

Essential Oils As green Pesticides

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ABSTRACT

Plant essential oils in general have been recognized as an important natural source of pesticides. Many plant essential oils show a broad spectrum of activity against pest insects and plant pathogenic fungi ranging from insecticidal, antifeedant, repellent, oviposition deterrent, growth regulatory and antivector activities. These oils also have a long tradition of use in the protection of stored products. Essential oil compounds and their derivatives are considered to be an alternative means of controlling many harmful insects and their rapid degradation in the environment. Recent investigations indicate that some chemical constituents of these oils interfere with the octopaminergic nervous system in insects. As this target site is not shared with mammals, most essential oil chemicals are relatively non-toxic to mammals and fish in toxicological tests, and meet the criteria for “reduced risk” pesticides. Some of these oils and their constituent chemicals are widely used as flavoring agents in foods and beverages and are even exempt from pesticide registration. This special regulatory status combined with the wide availability of essential oils from the flavor and fragrance industries, has made it possible to fast-track commercialization of essential oil-based pesticides. Though well received by consumers for use against home and garden pests, these “green pesticides” can also prove effective in agricultural situations, particularly for organic food production. Further, while resistance development continues to be an issue for many synthetic pesticides, it is likely that resistance will develop more slowly to essential-oil-based pesticides owing to the complex mixtures of constituents that characterize many of these oils. Ultimately, it is in developing countries which are rich in endemic plant biodiversity that these pesticides may ultimately have their greatest impact in future integrated pest management (IPM) programmes due to their safety to non-target organisms and the environment.

KEY WORDS : Essential oils, green pesticides, monoterpenes, phytochemicals, antifeedants, repellents, fumigants, commercialization.

INTRODUCTION

Green pesticides, also called ecological pesticides, are pesticides derived from organic sources that are considered environmentally friendly and cause less harm to human and animal health, to habitats, and to the ecosystem. Green revolution is defined as an increase in crop production because of the use of new varieties of seeds, the use of pesticides, and new technologies and improved management. Organic farming, “originally grown food,” is food grown and processed using no synthetic fertilizers or pesticides. Pesticides derived from natural sources (such as biological pesticides) may be used in producing organically grown food. Botanical insecticides are becoming a key element for pest control in organic agriculture and stored products. The use of essential oils or their components adds to this natural concept, owing to their volatility, limited persistence under field conditions, and several of them having exemption from regulatory protocols. Essential oil-based insecticides started two decades ago but have not reached their full potential. Essential oils are naturally occurring, pleasant-smelling, highly volatile liquids that are widely distributed in several plants. Eucalyptus oil, clove oil, and turpentine oil are a few examples of this class. Essential oils are produced in different parts of plants, such as buds, flower petals, bark, leaves, stems, seeds, roots, and resin or fruit rinds. They are concentrated volatile aromatic compounds that contain different functional groups, such as the alcoholic group in linalool (sandalwood oil and lavender oil), aldehyde group in citral (lemongrass oil), ester group in eucalyptus oil (wintergreen), hydrocarbon group in cymene, and phenolic group in eugenol (bay oil). An individual functional group or a set of functional groups imparts a peculiar, specific scented smell to an essential oil. A plant can be recognized or grouped on the basis of its specific scenting odor. Each and every plant species originates in a certain region of earth, acquiring particular environmental conditions, so the oil extracted from a given species possesses its own characteristic scenting smell. Essential oils are colorless in pure state but light yellow in crude state. They are soluble in organic solvents in all proportions. They are steam volatile, with decomposition in some cases. They impart stain on paper that disappears upon warming or solvent washing. Essential oils are frequently referred to as the “life force” of plants. A large amount (tons) of plant material is required to collect just a few hundred kilograms of oil, as each plant contains a low percentage of oil (0.01%–10%). Essential oils possess a wide range of therapeutic constituents, and these are often used for flavor, therapeutic purposes, or odoriferous characteristics in foodstuffs, beverages, medicines, and cosmetics. Pure oil is a complex mixture of certain molecules, and it cannot be duplicated. Recent investigations indicate that some chemical constituents of these oils interfere with the octopaminergic nervous system in insects. As this target site is not shared with mammals, most essential

oil chemicals are relatively nontoxic to mammals and fish in toxicological tests, and they fulfill the criteria for “reduced-risk” pesticides. As these oils are used in food and beverages, they are even exempt from pesticide registration. This special regulatory status, combined with the easy availability of essential oils from plant parts, has made it possible to fast-track commercialization of oilbased pesticides. Besides their use against home and garden pests, these green pesticides may also prove effective in agricultural situations, particularly for organic food production. It is a fact that synthetic chemical pesticides have been very effective, but the continuous resistance development is an issue for many of them. It is likely that resistance may develop more slowly to essential oil-based pesticides owing to the complex mixtures of many constituents of different functional groups. In developing countries that are rich in endemic plant biodiversity, the green pesticides may ultimately have their great impact in coming days in integrated pest management (IPM) programs due to their safety to nontarget organisms and the environment.

Natural products or eco-friendly pesticides are an excellent alternative to synthetic pesticides as a means to reduce negative impacts to human health and the environment. The move toward green chemistry processes and the continuing need for developing new crop protection tools with novel modes of action makes discovery and commercialization of natural products as green pesticides, an attractive and profitable pursuit that is commanding attention. The concept of “Green Pesticides” refers to all types of nature-oriented and beneficial pest control materials that can contribute to reduce the pest population and increase food production. Green pesticides are safe, eco-friendly and are more compatible with the environmental components than synthetic pesticides [1]. Thus in the present concept of green pesticides, some rational attempts have been made to include substances such as plant extracts, hormones, pheromones and toxins from organic origin and also encompass many aspects of pest control such as microbial, entomophagous nematodes, plant derived pesticides, secondary metabolites from microorganisms, pheromones and genes used to transform crops to express resistance to pests. More recently, the encouragement of use of products from natural resources and even the extremely biodegradable synthetic and semi synthetic products in pest management has been considered to constitute the umbrella of green pesticides [2-4].

Essential oils are defined as any volatile oil(s) that have strong aromatic components and that give distinctive odour, flavour or scent to a plant. These are the by-products of plant metabolism and are commonly referred to as volatile plant secondary metabolites. Essential oils are found in glandular hairs or secretory cavities of plant cell wall and are present as droplets of fluid in the leaves, stems, bark, flowers, roots and fruits in different plants. The aromatic characteristics of essential oils provide various

functions for the plants including (i) attracting or repelling insects, (ii) protecting themselves from heat or cold; and (iii) utilizing chemical constituents in the oil as defence materials. Many of the essential oils have other uses as food additives, flavourings, and components of cosmetics, soaps, perfumes, plastics and as resins. Typically these oils are liquid at room temperature and get easily transformed from a liquid to a gaseous state at room or slightly higher temperature without undergoing decomposition. The amount of essential oil found in most of the plants is 1 to 2%, but can contain amounts ranging from 0.01 to 10%. For example, orange tree produce different composition of oils in their blossoms, citrus fruits, and/or leaves. In certain plants, one main essential oil constituent may predominate while in others it is a cocktail of various terpenes. In *Ocimum basilicum* (basil) methyl chavicol makes up 75% of the oil, β -asarone amounts to 70-80% in *Acorus calamus* (Bach) rhizomes, linalool, in the range of 50-60%, occurs in coriander seed and leaf oils procured from different locations at different time intervals and is by far the most predominant constituent followed by *p*-cymene, terpinene, camphor and limonene. Interestingly 2-decenol and decanal were the other most predominant constituents in leaf oil [5]. However, in other species there is no single component which predominates. Most essential oils comprise of monoterpene compounds that contain 10 carbon atoms often arranged in a ring or in acyclic form, as well as sesquiterpenes which are hydrocarbons comprising of 15 carbon atoms. Higher terpenes may also be present as minor constituents. The most predominant groups are cyclic compounds with saturated or unsaturated hexacyclic or an aromatic system. Bicyclic (1, 8-cineole) and acyclic (linalool, citronellal) examples also make the components of essential oils. However, intraspecific variability in chemical composition does exist, which is relative to ecotype variations and chemotype races or populations.

PLANTS AND ESSENTIAL OILS

Essential oils are present in different parts of plants. A brief description of oil-containing plant parts is as follows:

- Leaves: Basil, bay leaf, cinnamon, eucalyptus, lemongrass, melaleuca, oregano, patchouli, peppermint, pine, rosemary, spearmint, tea tree, wintergreen, thyme, and so forth
- Flowers: Chamomile, clary sage, clove, geranium, hyssop, jasmine, lavender, manuka, marjoram, orange, rose, ylang-ylang, and so forth
- Peel: Bergamot, grapefruit, lemon, lime, orange, tangerine, and so forth
- Seeds: Almond, anise, celery, cumin, nutmeg, and so forth
- Wood: Camphor, cedar, rosewood, sandal, and so forth

- Berries: Allspice, juniper, and so forth
- Bark: Cassia, cinnamon, and so forth
- Resins: Frankincense, myrrh, and so forth
- Rhizome: Ginger, and so forth
- Root: Valerian, and so forth

Essential oils are significantly different from fatty oils, which are also found in parts of various plants. Essential oils are used by the plants and humans for very similar purposes, such as fighting infection, initiating cellular regeneration, and working as a chemical defense against fungal, viral, and animal foes. They also contain hormone-like compounds. Despite their foliar origins, the chemical structure of essential oils is similar to that of some of the compounds found in blood and tissues, which allows them to be compatible with our own physiology.

PHARMACOLOGICAL PROPERTIES OF ESSENTIAL OILS

Essential oils possess many pharmacological properties. Some properties are discussed briefly in the following sections.

ANTISEPTIC

Essential oils are active against a wide range of bacteria and also against antibiotic resistance strains. They are also known to control fungi and yeasts (Candida). Cinnamon, thyme, clover, Eucalyptus, culin savory, lavender, citral, geraniol, linalool, and thymol are well-known antiseptics. They are much more potent than phenol.

EXPECTORANT AND DIURETIC

The external application of essential oils like “L’essence de terebenthine” increases microcirculation and provides a slight local anesthetic action. Some essential oils are used in ointments, creams, and gels that are effective in relieving sprains and other articular pains. Eucalyptus or pine oils are administered orally to stimulate ciliated epithelial cells to secrete mucus. They are known to affect the renal system in order to increase vasodilation and, as a result, bring about a diuretic effect.

SPASMOLYTIC AND SEDATIVE

The essential oils from the Umbelliferae family (*Mentha* species and *Verbena*) are documented to decrease or eliminate gastrointestinal spasms. They are known to increase secretion of gastric juices. They are reported to be effective against insomnia.

OTHER RELATED PROPERTIES

Some essential oils are known to be anti-inflammatory and cicatrizing and acts as cholagogues.

PESTICIDAL PROPERTIES

A literature survey points out that the plants of the Myrtaceae, Lamiaceae, Asteraceae, Apiaceae, and Rutaceae families are thoroughly investigated for anti-insecticide activities against specific insect orders like Lepidoptera, Coleoptera, Diptera, Isoptera, and Hemiptera [6].: essential oils of *Artemisia* species are reported for vapor toxicity and repellent activities against coleopteran beetle, and essential oils of *Cinnamomum camphora*, *C. cassia*, and *C. zeylanicum* for repellent action against mosquitoest mosquito adults. Both field and laboratory experiments showed that β -ocimene is a good repellent to the leaf cutter ant and *Atta cephalotes*. The aphid can be captured in traps baited with carvone, which occurs in the essential oils of several plants of the Apiaceae. Linalool is reported to be a good repellent of aphids. A monoterpene, β -Thujaplicin is toxic to larvae of the old house borer. Cineole, geraniol, and piperidine extracted from bay leaves are good repellents of cockroaches. Linalool extracted from sour oranges is toxic to adult bean weevils, but it is attractant to male Mediterranean fruit flies. There is a growing interest in this area. Koul et al. [7] have reported that many plant essential oils show a broad spectrum of activity against pest insect and plant pathogenic fungi, including insecticidal, antifeedant, repellent, oviposition deterrent, growth regulatory, and antivector activities. These oils also have a long tradition percentages of mortality were found in tulsi oil and wintergreen oil at 76%–92% and 86%, respectively. These results suggest the presence of active principles in the plant oils. From another part of Asia, Tariq et al. [8] studied the Pakistanian *Acorus calamus* (Araceae), a locally available plant. The common name of *A. calamus* is sweet flag. They analyzed the essential oil obtained from *A. calamus* and found that it is a complex mixture of seven major compounds. This oil prevents cuts and wounds from fungal growth, and cuts and wounds heal rapidly compared with a control. They recommended this oil as a biopesticide in the agriculture and health sectors. of use in the protection of stored products. Some constituents of these oils also interfere with the octopaminergic nervous system in insects. As this target site is not shared with mammals, most essential oil chemical constituents are relatively nontoxic to mammals and fish in toxicological tests, and meet the criteria for reduced-risk pesticides. Some of these oils are widely used as flavoring agents in foodstuffs and beverages and are even exempt from pesticide registration. This special

regulatory status, combined with the wide availability of essential oils from the flavor and fragrance industries, has made it possible to fast-track commercialization of essential oil-based pesticides. They may be an integral part of future integrated pest management programs due to their safety to nontarget organisms and the environment. A team of researchers [9] working on biofertilizers and biopesticides has published a very clear-cut point of opinion. They have reported that the loss during growing crops and postharvest handling processing, storage, and distribution is 20%–60% of oil, depending on the facilities available, such as technical know-how provided by the government and the skill of users. Three major groups of enemies are fungi, insects, and rodents. Many synthetic insecticides are in use for the protection of stored cereals and pulses. The growing awareness of environment pollution and health hazards due to synthetic pesticides has prompted a search for alternative pesticides. Researchers and users are trying green pesticides and biopesticides for grain storage purposes, that is, for organic farming. One of the alternatives is oils from plant origin that have been found to possess pesticidal properties. They are easy to apply, leave harmless residues, and are safe to natural enemies of pests. However, a serious disadvantage of oil pesticides is they have an adverse effect on the germination power of the treated seeds. Pugazhvendan et al. [10] have tested the insecticidal and repellent activities of five plant oils, *Citrus aurantium*, *Cinnamomum zeylanicum*, *Gaultheria fragrantissima*, *Lavandula officinalis*, and *Ocimum sanctum*, against *Tribolium castaneum* by using a standard protocol in vitro. The maximum repellent activity was found to be in tulsi oil (0.5 µg). Wintergreen oil and lavender oil give a good response at a higher concentration. The toxic effect of essential oils, apart from the variability of phytochemical patterns, involves several other factors. The point of entry of the toxin is one of them. Commonly, essential oils can be inhaled, ingested or skin absorbed by insects (Ozols and Bicevskis, 1979). Survey of the literature on biopesticidal potential of essential oils from the year 2000 onwards indicates that the plants of families Myrtaceae, Lamiaceae, Asteraceae, Apiaceae and Rutaceae are highly targeted for anti-insect activities against specific insect orders like Lepidoptera, Coleoptera, Diptera, Isoptera and Hemiptera. Essential oils have been explored for repellent, fumigant, larvicidal and adulticidal activities against the insects of the above orders. Cineole, geraniol and piperidine found in Bay leaves (*Laurus nobilis*, Lauraceae) possess repellent properties towards cockroaches (Verma and Meloan, 1981). Female Caribbean fruit flies, *Anastrepha suspensa*, lay their eggs readily in ripe grape fruit but do not oviposit in immature grape fruit because of the presence of linalool, which is toxic to the eggs and larvae of insects. Limonene found in sour oranges (*Citrus aurantium*) is toxic to adult bean weevils (*Callosobruchus phaseoli*), but highly attractive to male Mediterranean fruit flies (Jacobson, 1982).

ESSENTIAL OILS AS GREEN PESTICIDES

Naturally green concept suggests the avoidance of use of any pesticide via public education and awareness-raising program, and also to inform public about the potential risk of pesticide use and alternatives that are available. In fact, such programs support the policy of “prudent avoidance”. Use of essential oils or their components add to this natural concept owing to their volatility, limited persistence under field conditions and several of them having exemption under regulatory protocols. Essential oils are usually obtained via steam-distillation of aromatic plants, specifically those used as fragrances and flavourings in the perfume and food industries, respectively, and more recently for aromatherapy and as herbal medicines. Plant essential oils are produced commercially from several botanical sources, many of which are members of the mint family (Lamiaceae). The oils are generally composed of complex mixtures of monoterpenes, biogenetically related phenols, and sesquiterpenes. Examples include 1,8-cineole, the major constituent of oils from rosemary and eucalyptus; eugenol from clove oil; thymol from garden thyme; menthol from various species of mint; asarones from bach; and carvacrol and linalool from many plant species. A number of source plants have been traditionally used for protection of stored commodities, especially in the Mediterranean region and in Southern Asia, but interest in the oils was renewed with emerging demonstration of their fumigant and contact insecticidal activities to a wide range of pests in the 1990s. The rapid action against some pests is indicative of a neurotoxic mode of action, and there is evidence for interference with the neuromodulator octopamine by some oils [11]. Several examples of essential oils like rose (*Rosa damascena*), patchouli (*Pogostemon patchouli*), sandalwood (*Santalum album*), lavender (*Lavandula officinalis*), geranium (*Pelargonium graveolens*) etc. are well known in perfumery and fragrance industries. Other essential oils such as lemon grass (*Cymbopogon flexuosus*), eucalyptus (*Eucalyptus globules*), rosemary (*Rosmarinus officinalis*), vetiver (*Vetiveria zizanioides*), clove (*Eugenia caryophyllus*) and thyme (*Thymus vulgaris*) are known for their pest control properties. While peppermint (*Mentha piperita*) repels ants, flies, lice and moths. Spearmint (*Mentha spicata*) and basil (*Ocimum basilicum*) are also effective in warding off flies. Similarly, essential oil bearing plants like *Artemisia vulgaris*, *Melaleuca leucodendron*, *Pelargonium roseum*, *Lavandula angustifolia*, *Mentha piperita* and *Juniperus virginiana* are also effective against various insects and fungal pathogens [12]. Studies conducted on the effects of volatile oil constituents of *Mentha* species are highly effective against *Callosobruchus maculatus* and *Tribolium castanum*, the common stored grain pests [13]. Essential oils derived from eucalyptus and lemongrass have also been found effective as animal repellents, antifeedants, insecticides, miticides and antimicrobial products; thus finding use as

disinfectants, sanitizers, bacteriostats, microbiocides, fungicides and some have made impact in protecting household belongings. Essential oil from *Cinnamomumzeylanicum*, *Cymbopogoncitratu*s, *Lavandulaangustifolia*syn. *L. officinalis*, *Tanacetumvulgare*, *Rabdosiamelissoides*, *Aconuscalamus*, *Eugenia caryophyllata*, *Ocimum*spp., *Gaultheriaprocumbens*, *Cuminumcymium*, *Buniumpersicum*, *Trachyspermumammi*, *Foeniculumvulgare*, *Abelmoschusmoschatus*, *Cedrus*spp. and *Piper* spp. are also known for their varied pest control properties. Citronella (*Cymbopogonwinterianus*) essential oil has been used for over fifty years both as an insect repellent and an animal repellent. Combining few drops each of citronella, lemon (*Citrus limon*), rose (*Rosa damascena*), lavender and basil essential oils with one litre of distilled water is effective to ward off indoor insect pests. The larvicidal activity of citronella oil has been mainly attributed to its major monoterpenic constituent citronellal [14]. Vetiver(*Vetiveriazizanioides*) essential oil obtained by steam distillation of aromatic roots contains a large number of oxygenated sesquiterpenes. This oil is known to protect clothes and other valuable materials from insect attack when placed in closets, drawers, and chests. Catnip (*Nepetacateria*) essential oil is highly effective for repelling mosquitoes, bees and other flyinginsects. The most active constituent in catnip has been identified as nepetalactone. It repels mosquitoes ten times more than DEET. It is particularly effective against *Aedesaegypti*mosquito, a vector for yellow fever virus. Oil of *Trachyspermum*sp. is also larvicidal against *A.aegypti*and southern house mosquito, *Culexquinquefasciatus*.

ESSENTIAL OIL CHEMISTRY

The volatile components of essential oils can be classified into four main groups: terpenes, benzene derivatives, hydrocarbons and other miscellaneous compounds (Haagen-Smit, 1948; Ngoh et al., 1998). Monoterpenoids are the most representative molecules constituting 90% of the essential oils and allow a great variety of structures with diverse functions. They are ten carbon hydrocarbon or their related compounds such as acyclic alcohols (e.g. linalool, geraniol, citronello), cyclic alcohols (e.g. menthol, isopulegol, terpeniol), bicyclic alcohols (e.g. borneol, verbenol), phenols (e.g. thymol, carvacrol), ketones (carvone, menthone, thujone), aldehydes (citronellal, citral), acids (e.g. chrysanthemic acid) and oxides (cinole). The main group is composed of terpenes and terpenoids and the other of aromatic and aliphatic constituents, all characterized by low molecular weight terpenes mainly the monoterpenes (C10) and sesquiterpenes (C15), but hemiterpenes (C5), diterpenes (C20), triterpenes (C30) and tetraterpenes (C40) also exist. Aromatic compounds occur less frequently than the terpenes and are derived from phenylpropane e.g. Aldehyde: cinnamaldehyde; Alcohol: cinnamic alcohol; Phenols: chavicol, eugenol;

Methoxy derivatives: anethole, elemicine, estragole, methyl eugenols; Methylene dioxy compounds: apiole, myristicine, safrole.

CHEMICAL COMPOSITION OF ESSENTIAL OILS

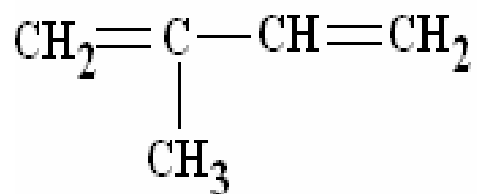
A pure essential oil is a complex mixture of more than 200 chemical compounds. Normally, it is a mixture of terpenes or phenylpropanic derivatives, in which structural differences between compounds are minimal. The components of an essential oil can mainly be classified into two groups:

1. Volatile fraction. Essential oil (90%–95% by weight) consists of hydrocarbons and terpenes and their oxygenated derivatives, such as camphor, along with acids, aliphatic aldehydes, ketones, alcohols, and esters.
2. Nonvolatile residue. Essential oil consists of hydrocarbons, fatty acids, carotenoids, sterols, waxes, and flavonoids. They comprise at maximum 10% weight of the oil.

VOLATILE FRACTION

HYDROCARBONS

Essential oils consist of chemical compounds containing hydrogen and carbon as their building blocks. The basic hydrocarbon found in plants is isoprene. It is also called hemiterpene. A fascinating area of research linking organic chemistry and biology is the study of the biogenesis of natural products: the detailed sequence of reactions by which a compound is formed in living systems, plant or animal. All the isoprene units in nature, it appears, originate from the same compound, “isopentenyl” pyrophosphate.



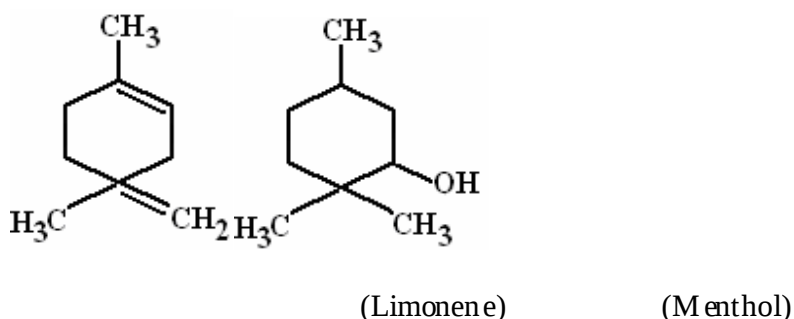
(ISOPRENE)

TERPENES

When two molecules of an isoprene unit join head to tail, the result is a monoterpene. Similarly, when three units join, it is a sesquiterpene, and when four units join, a diterpene [15–17].

MONOTERPENES

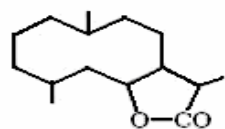
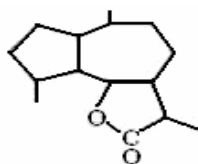
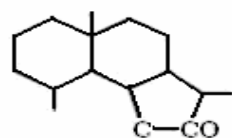
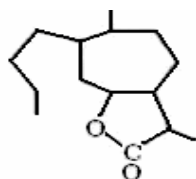
Monoterpenes are naturally occurring compounds consisting of 10 carbon hydrocarbons, the majority of which are unsaturated. Oxygenated derivatives of monoterpenes, such as alcohols, ketones, and carboxylic acids, are known as monoterpenoids. Monoterpenoids are the most representative molecules, constituting 90% of the essential oils, and allow a great variety of structures with diverse functions. The branched-chain 10 carbon hydrocarbons are composed of two isoprene units and are widely distributed in nature. More than 400 naturally occurring monoterpenes have been identified. Monoterpenes are linear derivatives, such as geraniol and citronellol; they can be cyclic molecules, such as menthol (monocyclic), camphor (bicyclic), pinenes, and ($\alpha\beta$)-pinene genera, as well. Thujone (monoterpene) is a toxic agent found in *Artemisia absinthium* (wormwood) from which the liqueur absinthe is made. Borneol and camphor are two common monoterpenes. Borneol, derived from pine oil, is used as a disinfectant and deodorant. Camphor is used as a counterirritant, anesthetic, expectorant, and antipruritic. Camphene and pinene are present in cypress oil. Similarly, camphene, pinene, and thujene are available in black pepper.



SESQUITERPENES

The sesquiterpenes (sesqui- = “one and a half”) are hydrocarbons of formula C₁₅H₂₄, or derivatives of them, which are very common in essential oils of plants. Sesquiterpenes are biogenetically derived from farnesyl pyrophosphate and in structure may be linear, monocyclic, or bicyclic. They constitute a very large group of secondary metabolites; some of them are reported to be stress compounds formed as a result of disease or injury. Sesquiterpenes are anti-inflammatory, antiseptic, analgesic, and

antiallergic. Lactones More than 500 compounds of this group are known. They are particularly characteristic of the Compositae but do occur sporadically in other families. They have been found to be of interest from a chemical and chemotaxonomic viewpoint. But they also possess many antitumor, antileukemia, cytotoxic, and antimicrobial activities. They may be responsible for skin allergies in humans, and they may also act as insect-feeding deterrents. Their classification is based on their carboxylic skeletons. For example, guaianolides, pseudoguaianolides, eudesmanolides, eremophilaolides, and xanthanolides can be derived from germacranolides. Lactones, farnesene, and β -caryophyllene are present in chamomile and lavender extracts and in basil and black pepper extracts, respectively.

**Germacranolides****Guaianolides****Eudesmanolides****Xanthanolides**

DITERPENES

Diterpenes are made up of four isoprene units. This molecule is too heavy to steam volatile in steam distillation process (diterpenes are high molecular weight compounds, so they may not be distilled by steam distillation), so it is rarely found in steam-distilled essential oils. Diterpenes occur in all plants and consist of compounds having a C₂₀ skeleton. About 2500 diterpenes are known (of 20 major structural types). Well-known diterpene derivatives are plant hormones, gibberellins, and phytol occurring as a side chain on chlorophyll. The biosynthesis occurs in plastids, and interestingly, mixtures of monoterpenes and diterpenes are the major constituents of plant resins. The diterpenes arise from metabolism of geranylgeranyl pyrophosphate (GGPP) in a manner similar to that of monoterpene. Sclareol in clary sage is an example of a diterpene alcohol. Diterpenes are antifungal, expectorant, hormonal balancers and hypotensive. They have limited therapeutic importance, and they are used in certain sedatives (coughs), as well as in antispasmodic antidiarrhetics.

ALCOHOLS

Alcohols exist naturally, as either free compound or part of terpenes. When a hydroxyl group is attached to terpene, the product is an alcohol. Alcohols have a very low or negligible toxic reaction in the body or on the skin. Therefore, they are considered safe to use. Examples of acyclic alcohols are linalool, geraniol, and citronellol. Cyclic alcohols are menthol, isopulegol, and terpineol. Bicyclic alcohols are borneol and verbenol. Other hydroxyl compounds, like phenols, are thymol and carvacrol. Linalool is found in ylang-ylang and lavender. Geraniol is found in geranium and rose. Nerol is found in neroli.

ALDEHYDES

Some of the common examples of aldehydes are citral and citronellal. Citral (geranial) is the aldehyde corresponding to geraniol, from which it may be prepared by careful oxidation. Citral imparts to oil of lemon its characteristic odor and is an important constituent of orange, mandarin, and certain kinds of eucalyptus oil. It is very abundant (70%–80%) in lemongrass and lemon balm. Citronellal is found in lemongrass, lemon balm, and eucalyptus. Aldehydes are antifungal, anti-inflammatory, antiseptic, antiviral, bactericidal, disinfectant, and sedative. Essential oils containing aldehydes are effective in treating Candida and other fungal infections.

ACIDS

Organic acids such as chrysanthemic acid, cinnamic acid, citric acid, and lactic acid in their free state are generally found in very small quantities in essential oils. They possess anti-inflammatory properties. They also act as components or buffer systems to provide a constant pH.

ESTERS

Esters such as linalyl acetate, geranylformate, and methyl salicylate are found in plants. Linalyl acetate and geranylformate are found in bergamot and geranium, respectively. Methyl salicylate is found in birch and wintergreen, which is toxic within the system. Essential oils containing esters are used for their soothing and balancing effects. Esters are effective antimicrobial agents. They are used medicinally as antifungals and sedatives, with a balancing action on the nervous system. Esters as such are free from precautions.

KETONES

Ketones such as carvone, menthone, and thujone are found in essential oils. Ketones assist the flow of mucus and ease congestion, so they are used for upper respiratory complaints. Essential oils containing ketones are beneficial for promoting wound healing and encouraging the formation of scar tissue. A few ketones, such as jasmine in jasmine oil, fenchone in fennel oil, carvone in spearmint and dill oil, and menthone in peppermint oil, are nontoxic. But generally, ketones are very toxic. The most toxic ketone is thujone, which is found in mugwort, sage, tansy, thuja, and wormwood oils. Other toxic ketones found in essential oils are pulegone in pennyroyal and pinocamphone in hyssops.

LACTONES

Lactones are cyclic esters, which may be obtained by dehydration of a γ - or δ -hydroxy acid. Treatment of lactone with base rapidly opens the lactone ring to give the open-chain salt. Lactones are anti-inflammatory, antiphlogistic, expectorant, and febrifuge. The essential oils containing lactones are known to be particularly effective for their anti-inflammatory action, possibly by their role in the reduction of prostaglandin synthesis and expectorant actions. Lactones possess stronger expectorant action than ketones.

OXIDES

such as cineole and camphor are also the constituents of essential oils. 1,8-Cineole, $C_{10}H_{18}O$, boiling point (b.p.) $174.4^{\circ}C$, occurs in eucalyptus oil. There is also 1,4-cineole, which also occurs naturally [18]. Camphor is obtained by distilling the wood and leaves of camphor laurel with steam. Camphor is used as a moth repellent, as a preservative in cosmetics, in medicine, and as a plasticizer in the manufacture of celluloid, smokeless powder, and photographic films. The essential oils containing camphor are useful for medicinal purposes.

ESSENTIAL OIL-BASED COMMERCIAL PRODUCTS

In spite of favorable mammalian toxicity of essential oils and their constituents, surprisingly few pest control products based on plant essential oils appear in the market [19–22]. This may be a consequence of regulatory barriers to commercialization (cost of toxicological and environmental evaluation) or the fact that the efficacy of essential oils toward pests and diseases is not apparent or as obvious as that seen with currently available products. Two American companies have recently produced the following products:

- Mycotech Corporation: An aphicide–miticide–fungicide, emulsifiable concentrate (EC) formulation, which consists of cinnamon oil with 30% cinnamaldehyde for greenhouse and horticultural use and for bush and tree fruits
- EcoSMART Technologies
- EcoPCO, which contains eugenol and 2-phenyl propionate for controlling crawling and flying insects
- EcoTrol Plus, an insecticide–miticide, which contains rosemary oil for horticultural crops
- Sporan, which contains rosemary oil for fungus
- Matran™, which contains clove oil for weed control

Many commercial products, like Buzz Away®, contain oils of citronella, cedar wood, eucalyptus, and lemongrass. Green Ban® contains oils of citronella, cajuput, lavender, safrole-free sassafras, peppermint, and bergapten-free bergamot oil. Skin-So-Soft contains some essential oils and stearates. Similarly, many other formulations have been developed by American and European companies on a small scale that contain either garlic oil or mint oil for pest control in the home and garden, or menthol for tracheal mite control in beehives. Italy has developed a formulation, ApilifeVar™, containing menthol and lesser amounts of cineol, menthol, and camphor, to control varroa in honeybees. In Asian countries, several blended formulations containing pleasant-smelling essential oils and chemical pesticides are used. Research work on new formulations and new technologies for storage and usage is being carried out in many laboratories in Canada, France, and Israel. The scarcity of the natural resource, the need for chemical standardization and quality control, and difficulties in registration are barriers to the commercialization of new products.

ADVANTAGES OF ESSENTIAL OIL-BASED PESTICIDES

- Broad-spectrum pesticides possess insecticidal, antifeedant, repellent, oviposition deterrent, growth regulatory, and antivector activities.
- They are useful in foodstuffs and stored foods.
- Reduced-risk pesticides are nontoxic to mammals and fish.
- They are widely used as flavoring agents in beverages and foodstuffs.

- Commercialization is possible due to abundant availability.
- Green pesticides are largely used against home and garden pests.
- There is slow pest resistance due to complex mixtures of several compounds.
- There is a unique impact on integrated pest management.
- There is limited persistence and high volatility.
- There is no harm to predators, parasitoids, and pollinators.

LIMITATIONS OF ESSENTIAL OIL-BASED PESTICIDES

- Few pest control products are available on the market.
- They have a lower efficacy than chemical pesticides.
- A greater application rate and frequent reapplication are required.
- There is poor specificity due to the presence of several compounds.
- There is a lack of sufficient supply, protection technology, and regulatory approval.
- There is inconsistency in raw material composition obtained from plants grown in different geographical, genetic, climatic, and seasonal areas.
- There is minimum involvement from low-budget companies.
- Oil can have an adverse effect on the germination power of the treated seeds.

CONCLUSION

Pesticides based on plant essential oils or their constituents have demonstrated efficacy against a range of stored product pests, domestic pests, blood feeding pests and certain soft bodied agricultural pests, as well as against some plant pathogenic fungi responsible for pre and post-harvest diseases. They may be applied as fumigants, granular formulations or direct sprays with a range of effects from lethal toxicity to repellence and/or oviposition deterrence in insects. These features indicate that pesticides based on plant essential oils could be used in a variety of ways to control a large number of pests. In terms of specific constraints, the efficacy of these materials falls short when compared to synthetic pesticides although

there are specific pest contexts where control equivalent to that with conventional products has been observed. Essential oils also require somewhat greater application rates (as high as 1% active ingredient) and may require frequent reapplication when used out-of-doors. Additional challenges to the commercial application of plant essential oil-based pesticides include availability of sufficient quantities of plant material, standardization and refinement of pesticide products, protection of technology (patents) and regulatory approval. Although many essential oils may be abundant and available due to their use in the perfume, food and beverage industries, large-scale commercial application of essential oil-based pesticides could require greater production of certain oils. In addition, as the chemical profile of plant species can vary naturally depending on geographic, genetic, climatic, annual or seasonal factors, pesticide manufacturers must take additional steps to ensure that their products will perform consistently. All of this requires substantial cost and smaller companies may not be willing to invest the required funds unless there is a high probability of recovering the costs through some form of market exclusivity (e.g. patent protection). Finally, once all of these issues are addressed, regulatory approval is required. Although several plant essential oils are exempt from registration in the United States, many more oils are not, and few countries currently have such exemption lists. Accordingly, regulatory approval continues to be a barrier to commercialization and will likely continue to be a barrier until regulatory systems are adjusted to better accommodate these products. In fact, pesticides derived from plant essential oils do have several important benefits. Due to their volatile nature, there is a much lower level of risk to the environment than with current synthetic pesticides. Predator, parasitoid and pollinator insect populations will be less impacted because of the minimal residual activity, making essential-oil-based pesticides compatible with integrated pest management programs. It is also obvious that resistance will develop more slowly to essential-oil based pesticides owing to the complex mixtures of constituents that characterize many of these oils. Ultimately, it is in developing countries where the source plants are endemic that these pesticides may ultimately have their greatest impact in integrated pest management strategy. It is expected that these pesticides will find their greatest commercial application in urban pest control, public health, veterinary health, vector control vis-a-vis human health and in protection of stored commodities. In agriculture, these pesticides will be most useful for protected crops (e.g. greenhouse crops), high-value row crops and within organic food production systems where few alternative pesticides are available. There are thus the opportunities like (i) changing consumer preferences towards the use of 'natural' over synthetic products; (ii) existence of and growth in niche markets, where quality is more important than price; (iii) strong growth in demand for essential oils and plant extracts; (iv) potential to

extend the range of available products including new product development through biotechnology; (v) production of essential oils and plant extracts from low cost developing countries.

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