Essential Oils

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Contributor: Robin Raveau , Joël Fontaine , Anissa Lounès-Hadj Sahraoui

Naturally produced by aromatic plants, essential oils (EO) contain a wide range of volatile molecules, including mostly secondary metabolites, which possess several biological activities. Essential oils properties such as antioxidant, antimicrobial and anti-inflammatory activities are known for a long time and hence widely used in traditional medicines, cosmetics and food industries. However, despite their effects against many phytopathogenic fungi, oomycetes and bacteria as well as weeds, their use in agriculture remains surprisingly scarce. The purpose of the present review is to gather and discuss up-to-date biological activities of EO against weeds, plant pathogenic fungi, oomycetes and bacteria, reported in the scientific literature. Innovative methods, potentially valuable to improve the efficiency and reliability of EO, have been investigated. In particular, their use towards a more sustainable agriculture has been discussed, aiming at encouraging the use of alternative products to substitute synthetic pesticides to control weeds and plant diseases, without significantly affecting crop yields.

essential oils | biological properties | crop protection | sustainable agriculture

1. Specificities of Essential Oils

Naturally produced by aromatic plants and commonly obtained by hydrodistillation or steam distillation, EO are synthetized by all aromatic plant organs, flowers, buds, leaves, seeds, fruits, roots and rhizomes, wood and bark in relatively small amounts. They are located and stored in secretory cells, cavities or canals, epidermic cells or glandular hairs[1][2].

Either colourless or with a colour ranging from pale yellow to brown, these oils are commonly liquid at room temperature, but densities may be very different, and some oils can be resinous or even solid[3]. Poorly soluble in water but highly soluble in organic solvents, they are classified as fat-soluble[4].

Essential oils are usually rich in various compounds, comprising 20 to 60 active substances, and in many cases, can be characterized by up to three major components, at a relatively high concentration compared to other compounds present in trace amounts[5][1] [2,3]. For example, linalool (68%) is found in *Coriander sativum* EO, limonene (54%) and α and β-pinene (respectively 7 and 3.5%) in *Pinus pinea* EO, carvacrol (65%) and thymol (15%) in *Origanum heracleoticum* EO and menthol (59%) and menthone (19%) are found in *Mentha x piperita* EO[1][6][7]. The major components found in EO are often responsible for their biological properties and can be gathered in two main groups:

- Terpene hydrocarbons, constituted of monoterpenes and sesquiterpenes. Monoterpenes represent 80% of the EO's composition[8][9].
- Oxygenated compounds, constituted mostly of alcohols, phenols, aldehydes and esters. The aromatic and oxygenated compounds occur less in EO than terpenes but are yet frequent[1][10].

The chemical composition of the EO varies, depending on the organ the EO is extracted from[10][11][12]. As an example, EO from *Salvia officinalis* displayed a significantly different composition, whether it was distilled from leaves, stems or flowers. In fact, α-thujone was the major identified compound, respectively representing 30, 55 and 18% of the EO compositions. Similarly, camphor which was identified in the EO distilled from the three different organs, varied from 19.5 to 3.5% (respectively in the EO from leaves and flowers[12]). In addition, for a same plant species, EO's yield and chemical composition are wildly variable under the influence of several parameters, depending on growth and development conditions of the plant they originate from, climatic conditions (temperature, rainfall, humidity, light intensity), culture site (soil composition, acidity, pollution and mineral nutrition availability), harvesting time[11][12][13] and the root colonisation by symbiotic microorganisms, in particular arbuscular mycorrhizal fungi[14][15]. Differences in terms of chemical composition also appear between plant species of the same genus and more precisely between varieties of the same plant species, especially regarding the main compounds' proportions[16][17].

Owing mostly to their volatile nature and to the thermolability of their components, EO are very susceptible to degradation[18][19]. First, because of the close structural relationship between molecules, they may easily convert into each other through different processes, triggered by various factors which may affect them during storage or use, causing their degradation[18][20]. This occasional degradation is possible to assess through several chemical indexes (peroxide index, acid index, etc.,), physical measurements (refraction index, density, ethanol miscibility, etc.) or chromatographic analyses[18][19].

Among all the degradation ways known, oxidation, isomerisation, polymerisation and dehydrogenation are the most frequent ones[18]. In practical terms, EO's degradation is affected by several chemical and environmental factors, influencing first the likelihood of EO to be altered and then the reaction's process. External factors including temperature, light and oxygen availability and the presence of impurities in EO as well as the nature of EO compounds and their structure may be determinant regarding EO's stability[18].

Chemical molecules are most of the time very susceptible to temperature variations. In lemon EO an increased temperature leads to a drop in geranial, neral and β-phellandrene concentrations, whereas an increase in *p*-cymene, limonene oxide and geranic acid amounts[21]. Besides volatilization, oxidation reactions may occur under thermic stresses. These reactions are divided into different categories: oxidative cleavage of carbon-carbon double bonds, dehydrogenation leading to aromatic cycle formation, epoxide formation and allylic oxidation resulting in alcohols, ketones and aldehydes apparition[22]. As an example, terpenoids are known to be both volatile and heat sensitive and may either be easily oxidized or hydrolysed, based on their structure[18].

Essential oils are also very sensitive to light radiation. More specifically, it has been shown that changes in EO composition occurred in light (in comparison with a storage in dark conditions), especially an oxidation of major compounds such as monoterpenes in EO from laurel and fennel. Oxidation occurs even in the dark, but at a relatively slower rate[23].

Isomerisation process is favoured by light radiations on EO as well. A modification in the composition of anise, clove or cinnamon EO, with the transformation of *trans*-anethole into *cis*-anethole as a striking feature, results in a highly increased toxicity and an unpleasant smell[24]. It is notable that for the same concentration, two aromatic molecules may have very different properties, especially olfactory ones (depending on volatility and molecular structure); if the perception threshold of the altered molecule is consequently lower for an organism, compared to the unaffected one, this might be sufficient to deteriorate the product and its efficiency[20][24].

The impact of light and temperature in presence of atmospheric oxygen has been investigated[9]. Even at low temperature, it has been shown that EO oxidation could occur and result in the formation of peroxide radicals and hydroperoxides. In fact, oxygen solubility in the EO increases with a decreased temperature (Henry's Law). For example, in rosemary, pine, lavender and thyme EO, higher amounts of peroxides were detected at low temperature[9].

According to the previous observations, it appears necessary to find optimal conditions for EO storage. Processing EO with a non-reactive gas has been investigated, but optimal storage conditions remain unclear and only a few EO or volatiles have been subject to storage experiments so far. Nonetheless, a storage at room temperature, in the absence of both oxygen and light are highly recommended[18][19]. In addition to the three external factors presented so far, EO are also susceptible to react with the packaging material or with impurities present in the EO's mix. Humidity rate and some metal contaminations may result in oxidation reactions, with the prior presence of hydroperoxides in the EO[25].

One should keep in mind that because of their potential degradation, EO properties may be severely affected[26]. There are numerous examples of flavouring agents losing their organoleptic properties and going through viscosity change, because of the alteration of the EO's main compounds[18].

2. Essential Oil's Use in Agriculture, against Plant Pathogens and Weeds

An increasing number of EO has shown an interesting activity from an agricultural consideration, against a broad spectrum of micro-organisms (bacteria, fungi, oomycetes), insects and weeds. In addition to their effectiveness against plant pathogens, their multiple mechanisms of action and a relatively low toxicity to mammals and human beings have in particular been highlighted[27][28]. In the recent years, a large number of studies have been focusing on EO use, as a source for new biopesticides for a more sustainable agriculture. Indeed, to limit crop yield losses and increase the agricultural productivity, integrated pest management programs have implanted the application of effective, environmentally safe biopesticides. However, a small number of them have been homologated and is permitted for use worldwide. This low number of EO homologated in agriculture for various biocide usages (herbicide, fungicide and insecticide) as well as being usable as growth regulator, is remaining surprisingly scarce.

This could be explained by the different constraints that EO are facing (lack of *in planta* and in field tests, lack of stability, complex and onerous commercialisation process).

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