coatings

Review

Functional Coatings by Natural and Synthetic Agents for Insect Control and Their Applications

Divan Coetzee *, Jiri Militky and Mohanapriya Venkataraman

Department of Materials Engineering, Technická Univerzita v Liberci, 460 01 Liberec, Czech Republic; jiri.militky@tul.cz (J.M.); mohanapriya.venkataraman@tul.cz (M.V.)
* Correspondence: divan.coetzee@tul.cz

Abstract: Insect repellent textiles offer protection against disease-causing vectors such as mosquitoes, flies, and ticks. Protection is based on the incorporation of insect repellent compounds present in plant oil derivatives or synthetic oils. The effectiveness and application of natural insect repellents such as citronella grass, lemongrass, rosemary, peppermint, holy basil, tea tree, neem, lavender, thyme, lemon eucalyptus, clove, and cinnamon oils, as well as synthetic compounds permethrin, allethrin, malathion, DEET, DETA, IR3535, and picaridin, are compared here. The insect repellent and insecticidal effectiveness of natural compounds in their pure form are very low due to their high volatility. The effectiveness has been greatly improved through slow-release systems such as encapsulation of the essential oils and is comparable to synthetic compounds used for insect control purposes. Due to the lasting toxicity of synthetic compounds to humans and the environment, the use of natural compounds should become a more preferred method of insect control.

Keywords: insect repellent; natural; essential oil; permethrin; allethrin; malathion; DEET; DETA; IR3535; picaridin; encapsulation; textiles

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1. Introduction

Insect repellent textiles are materials that offer a protective barrier against insects to prevent disease transmission through insect bites. These materials are typically in the form of nets, curtains, garments, military uniforms, textiles used around the home, etc. A material's insect repellence is typically achieved by incorporating synthetic or natural insecticidal or repellent substances into the textile materials. The textile products are thus classified as either insecticidal or insect repellent depending on the treatment. Currently, permethrin is mostly used by militaries to protect soldiers against anthropoid insects; however, this is a synthetic chemical that has raised some environmental concerns. The effectiveness of synthetic insect repellents has thus far overshadowed naturally derived repellents. Repellents are considered effective when repellence is achieved over a certain amount of time against arthropods. Arthropods are insects such as mosquitos, flies, ticks, fleas, lice, ants, chiggers, etc. Among these arthropods, mosquitoes are considered the deadliest since they account for the most deaths relating to an animal-to-human viral transmission. It is estimated that at least 2.5 billion people are at risk of contracting the Dengue virus which is a common virus transmitted by mosquitoes. Another common insect-transmitted virus is Malaria of which there are approximately 500 million cases annually. Of these cases around 90% occur in Africa, with 2.7 million malaria-related deaths. In Brazil, a newer mosquito-borne virus called Zika emerged and has been linked to various reports of people suffering from Guillain-Barre syndrome and birth complications [1].

These insects are attracted to carbon dioxide and lactic acid, which are present in the warm blood of living mammals. Some repellents function by masking the smell of these substances whilst others are disliked by mosquitoes, such as DEET, picaridin, DEPA, etc. Fragrance-type repellents can be microencapsulated into textile materials and provide a slow-release during wearing [1]. Both natural and synthetic insect repellents are oily substances due to their high vapor pressure. The mechanism of action relates to the formation of a vapor layer on the surface to which the repellent is applied, which creates an undesirable environment for the insects [2,3].

The effectiveness of repellents is tested through the cage, cone, or Excito chamber tests. The cage test provides very accurate data since it simulates a real scenario where the treated substance that covers the human skin and is inserted into the cage is supposed to repel insects. The human factor in this method is the main disadvantage. The cone test uses artificial or animal blood to lure the mosquitoes to the fabric sample, which is this method's advantage since it is safer. This method is less accurate than the cage test due to the absence of the human factor; it is, therefore, more suitable for testing the toxicity of treated material. The Excito chamber works on a mosquito movement principle, where the efficacy of a repellent is measured by the number of mosquitoes passing a treated material sample [1].

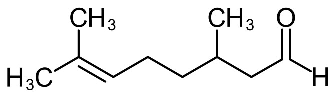
The use of chemical-based insect repellents has led to concerns of damaging ecosystems and being unsafe for humans, such as with the use of pyrethroid-based synthetic insecticides, which are considered neurotoxic [1]. Excessive use of synthetic insect repellents globally has led to the development of their resistance in insects as recent studies have shown [4–7]. Insect repellents for personal use such as DEET have been found to cause adverse skin reactions and therefore have limited the use of the active ingredient in products. Due to the mentioned concerns regarding synthetic insect repellents, there has been an interest to use more naturally derived compounds for insect repellence and to improve their effectiveness [1].

Due to the volatility of natural compounds used in natural insect repellents, extended-release systems have been developed. This resulted in natural compounds being incorporated into polymeric systems, representing around 28% of products of which about 20% are mixed with cyclodextrin. Most commonly, microencapsulation is used and represents about 28% of extended-release systems. Nanoencapsulation, nanoparticle, and microemulsion systems make up around 8% of products each, and 4% use solid lipid nanoparticles. Microencapsulation remains the most popular method to incorporate repellents into textiles and extend their active release time. More recently, solid lipid nanoparticles (SLNs) have attracted special interest. The lipid nanoparticles consist of a solid lipid matrix, which makes them different from nanoparticles. SLNs are used to overcome the limitations of other colloidal systems, such as emulsions, liposomes, and polymer nanoparticles. The advantages of the SLN system are a simple production method that uses biocompatible lipids, slow release of the active substances on the skin, and excellent physical stability. Encapsulation is most performed by coating the essential oils in a biopolymer such as polyvinyl alcohol. Biopolymers are well-suited for insect repellent encapsulation since the cell wall degrades upon exposure to the environment as well as being nontoxic. The slow release of insect repellent also reduces its acute toxicity thus reducing the possibility of dermal irritation [2]. Encapsulation is also performed using β-cyclodextrin which is commonly used for encapsulation of fragrance compounds. Cyclodextrins exhibit a hydrophilic exterior layer with a hydrophilic interior cavity in the cell membrane, making them favorable for encapsulation of oils. The capsules can be fixed to the textile by using cross-linking agents, such as poly carboxylic acids, to form chemical bonds between the capsule and applied materials [1,8,9]. Monochlorotriazine-β-Cyclodextrin has shown to exhibit a greater affinity for cotton fabrics compared to β-Cyclodextrin. This is due to its functionalization providing greater washing fastness [8]. Microcapsules produced using cyclodextrins are typically produced using the simple complexation technique. Emulsification is performed by emulsifying the essential oils with emulsifiers such as gum Arabic to form droplets in water before further processing. Emulsifiers such as proteins, polysaccharides, and phospholipids are used to stabilize emulsions, while the addition of surfactants reduces the interfacial tension in the solution [10]. Solvent evaporation is a common technique used to encapsulate essential oils with hydrophobic polymers. This is achieved by dissolving the encapsulation polymer in an organic solvent with the essential oil to create a solution that is immiscible in water. Microcapsules are produced by evaporation of the solvent. The solvent evaporation technique is an expensive method of encapsulation and is limited to the use of hydrophobic polymers. Recent advances in encapsulation have been made by utilizing interfacial polymerization [2]. Interfacial polymerization is a type of step-growth polymerization where the polymerization occurs between two monomers at the interface of two immiscible phases to form ultra-thin functional layers [11]. This technique offers a higher degree of control over the physical and chemical properties with milder reaction conditions. It is possible to achieve a high-loading factor of up to 480 g of active ingredient per liter of encapsulating material [12]. Ionic gelation involves the use of charged polymers to encapsulate essential oils. It is typically used with sodium–alginate biopolymer, which, with the essential oil, is dripped into a cross-linking solution to form the microcapsules. Complex coacervation is used to form microcapsules when the application requires high temperatures and humidity. It involves two differently charged biopolymers being linked in solution at the appropriate pH [10]. Spray drying is one of the oldest methods of microencapsulation dating back to the 1930s. It is a low-cost method with good scalability. The method involves at least two immiscible liquids that are well-dispersed to form an emulsion. The liquid emulsion is then sprayed or freeze-dried to obtain solid microcapsules. The active compound is encapsulated by a polymeric substance with which the monomer was present in the initial liquid emulsion. The spray-drying technique has one main disadvantage, which is that it could promote the release of volatile active compounds in the essential oils. This may occur due to the high temperatures of up to 140 °C used in the processing conditions. The effect can be minimized by controlling the inlet temperature and feed flow parameters. Freeze drying prevents the loss of volatile components. However, this process is time-consuming, energy-intensive, and more expensive compared to using heat in the spray dry method [13–15]. Microcapsules can be applied to textiles using conventional methods such as padding, bath exhaustion, spraying, or screen printing. Conventional methods of microcapsule incorporation rely on the impregnation of the material rather than physical bonding. This results in low washing fastness or microcapsule release from the material. The fastness can be greatly improved by using polymeric binders or resins on the material before applying the capsules, followed by a curing process. Ionic bonding can be used for textiles with surface potential. This involves synthesized nanoparticles or microcapsules containing cationic or anionic functional groups on the surface, such as in the case of chitosan biopolymer. This promotes strong ionic bonding between the functional groups of the textile and microcapsules. This method can be more advantageous compared to the use of polymeric binders or resins, which could hinder the active compound release kinetics of the microcapsules [16].

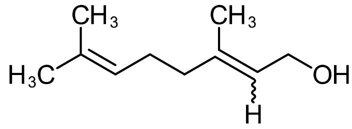
2. Natural Insect Repellents

2.1. Citronella Grass Oil

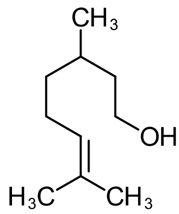
Citronella *Cymbopogon nardus* oil was originally registered by the U.S. Environmental Protection Agency as an insect repellent in 1948 and is commonly found in natural insect repellents. In the area of natural insect repellents, it is one of the most studied compounds in the field with varying results [17].



Citronellal



Geraniol



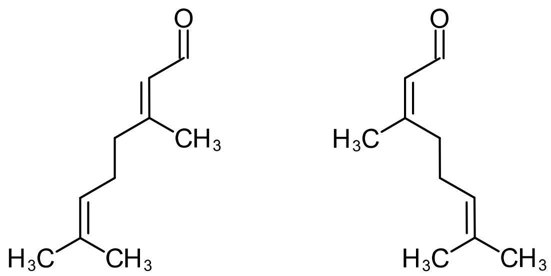
Citronellol

Citronellal (47.2%), geraniol (18.6%), citronellol (11.2%), in varying amounts depending on the harvest, are the main constituents of citronella grass oil. Studies have proven that citronella oil offers complete protection against common insects; however, this only lasts for up to two hours. This reduction in efficacy is due to the fast evaporation of citronellal. Improvements have been made by blending citronella oil with larger molecule substances or using encapsulation techniques to promote the slower release. Citronella oil has a wide range of bioactivity depending on the target organism. For up to 2 h, citronella oil exhibits the same mosquito repellent effectiveness of DEET. At concentrations exceeding 12.5%, the compound was found to be toxic to tropical horse tick larvae. It is also a known ingredient in some commercial insecticides. The insecticidal mechanism of citronella oil was found to be due to the blocking of the neural pathways, which disrupts the metabolism of the insect and deters feeding. Citronella essential oil also exhibits antifungal properties at concentrations as low as 400 mg/L against *Aspergillus Niger* or black mold on fruits. It was noted that at concentrations of 2.5 µl/ml and higher, citronella oil can be toxic to fruit and vegetables. In addition to citronellal and citronellol, citronella oil also contains nerol and elemol. These 4 compounds have proven to contribute to the antimicrobial properties of citronella oil with effective concentrations ranging between 1200–20,000 µg/mL. Within the concentration range both gram-positive and gram-negative human pathogens, namely *Acinetobacter baumanii*, *Escherichia coli*, *Enterococcus faecalis*, *Pseudomonas aeruginosai*, *Klebsiella pneumoniae*, *Serratia marcescens*, *Salmonella typhimurium,* and *Staphylococcus* were inhibited. The estimated acute toxicity of citronella oil is >5000 mg/kg. Some cases of dermatitis and eczema have been reported; however, this has been linked to higher concentrations of citronella oil in products. The allergic reactions associated with citronella oil can be attributed to neral and geranial present in the oil [18]. These compounds make up less than 20% of the oil's composition, respectively. More recently, the toxicity of citronella oil is being investigated on beneficial species in the environment [19].

Mixing citronella oil with larger molecules such as vanillin has been found to decrease volatility and improve protection over a longer duration [20]. Microencapsulation of citronella oil with β-cyclodextrin improved its efficacy to repel *Aedes aegypti* completely for more than 30 days on cotton fabric [21]. A study by Phasomkusolsil and Soonwera found that citronella grass oil acted as both a repellent and feeding deterrent against *Aedes aegypti*, *Anopheles minimus* and *Culex quinquefasciatus* [22]. Lis et al. microencapsulated citronella oil using β-cyclodextrin. The microcapsules were fixed to cotton and polyester fabrics by crosslinking with butane-1,2,3,4-tetracarboxylic acid, promoting an esterification reaction. It was determined that the chemical character of the fabric used influenced the release of the active substance. The hydrophobic nature of the polyester resulted in a faster release of an active substance compared to cotton. The polyester fabric released its maximum amount of citronella oil in 360 min compared to the cotton fabric sample at 660 min [9].

2.2. Lemongrass Oil

Various species of lemongrass exist; however, *Cymbopogon flexuosus* (red grass) is the variant that is commercially cultivated. The essential oil derived from this variant has higher solubility in alcohol, which makes it of higher commercial importance. Lemongrass essential oil contains between 75 and 80% citral with smaller amounts of linalool, geraniol, citronellol, nerol, 1,8 cineole, citronellal, linalyl acetate, geranyl acetate, apinene, limonene, caryophyllene, b-pinene, b-thujene, myrcene, b-ocimene, terpinolene, methyl heptanone, and a-terpineol [23].



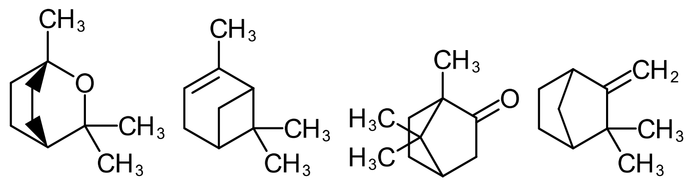
Citral A (Geranial) Citral B (Neral)

As in the case with citronella oil, lemongrass oils contain higher quantities of citral, which is comprised of geranial and neral, and have been associated with allergic reactions [18]. These compounds also contribute to the antibacterial properties of lemongrass oil. Lemongrass oil also poses broad-spectrum antifungal properties and has proven as an effective growth inhibitor of *Candidia* spp., which is a pathogenic yeast fungi [24].

Oyedele et al. dissolved varying concentrations of lemongrass oil in liquid paraffin and tested its repellency against *Aedes aegypti*. The authors' results indicated 100% repellency for one hour at concentrations of 20% and 25% lemongrass oil. At both concentrations, protection efficiency decreased to 94% after three hours before decreasing to 44% after five hours of exposure. Results for concentrations of 10% and 15% were relatively similar over the measured time; however, full protection was lost within the first hour. Compared to the control sample, which contained pure citral, the samples containing essential oil performed substantially better. This would suggest that other components present in the oil decreased the volatility thus increasing protection effectiveness. The authors used essential oil derived by hydro distillation of *Cymbopogon citratus*. It was noted that the lower effectiveness observed in the results compared to previous studies could be attributed to the difference in species of lemongrass used as well as the liquid paraffin [25]. Chauhan et al. determined that lemongrass oil exhibited 100% repellence against *Musca domestica* for 1 h at a repellent concentration of $RC_{95} = 0.010\ \mu L/cm^3$ [26]. Jovanovic et al. proved that microencapsulation of pure lemongrass oil with a biopolymer made from a combination of pectin and gelatin extended its protection effectiveness for up to 7 days compared to 2 h with the pure essential oil against the potato tuber moth, *Phthorimaea operculella* [27]. Soltanzadeh et al. encapsulated lemongrass essential oil with chitosan nanoparticles using an emulsification-ionic gelation technique. The highest encapsulation efficiency of 45% was obtained using a 1:0.75 chitosan-essential oil ratio with encapsulation efficiency decreasing at both lower and higher ratios. A loading percentage of 16.10% was obtained at this ratio. The authors did not test the effectiveness of the encapsulated essential oil against any insect vector; however, a slow-release mechanism was observed. The authors noted 3 stages of an essential oil release. At first, the essential oil was released at an exponential rate followed by the second stage of constant release. The third stage indicated an exponential decrease in the release rate. The amount of essential oil released was about 15% greater using an acetate buffer at pH = 3 compared to a phosphate buffer system at pH 7.4 [28]

2.3. Rosemary Oil

Rosemary (*Rosmarinus officinalis*) essential oil is mostly made by steam distillation of the fresh-flowering tops of the plant. The major active compounds in the essential oil include 1,8-cineole (eucalyptol, 24.6%), α-pinene (17.7%), camphor (12.4%), and camphene (11.3%). Due to the use of rosemary in food, it is considered to have minimal toxic effects on humans and there are no known allergic reactions associated with it [29].

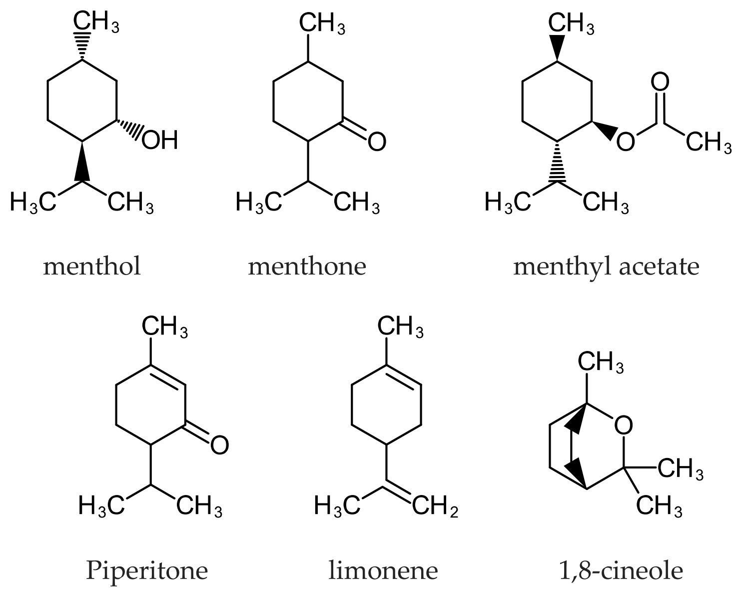


1,8-cineole α-pinene Camphor Camphene

Rosemary oil has proven to provide 100% protection for up to 8 h against *Culex quinquefasciatus* and *Anopheles stephensi* adult mosquitos [2]. When compared to 11 other plant-based essential oils, rosemary essential oil proved to be the most effective by providing 100% repellence against *Aedes aegypti* for up to 90 min. It also proved to be highly toxic to the first instar of *Aedes aegypti* larvae; however, it was nontoxic to later instars. Rosemary essential oil proved to be minimally toxic to *Culex quinquefasciatus* and *Anopheles stephensi* mosquito larvae [29]. Caballero-Gallardo et al. used rosemary and citronella essential oils in concentrations of 0.2, 0.4, 0.8, and 1.6% (*v/v*) in acetone with a 15% IR3535 control sample. Both rosemary and citronella essential oils provided 100% effective protection against *Ulomoides dermestoides* for up to 4 h at a concentration of 16 µL/mL. It was noted that at lower concentrations the insect repellency of rosemary essential oil was much less than that of citronella essential oil. The repellency results compared well against synthetic IR3535 whilst all three compounds indicated similar levels of toxicity against *Ulomoides dermestoides* upon contact. Citronella essential oil indicated no fumigation toxicity; however, 3% of the insects were killed using rosemary essential oil as a spray. Only between 24 h and 48 h did the fumigation toxicity of IR3535 exceed that of rosemary essential oil, which killed 25% of the beetles [30]. Singh and Sheikh encapsulated rosemary essential oil with a chitosan–gelatin biopolymer using a spray-drying process. The produced microcapsules were incorporated into linen fabric. After an encapsulation efficiency of 74% was obtained, the authors tested the material's insect repellent properties against *Anopheles* mosquitoes of unspecified variation. The unwashed material exhibited a 95% effective repellence which reduced to 90% after 20 wash cycles [31]. Ahsaei et al. produced microcapsules containing rosemary essential oil using octenyl succinic anhydride starch in a spray-drying process. The microcapsules were tested against the confused flour beetle *Tribolium confusum.* A mortality rate of 46.6% was observed after 15 days in storage. The authors obtained a maximum encapsulation efficiency of 32.8% and a maximum oil concentration of 0.134 g oil/g capsule [13].

2.4. Peppermint Oil

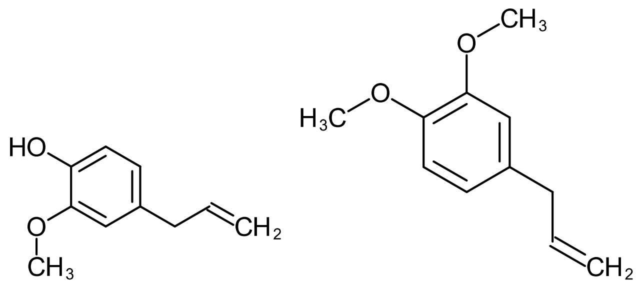
Peppermint (*Mentha* × *Piperita*) is a hybrid mint as it is a cross between water mint and spearmint. The primary components of peppermint essential oil were identified as menthol (35.21%), menthone (21.56%), menthyl acetate (6.90%), piperitone (5.60%), limonene (5.40%), and 1,8-cineole (5.30%) [32].



Chauhan et al. determined that peppermint oil exhibited 100% repellence against *Musca domestica* domestic house flies at a concentration of 0.010 μL/cm^3. It performed slightly better but comparable to lemongrass essential oil with a repellent concentration RC_{95} = 0.009 μL/cm^3 [26]. Benelli et al. tested the toxicity of peppermint essential oil on the 4th instar larvae of *Culex quinquefasciatus* and adult *Musca domestica*. Compared to 7 other essential oils, peppermint essential oil performed the worst against the larvae of *Culex quinquefasciatus* with an LC_{50} of 218.7 μL/L. It performed moderately against *Musca domestica* adult house flies with an LC_{50} of 59 μL/L [33]. Palermo et al. investigated the repellency of peppermint essential oil against the confused flour beetle *Tribolium confusum.* The repellent effectiveness of peppermint essential oil was moderate with an RC_{50} of 1.083 and 1.601 mg of essential oil over periods of 24 h and 48 h, respectively. It was outperformed by five other essential oils, which included rosemary essential oil. Although peppermint essential oil does not prove to be the most effective insect repellent, it is moderately effective as an insecticidal substance [34]. Gupta and Singh coated a cotton fabric sample with peppermint essential oil using a pad-dry-cure method. The authors extracted the essential oil from mint leaf powder with methanol to obtain a 15% concentration of the essential oil. A 25% concentration of the essential oil was applied to cotton fabric samples by padding for 90 min. This was followed by drying at 90 °C for 5 min. The samples were mordanted with 10% citric acid for 60 min, followed by curing at 120 °C for 2 min. The samples exhibited a 100% effective repellence towards an unknown mosquito vector after 9 wash cycles [35]. Rajkumar et al. encapsulated peppermint essential oil in chitosan nanoparticles by emulsifying the oil in water and forming the nanoparticles by ionic gelation. The particles were solidified by freeze drying at −35 °C for 72 h. The authors tested the insecticidal efficacy of the microcapsules against the red floor beetle *Tribolium castaneum* and rice weevil *Sitophilus oryzae.* The encapsulation efficiency ranged from 65–70% and the loading percentage from 12.31–13.92%. The encapsulated essential oil performed better than the pure essential oil, at LC_{90} = 57.47 μL/L air and LC_{90} = 98.35 μL/L air, respectively, against *Sitophilus oryzae*. The same was observed against *Tribolium castaneum* where the microencapsulated essential oil exhibited an LC_{90} = 66.45 μL/L air and the pure essential oil an LC_{90} = 101.85 μL/L air [36].

2.5. Holy Basil Oil

The main chemical components of holy basil *Ocimum tenuiflorum* oil were identified as eugenol (1.94–60.20%), methyl eugenol (0.87–82.98%), β-caryophyllene (4.13–44.60%), and β-elemene (0.76–32.41%). The eugenol components are responsible for the insect repellent properties of holy basil essential oil [37]. The large differences in eugenol content can be attributed to chemical composition changes during different harvest times [38]. The red holy basil *Shyama* variant is known to contain much higher quantities of eugenol compared to the *Rama* or white holy basil variant [39]. In addition to its insect repellent properties, holy basil essential oil is also a known antifungal agent [40].



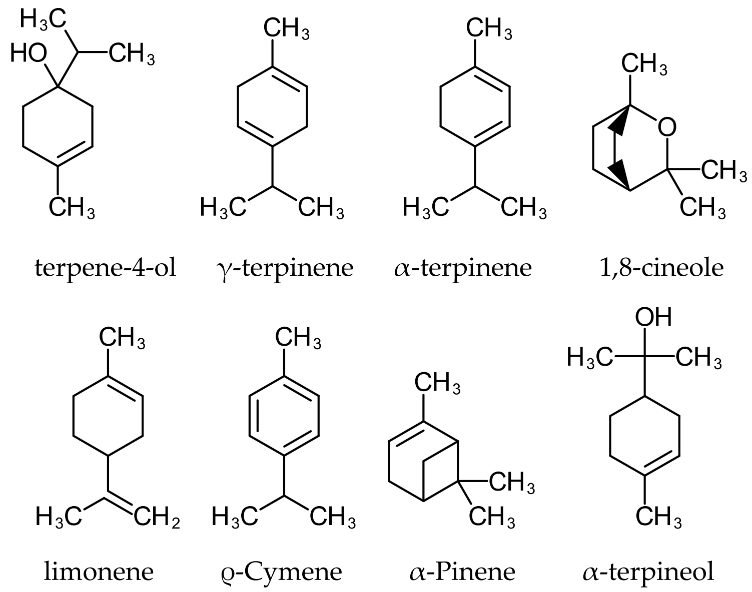
Eugenol Methyl Eugenol

Of the nine major constituents of essential oils, the benzene derivatives, which include eugenols, have proven to be more toxic to certain insects, such as the American cockroach *Periplaneta americana,* compared to terpenes such as cineole, limonene, p-cymene, and α-pinene. Methyl eugenol is also known for its knockdown activity as an insecticide [41]. Holy basil oil has proven to be 100% effective at repelling *Aedes aegypti* for up to 1 h whilst causing 100% mortality at 60 ppm against the 4th instar larvae [2,41,42]. At an LC_{50} = 0.07 ppm and LC_{90} = 0.12 ppm, holy basil essential oil successfully inhibited the growth of the 2nd instar larvae of *Aedes aegypti* [43]. Methyl eugenol does not repel all insects and can act as an attractant to honey bees such as *Apis mellifera* and lacewing *Ankylopteryx exquisite* [41]. Typically, essential oils with high eugenol content are associated with contact allergic reactions. Research suggests that this is not the case with essential oils derived from the basil plant family since its most common allergen-causing compound was identified as linalool [18,44,45]. Chenni et al. enhanced the effectiveness of holy basil essential oil by encapsulating the oil with maltodextrin or acacia gum biopolymers used in a 1:1 ratio. The authors followed the emulsification procedure, followed by freeze-drying to solidify the microcapsules. It was noted that the amorphous essential oil was dispersed in the amorphous acacia gum matrix which protected the loss of essential oil from exposure to heat and oxygen. The encapsulation efficiency and load percentage of the microcapsules were not determined. The authors tested the insect control properties of the microcapsules against lesser grain borer *Rhyzopertha dominica,* rice weevil *Sitophilus oryzae,* and the red flour beetle *Tribolium castaneum* by direct contact and ingestion toxicity assay. Results were dose-dependent with the best results obtained at a maximum tested dosage of 1 g/kg. The microcapsules exhibited insect mortality of 93.68% and 44.00% against *Rhyzopertha dominica* and *Sitophilus oryzae,* respectively, during the contact toxicity assay. Insect mortality caused by ingestion of microcapsules was determined to be 85.26% and 33.00% against the two species, respectively. This compared similarly to the pure essential oil with slight improvement. For the pure essential oil, the mortality by contact was determined to be 89.47% and 36.00% at the same dose of 1g/kg for each species, respectively. Mortality caused by ingestion was determined to be 83.16% and 29.00% against the two insect species, respectively. The authors noted no insect mortality for *Tribolium castaneum* [46]. It is expected that the microencapsulated essential oil would remain effective for a longer duration than pure essential oil due to the protection offered by the capsule.

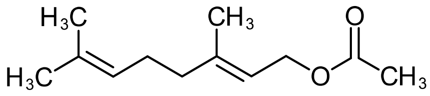
2.6. Tea Tree Oil

The tea tree *Melaleuca alternifolia* is a native plant to Australia which has been used for its medicinal properties over centuries. Major components of the oil include terpene-

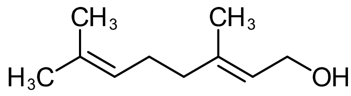
4-ol (>40%), γ-terpinene (>20%), α-terpinene (>9.0%), 1,8-cineole, limonene, ρ-Cymene, α-Pinene, and α-terpineol, representing less than 5.0% each [47].



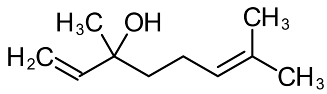
Tee tree oil has proven to provide 78% protection for 30 min against *Aedes aegypti,* also known as the yellow fever mosquito [2]. Shrestha et al. encapsulated tea tree oil with recrystallized β-cyclodextrin powder in its amorphous state, by adding water and ethanol using a direct mixing method. With the addition of water or ethanol in this method, significantly more tea tree oil was encapsulated compared to the traditional direct mixing method [47]. Beşen and Burcu successfully encapsulated tea tree oil with ethyl cellulose and applied it to 100% cotton fabric by padding. The material was tested for antibacterial effectiveness where it performed acceptably. This could also be promising for use as an insect repellent due to the slow-release properties of the microcapsules [48]. In a study by Edris et al., it was found that 1,8-cineole was the major constituent that was responsible for the insecticidal and repellent action against adult red floor beetles *Tribolium castaneum* and red imported fire ants *Solenopsis invicta.* The LC_{50} was determined to be 23.52 µL/mL [49]. Maguranyi et al. found that tee tree oil was one of the most effective essential oils studied by repelling *Aedes aegypti, Culex annulirostris,* and *Culex quinquefasciatus* for up to 38 min, 45 min, and 78 min, respectively. Lemon-scented tea tree *Leptospermum petersonii* performed the best in the study by repelling the aforementioned species for 38 min, 60 min, 98 min, respectively. The essential oils were diluted 5% *v/v* in *Simmondsia chinensis* carrier oil [50]. The chemical composition between regular tea tree oil and lemon-scented tea tree oil *Leptospermum petersonii* differs significantly. *Leptospermum petersonii* contains geranyl acetate (31.4%), geraniol (9.5%), linalool (5.1%) as oxygenated monoterpenes, and γ-terpinene (12.4%), terpinolene (9.3%), α-pinene (5.7%), p-cymene (5.6%), and (E)-β-Ocimene (5.1%), among other monoterpenes and hydrocarbons. It was stated that *Leptospermum petersonii* from Brazil and South Africa also contained considerable amounts of citronellal, geranial, and neral, which may have greater repellence properties [51].



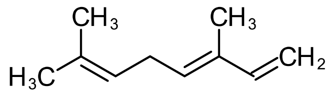
geranyl acetate



geraniol



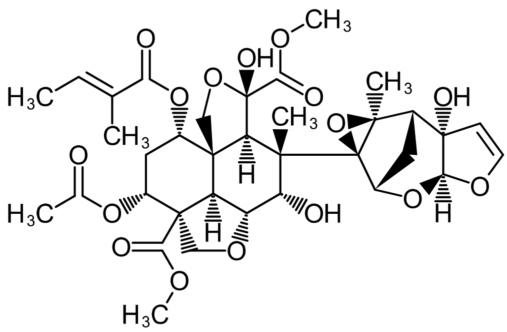
linalool



(E)-β-ocimene

2.7. Neem Oil

Neem oil Azadirachta *indica* is a known insect repellent and can be considered a natural alternative for DEET. Neem oil has low dermal toxicity, although when used in its undiluted form, it is known to cause allergic reactions and skin irritations. It is not approved by the EPA for use as a topical insect repellent [20]. Neem oil is used as the main ingredient in a wide variety of insecticidal products. Neem oil is typically obtained from the plant's seeds by solvent extraction using hexane. The main component responsible for its insecticidal properties is azadirachtin [52]. Azadirachtin is a mixture of 7 isomeric compounds which are labeled from azadirachtin-A to azadirachtin-G. Azadirachtin-A is present in the largest quantity in the oil and azadirachtin-E is regarded as the compound responsible for the oil's insect control properties [53]. Azadirachtin acts as a feeding deterrent by stimulating specific cells in mosquito chemoreceptors, which blocks the firing of sugar receptor cells that would stimulate feeding [54].

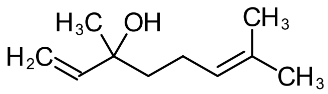


Azadirachtin A

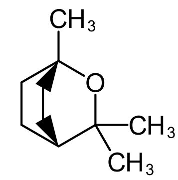
Kantheti et al. investigated the effectiveness of essential-oil-based insect repellents on cotton fabric and found that neem oil performed moderately against *Anopheles* mosquitoes with 65% effective repellence for 1 h. In the same experiment, holy basil essential oil performed slightly better with a repellence of 70% [55]. The concentration was not mentioned in the previous study; however, a study by Chio et al. confirmed that at 10% concentration, neem oil exhibited 100% repellence against the Asian tiger mosquito *Aedes albopictus*, comparable to a 15% solution containing DEET. At concentrations exceeding 2.5%, the effective repellence was over 90% for 1 h. The neem oil was diluted with methanol [56]. Neem oil is not approved for insect control by regulating agencies due to a lack of credible tests [57]. Gaydhane et al. produced electro-spun polyurethane nanofibers encapsulated with neem essential oil. Optimal results were obtained for fibers spun using polyurethane with 10% neem oil. Electrospinning was performed with 12 kV voltage, a solution flowrate of 12 μL/min, and a 15 cm distance between the needle tip and collector. The material was transformed into seed bags. After storage for 75 days, the material inhibited fungal growth with 90% efficiency as well as inhibiting seed germination. This was compared with commercial polypropylene seed bags of which 70% of the seeds contained black mold as well as the occurrence of seed germination [58].

2.8. Lavender Oil

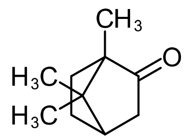
Lavender *Lavandula angustifolia* is part of the *Lamiaceae* family of plants. It is typically used as a food additive but is also renowned for its antibacterial, antifungal, insect repellent, insecticidal, and antioxidant properties. Major constituents of this variant include linalool (26–44%); however, species such as *Lavandula latifolia* and *Lavandula* × *intermedia* are known to contain 1,8-cineole (≤36%), camphor (≤15.3%), and borneol (≤4.9%). Linalool is considered the major component responsible for the insect-repellent effects of lavender essential oil [59]. In other species, 1,8-cineole, camphor, and borneol could have a synergistic effect on the repellent efficacy. The active compounds are produced in the structures of the leaves and on the plant surface. The oil is typically extracted from the leaves by steam distillation [60]. Kheloul et al. found that linalool was the major component in *Lavandula spica,* making up nearly 50% of the oil volume [61].



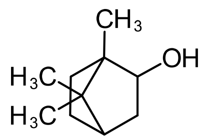
Linalool



1,8-cineole

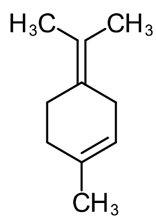


Camphor



Borneol

The lavender essential oil has proven to be 85.7% effective as a repellent against *Culex quinquefasciatus* for 8 h [2]. Kulkarni et al. investigated the repellence and larvicidal effects of lavender essential oils from *Lavandula gibsoni* against adult *Aedes aegypti and* its larvae, the larvae of *Anopheles sfttephensi,* and *Culex quinquefasciatus* mosquitoes. The species of lavender contained α-Terpinolene (22.22%) as the main compound, in addition to linalool (2.65%); however, no 1,8-cineole, camphor, or borneol was present. At 2.0 mg/cm^2, the essential oil of *Lavandula gibsoni* offered 100% protection for a period of 7 h and 15 min against adult *Aedes aegypti*. For comparison, DEET offered 100% protection for more than 8 h at 0.25 mg/cm^2. *Lavandula gibsoni* produced 100% mortality at 150 mg/L for the tested species, with LC_{50} values ranging from 48.32–62.79 mg/L [62].

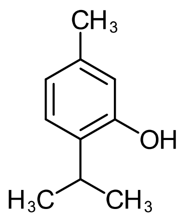


α- terpinolene

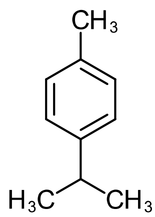
Cossetin et al. found that the *Lavandula dentata Lamiaceae* species contained largely 1,8-cineole (41.67%) in addition to camphor and linalool. The essential oil was toxic to *Musca domestica* and *Chrysomya albiceps* adults at concentrations of LC_{50} = 3.13 ± 0.64 and 1.39 ± 0.19%, respectively, at the live weight (l/v), using the superficial application test. Toxicity was also found using the oil-impregnated paper exposure test, with LC_{50} = 4.15 ± 0.64 and 5.14 ± 0.81%, respectively. At a concentration of 2.5% (m/v), the larvicidal effect was observed on third-stage *Musca domestica* larvae [63]. Lavender essential oils are mostly used for their long-lasting fragrance on textile products. The essential oil is typically coated onto cotton cellulose fabric using an exhaust method. In this process, the essential oil is emulsified using water and alcohol in the presence of a binder. This is followed by doping the fabric in the emulsion, after which it is dried and cured at 120 °C [64]. As in the case of most essential oils, their effectiveness can be prolonged by encapsulation. It was found by Aracil et al. that lavender essential oil encapsulated with melamine-formaldehyde exhibited much greater washing fastness when crosslinked with succinic acid compared to using an acrylic binder on cotton fabric [65].

2.9. Thyme Oil

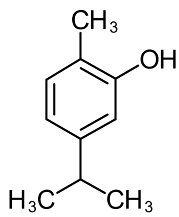
Thyme has a variety of species under the *Thymus* genus, while *Thymus vulgaris* and *Thymus zygis* are most used to obtain thyme essential oil via steam distillation. The main active compound responsible for the repellent and insecticidal effects of thyme essential oil is thymol (40.5%), which could be as high as 80% concentration. Other major compounds include p-cymene (23.6%), carvacrol (3.2%), linalool (5.4%), β-caryophyllene (2.6%), and terpinen-4-ol (0.7%). Other compounds present in smaller varying amounts may include borneol, 1,8-cineole, geraniol, various other terpenoids, alcohols, and esters [29,66].



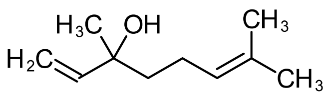
Thymol



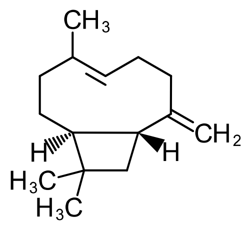
p-cymene



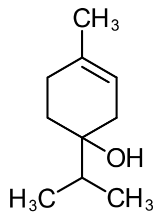
carvacrol



Linalool



(+)-β-caryophyllene



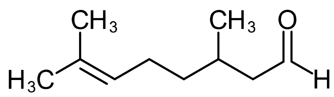
terpinen-4-ol

Thyme oil has been found to be an effective insect repellent for up to 3 h [20]. Kim et al. found that thyme oil was one of the more effective essential oils tested against sweet potato whitefly *Bemisia tabaci*. The results indicated an LC_{50} of 0.45 mL/cm^3 for red thyme, 0.46 mL/cm^3 for white thyme, and 100% mortality at a rate of 2.4 mL/cm^3 for the oil from both species [29,67]. It was found that at a concentration of 7 g/100 mL thyme oil, which was microencapsulated into a film by in situ polymerization using melamine-formaldehyde prepolymer as a wall material and pluronic F-127, tween 80, and sodium lauryl sulphate as emulsifiers, was more than 90% effective at repelling *Plodia interpunctella* for up to 4 weeks [68,69]. Maia et al. found that the biological activity of thyme essential oil was improved by microencapsulation with starch, which reduced the lethal concentration by a factor of three compared to nonencapsulated thyme essential oil. Due to the prolonged residual effect, the microencapsulated particles maintained the 3rd instar *Aedes aegypti* larval mortality of 100% for 10 days more than nonencapsulated thyme essential oil. The authors produced the microencapsulated particles using thermal extrusion, which is considered a novel technique to microencapsulate essential oils [70]. Barros et al. encapsulated thyme essential oil with maltodextrin using a spray-drying technique. The authors obtained an encapsulation efficiency of 89% with this technique.

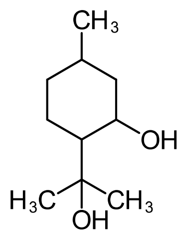
The microcapsules with a concentration of 5.0 L/t exhibited mortality of >80% for up to 70 days compared to pure thyme essential oil, which exhibited mortality of less than 20% against the maize weevil *Sitophilus zeamais* [71]. Thyme oil may cause allergic reactions such as dermatitis; however, it is generally considered safe to use. It was suggested during a cosmetic study that thymol did not produce any allergic reactions; however, it may react with other compounds to form a new product, which could generate a new allergen [72].

2.10. Lemon Eucalyptus Oil

Lemon eucalyptus *Corymbia citriodora* is known as an effective repellent since it contains around 85% citronellal. Due to the high volatility of citronellal, this repellent is only effective for up to 1 h. Kiplang'at and Mwangi found that at concentrations of 1%, lemon eucalyptus essential oil was more effective than neem oil at repelling *Aedes aegypti* mosquitos for 1 h with an effective repellence of 97.37% and 55.26%, respectively. Both essential oils were diluted with petroleum jelly [73]. Para-menthane-3,8-diol (PMD) is another compound present in lemon eucalyptus oil and, when isolated, it has been found to be an effective repellent for up to 7.5 h [17,20]. Laboratory studies confirmed that 30% PMD was as effective as 20% DEET against *Anopheles* mosquitoes. PMD-derived insect repellents have been associated with ocular irritation and have therefore been recommended not to be used close to the eyes [17]. Shah et al. developed an acrylic acid and acryloyl–PMD (30:70) copolymer containing approximately 11.5% PMD by free radical polymerization. The authors determined that the copolymer released around 45% of PMD over a period of 5 days. This had the potential to prolong repellent efficacy as well as reducing PMD associated allergic reactions since skin uptake was reduced [74]. A study by Maguranyi et al. found that eucalyptus essential oils were least effective at repelling *Aedes aegypti*, providing only 10 min to 25 min of protection. Lemon eucalyptus was the most effective against *Culex quinquefasciatus* by providing 100% repellence for 100 min. The essential oils were diluted at 5% *v/v* in *Simmondsia chinensis* carrier oil [50].



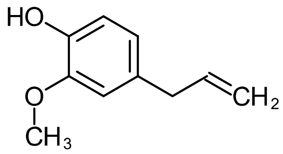
Citronellal



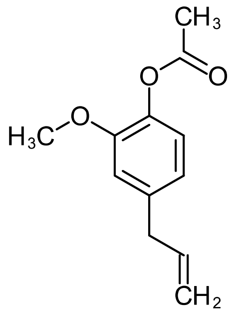
p-menthane-3,8-diol

2.11. Clove Oil

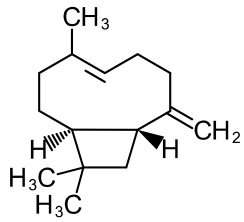
Clove *Syzygium aromaticum* is an aromatic flower belonging to the *Myrtaceae* family, which also includes eucalyptus. Eugenol (≤82%) is the major component in the oil with eugenol acetate, β-caryophyllene, and α-humulene making up less than 40% composition [18,75]. The essential oil is typically obtained by steam distillation; however, recent advances have been made using supercritical fluid extraction. The oil's mechanism of action is the interference with octopamine and gamma-aminobutyric acid receptors and transient receptor potential channels. Clove essential oil can increase permeability activity on the cell membrane, disrupt the cytoplasmic membrane, and inhibit proteins, ATPase, histidine decarboxylase, amylase, and protease enzymes [75].



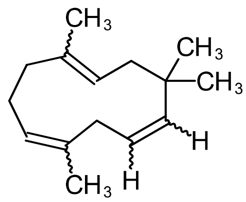
Eugenol



Eugenol acetate



(+)-β-caryophyllene

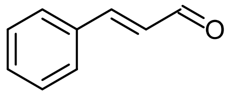


α-humulene

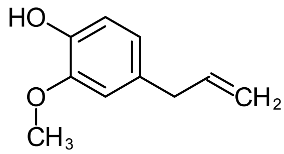
Sritabutra and Soonwera found that 10% clove oil mixed with olive oil offered full protection for about 76.5 min against *Aedes aegypti* mosquitoes. It was, however, much less effective against *Culex quinquefasciatus* mosquitoes, with an effective repellence of about 57 min compared to lemongrass and citronella grass oil, with effective repellences of about 97.5 min and 165 min, respectively [76]. Osanloo et al. investigated the larvicidal effects of clove essential oil compared to its isolated active compound, eugenol, against the 3rd and 4th instar larvae of *Anopheles stephensi.* In their study, the eugenol content in the clove oil used was 67%. The authors determined that clove essential oil and eugenol exhibited an LC_{50} = 57 and 93 ppm, respectively, while LC_{90} values were 86 and 158 ppm, respectively *against Anopheles* stephensi after exposure for 24 h. This would suggest that synergistic effects between the oil's components make it more effective compared to the isolated eugenol. The authors also noted that clove essential oil was more effective against the larvae of *Aedes aegypti* mosquitoes than *Culex quinquefasciatus* in their findings [77]. Clove oil has been found to cause various allergic reactions, which can be attributed to the high concentration of eugenol in the oil [18]. Hameed et al. encapsulated clove essential oil in electro-spun nanofibers. The authors used acetic acid and distilled water as solvents. Polyethylene oxide was used as a copolymer due to the poor chain entanglement of chitosan, making it unsuitable for electrospinning. Five percent chitosan and five percent polyethylene oxide solutions were prepared separately with water and acetic acid in a 50:50 ratio. The solutions were mixed and stirred together for 2 h. Concentrations of 0.5 and 1% clove essential oil were added to the polymer mixture in a 1:1 ratio, followed by mixing for 2 h. The authors did not state the electrospinning parameters used. The authors obtained an encapsulation efficiency of 87.6% and a loading of 8.9% clove essential oil in the fibers. The fibers released 79% of the original content over a period of 10 days at a pH of 5.5 [78]. The authors proved that the material produced inhibited fungal growth; however, the material could be promising for insect control purposes based on similar research [79].

2.12. Cinnamon Oil

Cinnamomum zeylanicum or Ceylon cinnamon is native to Southeast Asia. Its primary constituents are cinnamaldehyde (65–80%) and eugenol (5–10%) [43]. The oil is typically extracted via steam distillation with very good efficiency; however, Soxhlex extraction is also used [80].



(E)-cinnamaldehyde

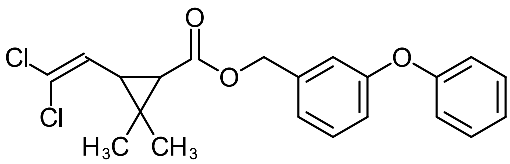


Eugenol

A study by Chaiphongpachara et al. proved that cinnamon essential oil was the most effective at eliminating *Aedes aegypti* larvae at LC_{50} = 0.03 ppm and LC_{90} = 0.04 ppm. It is known to also control the larvae of Culex tritaeniorhynchus successfully and *Anopheles subpictus*. In this experiment cinnamon essential oil outperformed holy basil essential oil as a larvicide against the 2nd instar larvae of *Aedes aegypti* [43]. Jo et al. developed a packaging material by microencapsulating cinnamon essential oil with polyvinyl alcohol using emulsification, which was coated onto polypropylene film by printing. The film was tested against *Plodia interpunctella* larvae. At a concentration of 2%, cinnamon essential oil >95% repellence was maintained for 30 days [68,81]. Nuraeni et al. proved that microencapsulation of cinnamon essential oil with PVA provided an effective slow release of volatile components for up to 59 days [82]. Cinnamon essential oil proved as a very effective repellent against *Aedes aegypti* mosquitoes with a repellent dosage (RD_{50}) of 75.92 mg. A major improvement was made by blending cinnamon essential oil with geranium and rosemary essential oils, which revealed a synergistic interaction, with an estimated RD_{50} of 29.50 mg [83].

3. Synthetic Insect Repellents

3.1. Permethrin

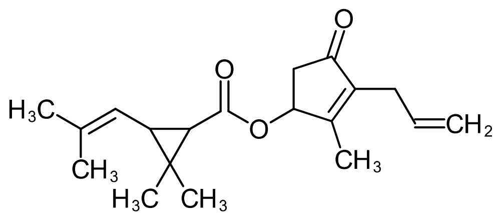


Permethrin

Permethrin is a synthetic pyrethroid with powerful insecticidal properties and was originally derived from the crushed dried flowers of the daisy *Chrysanthemum cinerariifolium*. Permethrin acts as a contact insecticide that causes nervous system toxicity. The chemical is effective against mosquitoes, flies, ticks, fleas, lice, and chiggers. Permethrin is toxic to arthropods but has low mammalian toxicity. It is poorly absorbed by the skin and is rapidly metabolized. Permethrins are non-staining, odorless, resistant to UV and heat degradation, and will remain effective for at least 2 weeks through several launderings. Permethrin is not used in products that can be applied to the skin but as a finish on textile materials [17]. It is typically applied directly to textile materials by exhaust or spraying methods. It can also be encapsulated to promote washing fastness [84]. Permethrin's method of action involves paralyzing the arthropod insect by inhibiting acetylcholinesterase and gamma-aminobutyric acid A receptors, which block sodium movement into neurons [85]. Ho et al. investigated the repellence efficacy of permethrin against an unknown mosquito type. The authors used a 100% cotton-knitted fabric and sprayed it with permethrin and DEET insect repellents at a dosage of 150 g/m^2. Permethrin maintained an effective repellency of >80% over a period of 4 days. This decreased to just under 80% after 7 days and from 30–40% after 10 days. The average repellency of permethrin was 74.48% over the 10-day period whereas the average repellency for DEET was only 18.1%. The effectiveness of DEET was initially high with a repellency of >70% for the first 12 h and exponentially decreased afterwards. This can be explained by the low volatility of permethrin since it has a lower vapor pressure of 2.15×10^{-8} mmHg at 20 °C compared to that of DEET, which is 5.6 × 10^{-3} mmHg at 20 °C. Therefore, the repellent effect of permethrin is longer than that of DEET. Another reason why permethrin is more suitable for use on textiles is that it has a lower water solubility compared to DEET [86]. Permethrin encapsulated with ethyl cellulose using the coacervation method has proven to remain effective for up to 20 wash cycles [84]. Ghamari et al. proved that permethrin encapsulated using polymethyl methacrylate was able to maintain 20% of its original concentration of permethrin on cotton fabric after 50 wash cycles. The microcapsules were produced using a conventional solvent evaporation process [87].

3.2. Allethrin

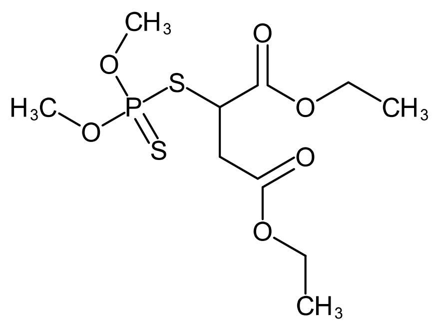
Allethrin is a common ingredient in vaporizer repellents and was one of the first synthetic pyrethroids to enter commercial use. It is suggested to have the same mechanism of action on insects as permethrin since both compounds are classified as type I pyrethroids [88,89]. It is considered safe for use except for children. Allethrin has low toxicity for humans and birds. It is mildly toxic to bees and very toxic to cats and aquatic animals [90]. Sayono et al. found that allethrin in aerosol form was more effective at controlling *Aedes aegypti* mosquitoes than those from the *Culex* gene [91]. Allethrin can be sprayed onto textiles and, at concentrations ranging from 250–1500 mg/m^2, has proven to be effective at repelling and killing mosquitoes [57].



Allethrin

3.3. Malathion

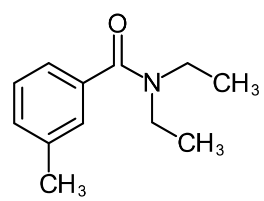
Malathion is an organophosphate insecticide. Malathion is typically used to eradicate mosquitoes in agriculture, residential landscaping, public recreational areas, and public health pest control programs. It is produced by condensation of dimethyl dithiophosphoric acid with diethyl maleate. The product is a chiral compound and its racemic mixture is used. Malathion acts as an acetylcholinesterase inhibitor, meaning it binds irreversibly to numerous sites on the cholinesterase enzyme where it releases peroxide. The formed phosphoric ester group is strongly attached to the cholinesterase enzyme where it irreversibly deactivates it. This reaction causes a quick spike of acetylcholine concentration at the synapse, which is the junction between the nerve and muscle. After stimulating the muscle response, the cholinesterase enzyme breaks down the acetylcholine, terminating muscle stimulation. When the enzyme is disabled, excessive neural responses across synapses are triggered, which leads to uncontrollable muscle movement and leads to paralysis, and death [90]. Malathion is not recommended for indoor use. Humans can metabolize the compound easily with minimal effects in low dosages. Poisonings do occur with acute effects ranging from disorders of the nervous and reproductive systems to skin irritations. Malathion decomposes to malaoxon, which is several times more toxic than the parent compound that can especially affect aquatic ecosystems [92,93]. Malathion is not applied to materials but can be present in textiles when fibers are harvested.



Malathion

3.4. DEET (N,N-Diethyl-Meta-Toluamide)

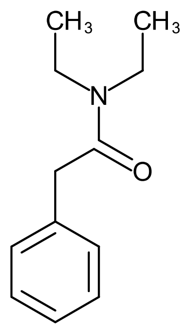
DEET has been commercially available since 1956. Over 200 products currently on the market contain DEET. These range in concentrations from 5–100%. Typically, products containing DEET concentrations of 10–35% will provide adequate protection. Efficacy and duration would typically increase with concentration and plateau at around 50%. At concentrations exceeding 50%, rare cases of vesiculobullous skin necrosis, residual scarring, and erythema have been reported by patients [85]. Improper use of DEET has been associated with neurotoxicity, while irritative contact dermatitis is a known allergic reaction [94]. DEET has been recommended for use to prevent West Nile virus and Lyme disease since it acts as an effective tick repellent and is considered safe enough to be used during pregnancy. DEET at a concentration of 23.8% exhibited complete protection from *Aedes aegypti* mosquitoes for a mean protection time of 301.5 min. At concentrations of 20% and 6%, the mean protection time for DEET was 234.4 min and 112.4 min, respectively [85,95]. A study by Goodyer and Schofield found that at concentrations of 25% DEET and picaridin, the latter outperformed DEET. The picaridin provided complete protection for up to 5 h against *Aedes taeniorhynchus* black salt marsh mosquito compared to 4 h with DEET. The same trend was observed with different concentrations tested. Real-world protection might depend on various factors such as the applied repellent dosage and the species that would be repelled. Another factor is that commercial products may contain up to 50% DEET and up to 30% picaridin. This would suggest that DEET would be a more effective insect repellent than picaridin at concentrations exceeding 30% [96]. DEET is believed to interfere with an insect's olfactory system, which is comprised of carbon dioxide odorant receptors and ionotropic receptors. This makes it difficult for an insect to detect carbon dioxide from a potential feeding source [97]. Improvements have been made using microencapsulation technology. Cecone et al. developed electro-spun pyromellitic dianhydride and β-cyclodextrin-based nano sponge microfiber containing DEET, which slowly released DEET for up to 2 weeks [98]. DEET acts as a plasticizer, which means it can cause damage to synthetic materials. However, it is not known to cause any damage to natural fibers [86].



DEET

3.5. DEPA (N.N-Diethyl Phenylacetamide)

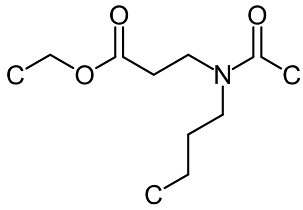
DEPA was developed as a broad-range insect repellent in India due to the unavailability of a chemical component to produce DEET. It is very economical and safe for human use. It has proven to be effective against *Aedes aegypti* and *Culex quinquefasciatus* mosquitoes. As an alternative to DEET, it performs very similarly, with repellence for up to 8 h. DEPA treated cotton and polycotton fabrics loaded with 10% (*w/w*) repellent effectively repelled *Aedes aegypti* and *Culex quinquefasciatus* mosquitoes for up to 30 and 36 days, respectively. The half-lives of the treated materials were determined to be 11 and 5 days against each species, respectively. Toxicity observed in rat studies for DEPA and DEET was LC_{50} = 900 mg/kg and 3664 mg/kg orally and 3500 mg/kg and 4280 mg/kg, respectively [99,100]. Balaji et al. developed microencapsulated DEPA by polymerization with ethylene glycol followed by phase inversion temperature emulsification. The nano capsules were incorporated into the cotton fabric using alginate crosslinking. This improved the bio efficacy of DEPA against *Culex quinquefasciatus* larvae and adult mosquitoes at lower exposure concentrations. The LC_{50} was determined to be 0.055, 0.208, and 1.397 mg/L and 0.023, 0.144, and 0.260 mg/L for Bulk-DEPA and Nano-DEPA against the 1st, 2nd, and 3rd instar larvae, respectively. For adult mosquitoes, the LC_{50} was 55.168 and 33.277 mg/L for Bulk-DEPA and Nano-DEPA, respectively [101].



DEPA

3.6. IR3535 (Ethyl Butylacetylaminopropionate)

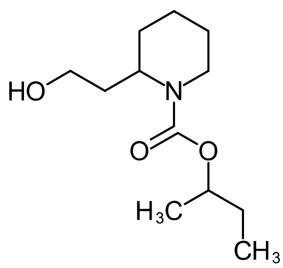
IR3535 was first used to reinforce skin emollients and moisturizers with insect repellent properties. IR3535 is colorless, almost odorless, and biodegradable; however, it is known to cause damage to natural and synthetic materials. Its concentration in products typically doesn't exceed 19.7%, making it less effective than products that contain higher concentrations of picaridin and DEET. It is known to be most effective against *Culicine* mosquitoes, which are arbovirus vectors [85]. Feuser et al. found that at a concentration of 15%, IR3535 exhibited an effective protection time of 362 min against *Aedes aegypti* mosquitoes. IR3535 was comparably effective with picaridin since 10% of IR3535 completely repelled *Aedes aegypti* mosquitoes for 356 min effectively whilst 10% of picaridin completely repelled the mosquitoes for 351.5 min [102]. The method of action of IR3535 is not well understood; however, it is believed to be similar to that of DEET involving interference with an insect olfactory system [85]. Dos santos et al. produced methyl methacrylate and styrene sulfonic acid sodium salt hydrate microcapsules containing IR3535. This was produced by emulsion polymerization with sodium persulfate as initiator and in absence of surfactant. The authors obtained a concentration of 12.2% encapsulated IR3535. Microcapsules were fixed to 100% cotton fabric by the exhaust method in a 1:20 liquor ratio. The treated samples maintained 100% repellency for up to 72 h. The treated textile exhibited a dose-dependent 100% knockdown time of approximately 87.5 min and 57.0 min against *Aedes aegypti* mosquitoes at 1.59 and 10.02 g/m^2 concentration on fabric samples, respectively. One hundred percent kill times were determined to be about 120 min and 75 min, respectively, at each concentration of IR3535 on fabric, respectively [103].



IR3535

3.7. Picaridin (2-(2-Hydroxyethyl)-1-Piperidine Carboxylic Acid 1-Methylpropyl Ester)

Picaridin is mostly used in Europe and Australia as an active ingredient in insect repellent products. Its popularity stems from the fact that it is more cosmetically pleasant to use. Picaridin is odorless, less likely to cause skin irritations, and does not damage synthetic or natural materials. Its concentration in commercial products typically does not exceed 30%. Picaridin has proven to be most effective at repelling *Culicine* mosquitoes, which are responsible for spreading arbovirus, and is also effective against *Anopheline* mosquitoes, which are known malaria vectors [85]. It has been suggested that picaridin was a more effective repellent than DEET at similar concentrations and with lower toxicity [96,100]. Recent studies support this statement as it was found that 20% picaridin effectively repelled *Aedes aegypti* mosquitoes with a protection time of 410.4 min compared to 20% DEET with a protection time greater than 380 min [102]. Picaridin's method of action is not well understood; however, it is believed to be similar to that of DEET involving interference with an insect olfactory system [97]. Picaridin is mainly used in skin lotions; however, Ryan et al. produced microencapsulated picaridin in nylon 6.6 fibers by electrospinning. The authors produced both monofilament- and coaxial-spun fibers for evaluation. The fibers were loaded with up to 50 wt% picaridin to nylon. It was noted that the monofilament fibers exhibited an effective slow-release mechanism by releasing picaridin for an excess of 300 min at 100 °C in ambient conditions. The coaxial fiber prevented the effective release of picaridin due to the barrier created by the encapsulating nylon. Both fiber types were electro spun at 15 kV at a flow rate of 15 µL/min and a needle to collector distance of 10 cm. For the coaxial-electro-spun fiber, the inner needle used had dimensions i.d./o.d. = 0.411/0.711 mm and the outer needle i.d./o. d. = 2.16/2.77 mm. Both fiber types were dried for 24 h in ambient conditions after spinning [104].



Picaridin

4. Conclusions

Several essential oils share similar components such as linalool, 1,8-cineole, camphor, borneol, eugenol, and various terpenes. Constituents within a specific essential oil also include isomeric compounds such as carvacrol and thymol, which are monoterpene derivatives of cymene. It was derived from this research that, as pure essential oil, lavender essential oil provided the longest protection lasting up to 8 h. As an isolated compound, the same conclusion was made with PMD from lemon eucalyptus oil. Essential oils performed remarkably better than isolated ingredients derived from the oil due to synergistic effects between the oil components. Further synergy was discovered when essential oils were blended to provide more broad-spectrum insect control. The long-lasting effectiveness of synthetic compounds for insect control has always justified their use over natural compounds, such as essential oils. This was also their main disadvantage due to the long-term effects synthetic compounds have on the environment. It is therefore beneficial to consider more natural approaches for insect control. It was discovered that the main disadvantage of natural insect repellents, such as essential oils, is their volatile nature, which reduces their insect control effectiveness. This has been largely overcome with improvements such as encapsulation, adequate textile impregnation, and fixation. The use of biopolymers enhances the environmental benefits of these materials further, justifying the use of essential oils for insect control compared to synthetic compounds.

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