Green Pesticides Handbook
Essential Oils for Pest Control

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Green Pesticides for Organic Farming: Occurrence and Properties of Essential Oils for Use in Pest Control

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1.1 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.

1.2 Definitions

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.

1.3 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.

1.4 Technology of Using Eucalyptus Oil

Eucalyptus oil can be applied externally and internally (inhalation) both ways. Inhalation is more effective than external use, but great care is required during inhalation to avoid harmful effects (skin irritation, etc.) caused by the excess concentration of vapors of the oil. The oil is used in body oils, compresses, cosmetic lotions, baths, hair rinses, perfumes, and room sprays, and for inhalation by steam.

For example, generally, 1%–10% solutions of eucalyptus oil are used in base oils like almond, jojoba, or kernel. A very pleasant method of inhalation may be created by using a diffuser or oil lamp for releasing eucalyptus oil vapors into a given atmosphere.

1.5 Aromatherapy

Aromatherapy may be defined as "the treatment of anxiety or minor medical conditions by rubbing pleasant-smelling natural oils into the skin or breathing in their smelling vapors." For example, nose infection due to cold can be cured by smelling jasmine flowers. In other words, aromatic essential oils are used to benefit the body in emotional and physical health and beauty. It has been investigated that our sense of smell plays a significant role in our overall health.

Many essential oils have medicinal properties, and they have been used in medicines since ancient times until today. Essential oils are complex mixtures, so different essential oils have diverse medicinal properties. For example, a great number of essential oils possess antiseptic properties.

1.5.1 History of Modern Aromatherapy

The distillation of rose essential oil was carried out first by the Persian philosopher Avicenna (980–1037 AD). He extracted the essence of rose petals through the "enfleurage process." This pioneering work and subsequent use of rose oil in perfume led him eventually to contribute a book on the healing properties of essential oil of rose [1].

In the early twentieth century, a French chemist, Rane-Maurice Gattefosse, began a new chapter in science, which he called "aromatherapy." He was struggling with his studies, and his arm was suffering after a burning accident in his laboratory. After several accidental burnings, he thrust his arm into the nearest available liquid, which happened to be a tub full of lavender oil. The quick healing of his arm by this oil surprised and impressed

Dr. Gattefosse, so he spent his life in researching the value of essential oils [2]. His work made aromatherapy popular and well known in Europe.

1.5.2 Mechanisms of Aromatherapy

An essential oil, either inhaled or taken by the olfactory system directly, goes to the limbic system of the brain. The brain responds to the particular scent and then affects our emotions and chemical balance. The essential oils are absorbed by the skin and carried throughout the body parts (internal organs) via the circulatory system. Due to the uniqueness of each person's system, one particular oil sample may not suit all people; that is, the benefits depend on the unique nature of an individual's response to an aromatic stimulus. Thus, by choosing one or more oils, one can experience beneficial effects promoting overall health and even specific targets.

1.6 Pharmacological Properties of Essential Oils

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

1.6.1 Antiseptic

Essential oils are active against a wide range of bacteria and also against antibioresistance 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.

1.6.2 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 vasodilatation and, as a result, bring about a diuretic effect.

1.6.3 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.

1.6.4 Other Related Properties

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

1.7 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 [3]. The following essential oils have been reported for their insecticidal activities: 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 mosquitoes. The toxic effect of essential oil of *Curcuma zedoaria* (with an LC_{50} of 5.44–8.52 μg/mg) was determined against 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. [4] 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 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 [5] 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. [6] have tested the insecticidal and repellent activities of five plant oils, *Citrus autantium*, *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 (10 μl). The maximum 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. [7] 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. Systematic control of root knot nematode was also recorded in cotton and brinjal plants by using 0.25% solution. The scale insects were also controlled by the same systematic method by using 0.5% solution in the infected cotton plants. Control of mealy bugs on cotton brinjal and *Abutilon indicum* was achieved by a 0.5% solution spray, repeated weekly for 1 month in Sindh and Baluchistan. They recommended this oil as a biopesticide in the agriculture and health sectors.

1.8 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, waves, and flavonoids. They comprise at maximum 10% weight of the oil.

1.8.1 Volatile Fraction

1.8.1.1 Hydrocarbons

Essential oils consist of chemical compounds containing hydrogen and carbon as their building blocks. The basic hydrocarbon found in plants is isoprene, $CH_2{=}C(CH_3)CH{=}CH_2$. 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.

1.8.1.2 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 [8–10].

1.8.1.2.1 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 (α,β)-pinene genera, as well. Thujone (monoterpene) is a toxic agent found in *Artemisia absinthium* (wormwood) from which the liqueur absinthe is made. Boreol 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.

1.8.1.2.2 Sesquiterpenes

The sesquiterpenes (*sesqui-* = "one and a half") are hydrocarbons of formula $C_{15}H_{24}$, or derivatives of them, which are very common in essential oils of plants. Sesquiterpenes are biogenetically derived from farensyl 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.

1.8.1.2.3 Sesquiterpene 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.

1.8.1.2.4 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 C_{20} 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 geranyl geranyl 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 antioxiolytics.

1.8.1.3 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.

1.8.1.4 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.

1.8.1.5 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.

1.8.1.6 Esters

Esters such as linalyl acetate, geranyl formate, and methyl salicylate are found in plants. Linalyl acetate and geranyl formate 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.

1.8.1.7 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 non-toxic. 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.

1.8.1.8 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.

1.8.1.9 Oxides

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°C, occurs in eucalyptus oil. There is also 1,4-cineole, which also occurs naturally [11]. Camphor is obtained by distilling the wood and leaves of camphor laurel with steam. Camphor is used as a moth repellant, 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.

1.9 Mode of Action of Essential Oils

Essential oils are volatile complex mixtures of several compounds, so many of their chemical constitutes serve as chemical messengers for insects and other animals [12]. Efforts have been made to elucidate the target sites and mode of action for the monoterpenoids, and limited success has been obtained. Most monoterpenes are cytotoxic to plants and animal tissues, causing a drastic reduction in the number of intact mitochondria and Golgi bodies, impairing respiration and photosynthesis and decreasing cell membrane permeability. It is also known that most monoterpenes serve as a signal of relatively short duration, making them especially useful for synomones (and alarm pheromones).

1.9.1 Insecticidal Action

Evans has demonstrated that a monoterpenoid (linalool) acts on the nervous system by affecting ion transport and the release of acetylcholine esterase in insects [13]. In insects, octopamine acts as a neurotransmitter, neurohormone, and circulating neurohormone–neuromodulator. When octopamine interacts with at least two classes of receptors, octopamine-I and octopamine-II, it exerts its effects [14]. The interruption in the functioning of octopamine results in a total breakdown of the nervous system in insects. Therefore, the octopaminergic system of insects represents a biorational target for insect control. The lack of octopamine receptors in vertebrates likely accounts for the profound mammalian selectivity of essential oils as insecticides. Many constituents of essential oils have been demonstrated to act on the octopaminergic system of insects [15]. Enan [16] has also shown that eugenol mimics octopamine in increasing intracellular calcium levels in cloned cells from the brain of *Periplaneta americana* and *Drosophila melanogaster*, and this was also found to be mediated via octopamine receptors. It has also been reported that the toxicity of eugenol was increased in mutant *D. melanogaster* that were deficient in octopamine synthesis, suggesting that the toxicity is mediated through the octopaminergic system, although this was not the case for geraniol. It was suggested that these cellular changes induced by eugenol are responsible for its insecticidal properties. Another research group [17] reached a similar conclusion, suggesting possible competitive activation of octopaminergic receptors by essential oil. They recorded significant effects at low concentration in the abdominal epidermal tissue of *Helicoverpa armigera*.

1.9.2 Repellent Action

It is known that the repellent molecules interact with the female mosquito olfactory receptors and thereby block the sense of smell. It is also known that the hairs on the mosquito antennae are temperature and moisture sensitive. Little is known about the receptors responsible for the repellent response in cockroaches. Literature [18] shows that oleic acid and linoleic acid are listed in death recognition and death aversion (repellency) in cockroaches, and the term *necromone* has been proposed to describe a compound responsible for this type of behavior. Essential oils seem to have good repellent potential, as they possess a characteristic smell and volatile nature. Unfortunately, no appreciable work has been reported in this direction.

1.9.3 Fumigant Action

Many essential oils have been claimed to be used as fumigants [19]. Essential oils obtained from *Artemisia annua*, *Anethum sowa*, *Curcuma longa*, and *Lippia alba*, and isolates such as d-limonene, carvones, and 1,8-ceneole, are well documented as fumigants. It seems that the route of action for these oils is in the vapor phase via the respiratory system. Unfortunately, the exact mode of action is unknown.

1.10 Phytotoxicity and Safety

Although commonly considered safe, oils can injure susceptible plants. The effects of plant injury or phytotoxicity may be acute or chronic. The injury may include leaf scorching and browning, reduced flowering, and stunted growth. Phytotoxicity may be associated with plant stress, ambient temperature and humidity, application rate, and nature of formulation. It may vary among plant species and cultivars. However, the plant phytotoxicity of essential oils is lower than that of mineral oils. Many of the essential oil formulations, for example, a natural repellent such as eucalyptus oil reported for use against mosquitoes, can serve as attractants to another blood-feeding pest, namely, midges. For a long time, the oil of the tea tree, *Melaleuca alternifolia*, has been used in Australia as a traditional remedy for insect bite relief. It has now been found to be responsible for contact dermatitis in humans [20]. Oil degradation products such as peroxides, epoxides, and endoperoxides may be responsible for this erratic behavior. Another constituent, d-limonene, of essential oils of lemon, orange, mandarin, and grapefruit, has been recommended as a pesticide for the indoor control of pests. It has also been reported that d-limonene causes dermatitis [21]. An active ingredient of *Artemisia absinthium*, thujone is a potent neurotoxin impacting the γ-amino butyric system [22]. In addition, a major constituent of *Mentha pulegium* oil, pulegone (insecticide), is oxidized upon ingestion by the cytochrome P-450 system into toxic metabolites, including methofuran [23]. These metabolites bind to proteins to cause loss of oxygen of organ function, seizures, acute poisoning, and death. These problems commonly occur whenever pesticides are used. Therefore, the following safety measures may be observed. When pesticidal oils are to be used, it is especially important to read and follow the label instructions and recommendations. Manufacturers are assumed to provide useful information based on extensive testing. In the case of repellent applications, the repellent formulations may be applied at levels lower than those of compounds that have been found to be acutely toxic, thereby lowering the pesticide load on the environment. Oils may separate from the carrier, so agitation is necessary to keep oil in the solution. Oils evaporate quickly and do not generally contaminate the environment, including soil and water, resulting in minimum risk to nontarget organisms and the environment. A proper storage procedure may be followed to preserve essential oil pesticides.

1.11 Indoor Reactions

Unsaturated monoterpenes interact with oxidants such as ozone, hydroxyl, and nitrate radicals in common places, and they produce a variety of secondary organic pollutants in the gaseous and particulate phase. In places like modern India (Hindustan), where overcrowded small houses (flats) are fully equipped with electrical and electronic devices and have limited cross-ventilation, the indoor air is ionized. In ionized air, the reactions discussed above are prone to occur. The oxidation products, such as d-limonene, α-pinene, and linalool, including aldehydes, ketones, and organic acids, have been tested in indoor air [24–26]. One of the major pollutants in the above reactions is formaldehyde. The fine particulate particles penetrate into the lower respiratory system, and they also cause skin irritation [27]. Therefore, attention is required, especially when essential oils are exposed to higher temperature during uses and storage.

1.12 Synergistic Formulations

A synergist is also called an activator or adjuvant. *Synergetic* or *synergic* means working together. These terms are derived from the Greek word *synergid*, which means cooperation (*syn* = “together,” *ergon* = “work”). Synergists are chemicals that have little or no insecticidal activity of their own but, when added to an insecticide, enhance its toxicity manifold. Thus, the synergistic formulation or combination is to reduce the dose of insecticide and thereby reduce the risk of developing resistance and environmental pollution. A broad array of pest-repellent products, including homemade herbal teas, plant extracts, fermentation products (vinegar), and industrial clay and rock powder products (kaolin), are being used in home gardens and organic farming. Now, the use of homemade products is fast declining because of the commercialization of standardized industrial products. The damage to cotton by the bollworm, *Helicoverpa armigera*, can be controlled by formulation of conventional insecticides at 50% of the recommended concentration by combining extracts of three local plants (*Azariracthta indica*, *Khaya senegalensis*, and *Hyptis sauveolens*). This admixture or formulation provides greater efficacy than that of the insecticide alone. It has been reported that low pH and salinity (5%) significantly affect the activity of essential oils such asthyme, anise, and saffron [28]. A proprietary monoterpene mixture containing 0.9% active ingredient has been developed for use against foliar feeding pests [29]. EcoSMART Technologies has developed a distinct combination of different essential oils that appreciably enhances the activity of these oils against insects (EcoPCO).

1.13 Structure–Activity Relationships

Recently developed computer-based theoretical modeling methods, such as quantitative structure–property relationship (QSPR) analysis and structure–activity relationship (SAR) analysis, are applied to the prediction and characterization of chemical toxicity of essential oils [30]. Ngoh et al. [31] have evaluated nine essential oil constituents composed of benzene derivatives and terpenes for toxic properties against *P. americana*. They found that benzene derivatives, namely, eugenol, isoeugenol, methyl eugenol, safrole, and isosafrole, are generally more toxic and a better repellent of *P. americana* than the terpenes, such as cineole, limonene, p-cymine, and α-pinene. The distance of the side-chain double bond from the aromatic ring and the substitution of the methoxy group may be responsible for their toxicity and repellency. Similarly, Aggarwal et al. [32] have evaluated L-menthol extracted from *Mentha arvensis* and its seven acyl derivatives for their bioactivities against four stored product insects. They found that the number of methyl groups in the side chain is responsible for the better activity of the derivatives than that of L-menthol. (L-menthol crystals by Sigma-Aldrich are available.)

1.14 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 [33–36]. 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 aphidicide–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 bergaptene-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.

1.15 Prospects of Essential Oils

A literature survey from 2004 to 2014 shows that several symposia [37,38] have been organized and numerous patents [39,40], books [41–43], and reviews [3,4,44,45] have been published on the preparation of admixtures (formulations) and their monitoring for different domestic and agricultural purposes, and on the fabrication of equipment such as sprayers for the application of liquid formulations of essential oil pesticides. The following patents reflect the genuineness of the research work:

- A formulation containing eucalyptus oil, pyrethroid oil, and borax is used for wood preservation and other building materials [46].
- Veneer-faced panels can be protected against insects by deep impregnation of the polymer layer with *Thujopsis dolobrata* essential oil [47].
- The biorational repellent based on nepetalactone and dihydronepetalactone from *Nepeta cataria* is used against cockroaches, mosquitoes, mites, ticks, and other household insects [48].
- Similarly, nootkatone from vetiver oil and its derivatives tetrahydronootkatone and 1,10-dihydronootkatone are used as a repellent against mosquitoes, cockroaches, termites, and ants [49].
- Thyme oil and monoterpenoids like thymol, anethole, eugenol, and citronellal are used against cockroaches and green peach aphids [50].
- Citronellal, citronellol, citronellyl, or a mixture of these is used against the human louse [51].

Recent patents involving essential oils show that the majority of the inventions are focused on household uses. Some patents are in the area of the protection of domestic animals. Many patents are related to the preservation of cloth from destruction by moths and beetles. A good number of patents are related to the protection of agricultural produce, foodstuffs, and building materials.

1.16 Global Essential Oil Pesticide Market

Annual sales of essential oils are estimated to be US$700.00 million and a total world production of 45,000 tons. About 90% of this production is focused on mint and citrus plants [45]. The global market for essential oils is increasing day by day. This is due to the fact that essential oils are considered a new class of ecological products for controlling pests. Therefore, the production of safe and scientifically approved herbal products may be given priority. There has been a regular growth of 7%–10% in the production of crop-protecting products during the last 40 years. It comes out to be a total turnover of $25 billion. The growth is partly due to a deep reorganization of the industrial sector because of takeovers and amalgamations of companies and partly due to modifications in the number and nature of commercialized pesticidal molecules. The expensive cost of commercialization licenses and the numerous cases of ecotoxicity or toxicity of pesticides to mammals that occurred in the past are responsible for this change.

One more economic aspect, the continuous and bulk requirement of raw materials, is important to producers. In order to fulfill this requirement, large-scale cultivation is required, which in turn generates good business opportunities and human resource development.

1.17 Registration of Green Pesticides

The plant protection process is profit-induced poisoning of the environment. Therefore, policies to reduce the use of plant protection products, especially chemical pesticides, are being developed globally. On the other hand, to feed the ever-growing world population, plant protection and food preservation agents are genuinely needed. In order to meet such aims and objectives, viable low-risk alternative products need to be developed and authorized by their proper registration. At present, the regulatory procedures based on synthetic chemical pesticides have been regarded as a barrier to the commercialization of green pesticides. Steps are being taken to encourage the development of green pesticides by proposing reduced data requirements. The Organisation for Economic Cooperation and Development (OECD), under the Pesticide Programme, has been working on the harmonization of its plant protection product review procedures, sharing the evaluation of plant protection products and proposing policies for the reduction of risks associated with plant protection product use. The OECD has maintained its active role in this area, developing a guidance document for the preparation of a dossier to support pheromones and other semiochemicals [52]. They recognize that semiochemicals act by modifying the behavior of pest species rather than killing them and may be target specific. They are used at very low rates, are nontoxic, and dissipate rapidly. Therefore, they can be regarded as low risk, and the data requirements are not as enormous as for synthetic chemical pesticides.

It has been proposed that semiochemicals may be exploited as pest management agents by synthesizing their derivatives and analogues using simple procedures and environment-friendly, as well as remunerative, approaches [53].

The naturally available terpenoids can be derivatized to molecules possessing pesticidal characteristics by using the structure–activity relationship approach. Monoterpenoids can be selected as lead compounds for the production of new pest management agents because of their bulk availability in plants [54].

1.18 Extraction Methods

Many techniques are available for the extraction of essential oils. One technique may produce nicer-smelling oil, while another yields oil with greater aromatherapeutic value. It turns out that essential oil production, like wine making, is an art form as well as a science. Therefore, the procedure applied for oil extraction from plant is important because some processes use solvents that can destroy the therapeutic properties. Some plants, especially flowers, do not lend themselves to steam distillation. Their fragrance and therapeutic essences cannot be completely released by water. For example, jasmine oil and rose oil are often found in "absolute" form. Thus, selection of the method is based on the experience of the user, as well as the application of the product. Therefore, each method has its own merit and importance in the processing of aromatherapy-grade essential oil. A few techniques are described briefly:

- *Maceration*: The plant is soaked in vegetable oil, heated, and strained at a temperature suitable for massage. It gives infused oil rather than an essential oil. It is one of the oldest herbal oil massage treatments.
- *Expression method*: In the expression method, the fruit is halved, placed in water for some time (5–6 hours), and then pressed against a sponge to eject oil.
- *Cold pressing*: This method is used to extract the oil from the rind of citrus, such as orange, lemon, grapefruit, and bergamot, by simply pressing the rind. The rind may be ground or chopped, and then be pressed to obtain a good yield. Thus, the product is a watery essential oil, and the water may be removed as an aqueous layer by keeping the sample for some time. The product obtained by this method possesses bright, fresh, uplifting aromas that smell similar to those of ripe fruit. However, the products have a relatively short life (±6 months).
- *Distillation method*: Essential oils are steam-volatile compounds, so the steam distillation is an affordable, readily available, and commonly used method for their extraction from plant material. To streamline the functioning and cost of the equipment, several modifications are made in the preliminary equipment of steam distillation. Some of the techniques are
    - *Hydrodistillation*: This is a simple method that is still used in places where sophisticated and costly equipment is not available; it is used in third world countries. The weakness of the method is that it can run dry i.e., no proper way to check water level or water presence or be overheated, burning the aromatics and resulting in an essential oil with a burnt smell. Hydrodistillation (HD) is generally used for spice powders and ground wood, roots, or nuts.
    - *Steam distillation*: This is the most commonly used technique for the extraction of essential oils. In this method, the distillation is carried out under atmospheric pressure and then the condensate is fractionated. Generally, plants or flowers are placed on a screen, and then steam is passed through the biomass. The steam is charged with the essence, and then steam passes through the area, where it cools and condenses. The aqueous layer containing essential oil is separated and bottled. As the plants contain essential oil in traces, several hundred pounds may be needed to produce a single ounce.
    - *Turbo distillation*: Another commonly used technique, turbo distillation extraction is used for hard-to-extract or coarse plant material, such as bark, roots, and seeds. In this method, the plant material is soaked in water and then the steam is circulated through the soaked material. The water and steam are

continually recycled through the plant material in order to perform rapid and efficient extraction.

- *Cold fat extraction or enfleurage method*: In cold fat extraction method, an extracting mixture that consists of tallow (one part), lard (two parts), and benzoin (0.6%) is spread in thin layers on rectangular wooden frames over which flower petals are distributed and allowed to remain there for about 8–10 weeks. During this period, the fat becomes saturated with oil. The alcoholic solution of the fat extract deposits on cooling, leaving oil in the solution. The solvent is removed by evaporation and the oil is recovered.
- *Extraction with volatile solvent*: The extraction is carried out with volatile solvent, such as petroleum ether, and the solvent is removed by evaporation. The oil is generally obtained in a semisolid form because of accompanying wax. The residue is treated with alcohol and filtered, and the alcohol is removed to obtain the oil. This method is not considered to be the best extraction method due to the fact that traces of solvent may be as impurities, which could cause allergies and affect the immune system.
- *Supercritical carbon dioxide extraction*: The recently developed techniques are carbon dioxide fluid extraction (CFE) and supercritical carbon dioxide fluid extraction (SCFE). Both techniques involve the use of carbon dioxide as the solvent, which carries the essential oil from the raw plant material. The low-pressure carbon dioxide extraction involves chilling carbon dioxide (35°F–55°F), which is pumped through the plant material at about 1000 psi. The carbon dioxide under these conditions condenses to a liquid. SCFE involves carbon dioxide heated to 87°F and pumped through the plant material at around 8000 psi. The carbon dioxide becomes a dense fog or vapor under these conditions. In both processes, when pressure is released, the carbon dioxide escapes as a gas, leaving the essential oil behind. These are ultrasensitive and high-priced methods, as they are working at low temperature and low pressure. However, they give good-quality essential oil, possessing the essence, as well as the therapeutic value, of the original plant.
- *Solvent-free microwave extraction*: Solvent-free microwave extraction (SFME) is a combination of microwave heating and fry distillation, performed at atmospheric pressure without adding any solvent or water [55]. The isolation and concentration of volatile compounds are performed by a single stage. SFME has been compared with a conventional technique, hydrodistillation, for the extraction of oil from three aromatic herbs: basil (*Ocimum baslicum*), garden mint (*Mentha crispa*), and thyme (*Thymus vulgaris*). The essential oils extracted by SFME for 30 minutes were quantitatively (yield) and qualitatively (aromatic profile) similar to those obtained by conventional hydrodistillation for 4.5 hours. The SFME method yields an essential oil with higher amounts of more valuable oxygenated compounds, and allows substantial savings of cost, in terms of time, energy, and plant material. SFME is a green technology and appears as a good alternative for the extraction of essential oils from aromatic plants. However, no comments have been made about the applicability of this technique on the spot, that is, plant-growing agricultural field where sophisticated facilities are not available or have not been installed so far, especially in the third world countries.

1.19 Methods of Analysis

Some new techniques have been developed for the estimation of essential oils. Most of the already known methods have been modified for use in essential oil analysis. A brief description of the currently used methods is given.

1.19.1 Gas Chromatography

Gas chromatography (GC) with a fused-silica capillary column and flame ionization detector (FID) is the routinely used method for use in essential oil analysis. In third world countries, this instrument in installed in the market of small places (in India, gas chromatography is used to fix the price of the oil; prior to the sale of oil, its chromatograph is seen, i.e., analyze the oil by gas chromatography to fix its price) to evaluate the price of essential oils. GC with capillary columns is quick in producing results. It can easily detect and identify major components of the oil, and gives good authenticity of the oil. Although the technique has no limitations, many minor components of essential oil (<0.01%) do not register on the chromatogram. The packing materials of the column are variable, depending on the polarity of the components to be separated, which varies from sample to sample. The chiral phases (mostly based on cyclodextrin derivatives) provide better resolution of the enantiomers of a volatile complex mixture because of the large changes in solute relative retention time. Gas chromatography with mass spectrometry (GC-MS) gives better resolution than GC alone. The information obtained from GC-MS analysis is sufficient to estimate whether the product is genuine. If the product is adulterated, the nature and level of adulteration is detected. A selective and accurate separation is absolutely necessary to decide the price of oil in industries [56,57].

1.19.2 Thin-Layer Chromatography

Thin-layer chromatography (TLC) is a simple and inexpensive tool of analysis. It is used in laboratories where either sophisticated or costly instruments have not been installed or repair facilities are not available. TLC can be installed with a minimum budget and operated by a semiskilled technician. It gives fairly good results for semiquantitative analysis. Now, it has been replaced by high-performance thin-layer chromatography (HPTLC), which gives accurate and reproducible results. TLC can be applied to analyze volatile essential oils after their conversion to nonvolatile substances by derivatization. HPTLC, with all its advantages, may be seen as a complementary technique, but a standard method suitable for all essential oils is still missing. HPTLC is a rapid, reliable, cost-effective, and extremely flexible method of analysis. The results are fast and clearly visible. With the introduction of automated equipment, chromatograms can be well documented, and this method fulfills the good manufacturing practices (GMP) guidelines [58,59].

1.19.3 High-Performance Liquid Chromatography

High-performance liquid chromatography (HPLC) is a modern, sophisticated, and ultrasensitive technique, but it is costly. It gives better resolution and is used to identify the minor constituents of essential oils that are not registered by GC-MS. HPLC is one of the most precise techniques for quantitative determination of plant constituents (complicated matrixes). A validated HPLC method for the assay of thymol and carvacrol in *T. vulgaris* oil has been introduced, and concentrations of these two phenolic compounds in the essential oil obtained by HPLC are compared to those obtained by the GC method [60]. The analysis of orange and mandarin essential oils (nonvolatile fraction) was carried out by HPLC in normal and reverse phase modes with ultraviolet (UV) and spectrofluorimetric detection in series. For the identification of chromatographic peaks, a preparative HPLC was used, and the purified fractions were analyzed by GC-MS and by LC-MS. Some flavones were identified in these oils [61].

1.19.4 Current Methods

The limitations of GC and GC-MS have pushed chromatographers to dig deep in search of better methods to analyze essential oil volatiles, such as improvement in sample preparation prior to injection methods, such as solid-phase matrix extraction (SPME), headspace GC, or coupling of analytical instruments to increase the separation power of one-dimensional techniques. In the area of high-speed gas chromatography, over the past few years, instruments and methods have been developed to dramatically increase the analysis speed of capillary GC. Efforts have also been made to develop techniques such as multidimensional gas chromatography (MDGC), comprehensive multidimensional chromatography (CMC), and comprehensive two-dimensional superfluid chromatography and gas chromatography (SFCXGC) [62,63].

1.20 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.

1.21 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.

1.22 Conclusion

In this area, several books have been published [64–78]. Many books have been written on topics such as essential oils and their use as pesticides. However, none of the books do what the *Green Pesticides Handbook* does—covers some pesticidal essential oils that can really protect foodstuffs. Experts from all over the world were invited to contribute chapters in order to make this handbook readable and useful to farmers, industrialists, producers, students, researchers, and teachers.

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