificity in their performance, pathogens develop less resistance to microbial products, and respect for the environment, as they are produced naturally (Fernández and Juncosa 2002).

Among the parts of the plant, the leaves were described as the main organs for the extraction of allelopathic compounds, which were treated as a crude extract without necessarily having described the major compounds, the essential oils extracted by hydrodistillation or others, such as maceration, extraction by solvent. Although other parts of plants such as seeds, roots, stems, among others show allelopathic behavior, the extraction of compounds from the leaves is the most common way to obtain these products, since the leaves are usually easier to access for the practice of collection (Zanfano et al., 2022).

| Species | Family | Tissue | Sample | Reference |
|-------------------------|---------------|------------------------|-----------------|------------------------|
| Sesamumindicum | Pedaliaceae | Root, stem and leaf | Aqueous extract | Zhao et al., 2022 |
| Olea capensis | Fabaceaea | Leaves | Aqueous extract | Miles et al., 2022 |
| Azadirachta indica | Meliaceae | Leaves | Aqueous extract | Cardozo et al., 2019 |
| Coffeaarabica | Rubiaceae | Leaves | Aqueous extract | Rodrigues et al., 2011 |
| Alpinia zerumbet | Zingiberaceae | Leaves | Essential oil | Almeida et al., 2019 |
| Pinus taeda | Pinaceae | Leaves | Aqueous extract | Sartor et al., 2009 |
| Morindacitrifolia | Rubiaceae | Leaves | Essential oil | Costa et al., 2016 |
| Achyroclinesatureioides | Asteraceae | Leaves | Aqueous extract | Baseggio et al., 2019 |
| Cymbopogonnardus | Poaceae | Leaves | Essential oil | Hirata et al., 2018 |

Table 1: Plant species and their parts with potential use for bioherbicide

3. Physiological effects

3.1. Inhibition of seed germination

The large-scale use of agrochemicals causes environmental and human health risks. This has aroused the need for investments in technologies that make the production of agricultural systems more efficient. In this sense, research involving the interaction of active principles of plants with pesticide potential has shown promising results (Pacheco and Buzea, 2018; Prata et al., 2018), also stand out as an environmentally friendly alternative (Table 2).

| Bioherbicide | Target species | Dose | %G | | Reference |
|-----------------------------|----------------------------|----------|-------|----|---------------------------|
| | | | С | T | |
| Pistaciaintegerrima | Bromusdiandrus | 25% | 33.33 | 20 | Zanfano et al., 2022 |
| Helianthusannuus | Sinapis alba | 10% | 95 | 25 | Rys et a1., 2021 |
| Portulaca oleracea | Brassica napus | 6% | 80 | 0 | Hamad et al., 2021 |
| Coffea arabica | Glycine max | 100% | 95 | 10 | Rodrigues et al., 2011 |
| Alpinia zerumbet | Lycopersicum esculentum | 1% | 100 | 1 | Almeida et al., 2019 |
| Pinus taeda | Avena strigosa | 100% | 37 | 7 | Sartor et al., 2009 |
| Morinda citrifolia | Zea mays | 20% | 97 | 0 | Costa et al., 2016 |
| Achyrocline satureioides | Triticum aestivum | 20% | 96 | 88 | Baseggio et al., 2019 |
| Cymbopogon nardus | Bidens pilosa | 1.5 mL/L | 85 | 55 | Hirata et al., 2018 |
| Cymbopogon nardus | Megathyrsus maximus | 1.5 mL/L | 83 | 3 | Hirata et al., 2018 |

Table 2: Seed germination response exposed to bioherbicide extracts

Percentage germination (%G); control (C); treatments (T).

In view of this, another indispensable parameter to be investigated is the toxicity of the constituents of natural products to non-target organisms and human health, especially if the purpose is its use as a more environmentally friendly pesticide, that is, a biopesticide. The term biopesticide should be interpreted as a technological mechanism, from plant derivatives, microorganisms or biochemical substances that aim to reduce, eliminate and/or control target organisms (pests), implying a different technique from conventional agricultural practices with industrial agrochemicals (Ferraz et al., 2021).

The use of essential oils in agriculture also stands out as an agent for controlling pathogens and invasive plants, as these compounds inhibit seed germination and/or the development of other plants that are nearby (Werrie et al., 2020; Maes et al., 2021). Study species Brassica pekinensis, Lactuca sativa, Oryza sativa, Portulaca oleracea, Oxalis corniculata and Setariaviridis showed reduction and/inhibition in germination when exposed to aqueous extract, pure ethanol and ethanol/water from Artemisia argyi leaves (Li et al., 2021). Results by Setyowati et al. (2021), describe the bioherbicidal activity of Sorghum root extract with effect of reducing the germination of Oryza sativa and Vigna radiata.

Considering the diversity of flora (especially tropical flora), compounds with properties for applications such as bioherbicides are produced, however, most of them lack certification to reach the level of production. This can be verified by the registration of active ingredients used in commercialized biopesticide products, which is prepared by the United States Environmental Protection Agency.

3.2. Enzymatic inhibition

Among the effects on plants caused by the application of EOs are the changes in enzymatic activity (Zhao et al., 2017). These changes of increase or decrease in enzyme activity occur due to the mechanism of recognition of stress compounds in plant metabolism. According to Fu et al. (2017), reactive oxygen species (ROS) are the first signaling for abnormalities in

plant metabolism. Initially, the oxygen produced by the photosynthetic reaction can be converted to reactive forms such as superoxide ion $(O2 \square)$, singlet oxygen (O2), peroxide ion (O2), hydrogen peroxide (H2O2) and hydroxyl radical $(HO \square)$ during electron transfer reactions (Apel and Hirt, 2004). It is important to define that the low content of ROS perform a signaling function to the damage caused by oxidation in plant cells. However, high ROS contents (oxidative burst) are harmful to seeds, leading to irreversible phytotoxicity such as loss of phospholipids, imbalance of fatty acids and disruption of plasma membranes (Hasanuzzaman et al., 2020).

The ROS cleaning mechanism in plants includes enzymatic and nonenzymatic activity and their action occurs in specific cellular compartments. Non-enzymatic detoxification includes the action of flavonoid, phenolic and carotenoid compounds linked to primary defense against biotic and abiotic stresses, in addition to being directly linked to light stress (Santos et al., 2020).

The enzymatic defense of ROS includes the action of superoxide dismutase (SOD), catalase (CAT), peroxidase (POD) and peroxidase ascorbate (APX). Based on the process of formation and defense of ROS, a sophisticated interaction between reactive molecules and antioxidant enzymes acts. As the formation of superoxide ion (O2 |) is associated with damage to the plasma membrane (Gomes and Garcia, 2013), consequently, the control occurs through the enzyme superoxide dismutase (SOD), which catalyzes the reaction transforming O2□ into molecular oxygen. (O2) and hydrogen peroxide (H2O2). However, the reaction promoted by SOD generates another ROS that is even more harmful to germination, with H2O2 being linked to membrane deterioration by the association of O2 molecules on fatty acids. The activated enzymes catalase (CAT) and peroxidase (POD) act in the detoxification of H2O2. The loss of CAT and POD activity is related to cellular deterioration, that is, lipid peroxidation occurs and, therefore, leads to loss of germinal potential. As soon as the H2O2 continues in the intercellular medium, it triggers the enzyme ascorbate peroxidase (APX) that uses the H2O2 electron oxidation reaction medium that results in the release of H2O (Kurutas, 2015; Moraldes and Bosch, 2019) (Figure 1).

Studies are reported in the literature on the effect of oils on plant enzyme activity. (Benchaa et al., 2018; Gharsan et al., 2022). Han et al. 2021, points out that the antioxidant activity of SOD and POD enzymes were reduced in seeds of Poa annua, Setaria viridis, Amaranthus retroflexus and Medicago

sativa species exposed to different concentrations (0.25; 0.50; 1; 2; 5 mg mL \square 1) of Ambrosia artemisiifolia L. essential oil, therefore, the analysis of the enzyme activity of plants exposed to EOs provides reliable answers, in order to attribute reliability in the data set to obtain a new bioherbicide.

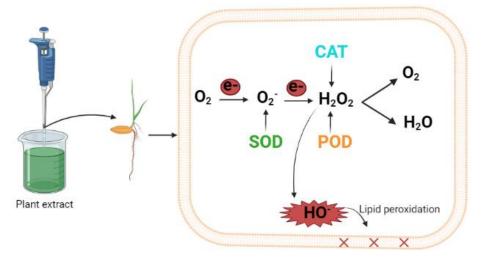


Figure 1: Mode of action of antioxidant enzymes in the presence ROS.

3.3. Effect on photosynthesis

Plant compounds act directly on the photosynthetic apparatus, altering the photosynthesis yield, pigment content and consequently plant development (Travaini et al., 2016; Radhakrishnan et al., 2018; Hasan et al., 2021). Such compounds present in plant extracts are classified by phenolics, flavonoids, alkaloids, terpenoids (Alternimi et al., 2017). Therefore, understanding the interaction of bioactive compounds in the photosynthetic apparatus strengthens its importance for new formulations of bioherbicides (Jinxin etal., 2022).

Results by Al-Johani et al. (2013), show that extracts of Chenopodium murale inhibited photosynthesis of Hordeum vulgare plants and significantly reduced the chlorophyll content. Chlorophyll a and chlorophyll b content were reduced in plants of Raphanus sativus variety sativus treated with aqueous extract of Hypericum perforatum (Hypericaceae) (Godlewska et al., 2021). The application of extracts from roots of Helianthus annuus L. in sinapis alba seeds decreased the parameters of maximum fluorescence (Fm) and initial fluorescence (Fo)(Pula et al., 2020).

In view of this, the chlorophyll fluorescence technique helps in the investigation of the effects of plant extracts and is advantageous to fill knowledge gaps, since the advance in the management of crop groups requires increasingly friendly sources with the environment. Study by Carvalho et al. (2016), investigated the site of interaction of plant extracts Plucheasagittalis, and leaves of Cecropia palmata and Brachiaria brizantha in photosystem ii of Spinacea oleracea through chlorophyll a fluorescence, the level of Fm decreased in treated plants, while control plants maintained optimal levels of fluorescence.

4. Conclusion and future prospective

The application of synthetic herbicides has been increasing the population's concern for a healthier diet and better environmental quality, with this the search for alternative inputs has been growing in the market. Therefore, allelopathic effects related to plants' bioactive secondary compounds have shown promising results as bioherbicides are considered less aggressive to the environment and non-target organisms. Although the idea of substituting completely the conventional agrochemical pesticides for biopesticides seems to be in a distant future, the use of these natural compounds is reality, especially for organic systems of production. However, the incorporation of biopesticides for use in large-scale agriculture needs to break some barriers

since the tradition of farms using agrochemicals with faster and visible results, the market power of the agricultural inputs companies, the gaps of knowledge about natural compounds and target organisms, and other challenges. Finally, despite the difficulties, natural compounds generate some commercial and environmental perspectives, since their use is considered a sustainable method. Studies are still needed on the subject, to facilitate the creation of methods to integrate these compounds in the production chain, reducing costs, as well as inducing consumers to give preference to agrochemical pesticide-free food, also contributing to the incorporation of technology in agricultural production systems, an important step to Brazil in front of the challenger of reducing to zero deforestation until 2030 allied to the increase in food production.

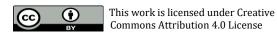
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