Volatile chemical composition of *Piper sancti-felicis* Trel essential oil and its biocidal action against *Tribolium castaneum* (Herbst)

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**ABSTRACT.** This research assessed the fumigant activity of the essential oil from *Piper sancti-felicis* Trel and five of its components on the *Tribolium castaneum* (Herbst) biological model. Hydrodistillation was used for extraction of the essential oil, with separation and identification of the compounds through gas chromatography coupled to mass spectrometry (GC-MS). The fumigant was evaluated through gas dispersion on the *T. castaneum*. The majority compounds found in the EO were β-nerolidol (15.4%), 5-carene (14.9%), p-cymene (9.1%), spathulenol (8.2%), α-cubebene (6.2%) and calamenene (5.2%). *Piper sancti-felicis* displayed fumigant activity with a LC₅₀ = 108.5 μg L⁻¹ air, and other individual monoterpenes tested such as α-terpinolene (LC₅₀ = 110.1 μg L⁻¹ air), p-cymene (LC₅₀ = 120.3 μg L⁻¹ air), 5-carene (LC₅₀ = 130.6 μg L⁻¹ air), (R)-limonene (CL₅₀ = 189.6 μg L⁻¹ air), and α-pinene (LC₅₀ = 213.1 μg L⁻¹ air), were significantly less toxic than methyl pyrimiphos used as a positive control, CL₅₀ = 87.4 μg L⁻¹ air. The essential oil of *P. sancti-felicis* can be considered as a natural source of biocides.

**Keywords:** essential oils; *Piper sancti-felicis*; toxicity; fumigant; *Tribolium castaneum*.

**Introduction**

Agricultural products grown in temperate and warm climates have been reported to suffer numerous losses, which can fall into a range of between 10 to 50% (Dissanayaka, Sammani, & Wijayaratnne, 2020). Some of such damages are caused by different types of blights, which attack food during harvest, production and storage. Due to this, the food manufacturing industry has chosen to take control measures against insects to guarantee the health of food in its manufacturing process. The problem lies in the infestation of the product when exiting the facilities and upon being stored in various points of sale (Rajabpour, Mashahdi, & Ghorbani, 2019).

*Tribolium castaneum* (Herbst) (Coleoptera: Tenebrionidae), is considered one of the insects that causes the most concern in the food industry and generates the contamination of a considerable number of stored foods, such as cereals, legumes, grains, spices, among others. *T. castaneum* is known as the red flour beetle and has been declared the culprit of the loss of grain weight, the decrease in its nutritional and industrial properties, the production of toxic quinones contaminating flour and its products, and of allergy in individuals who consume food products of this type (Ahmadi, Abd-allah, & Moharramipour, 2013).

In order to minimize these economic losses generated by such insects, the use of different pesticides has been implemented. In doing this, the United Nations Food and Agriculture Organization (FAO) has defined such pesticides as substances consisting of synthetic chemical components with the ability to control, repel or destroy any pest or microorganism capable of contaminating and devastating plant species and their respective products (Opit, Phillips, Aikins, & Hasan, 2012). Among the most used pesticides are organophosphates, neonicotinoids, substitute benzene, pyrethroids, among others (Jactel et al., 2019). However, most of these are in no case beneficial for the environment and the health of animals and humans, besides causing for adverse effects such as pesticide residue in the environment, food, impact on non-target species, low degradation, bioaccumulation, resistance in insects and management risks, among others (Arredondo, Hurtado, & Castañeda, 2011; Daglish, Nayak, Pavic, & Smith, 2015).
Due to the above, there is a global interest in the search for alternatives to replace chemical pesticides in order to reduce the consequences caused by them; currently, a growing trend towards the use of plant products has emerged, the most outstanding of which is the current research in essential oils and their components on account of their fumigant action, as well as other advantages over conventional products in terms of rapid degradation, local availability and low toxicity to mammals, among others (Guo et al., 2015; Yang et al., 2015; Liang et al., 2017).

This has led to the active search for available alternatives in order to replace synthetic pesticides. The use of biopesticides for insect control in cereal storage has grown worldwide (Pimentel, Faroni, Tótola, & Guedes, 2007; Opit et al., 2012), through the use of essential oils as botanical pesticides (Jaya, Prakash, & Dubey, 2014; Yang et al., 2015; Hu, Wang, Dai, & Zhu, 2019; Baccari et al., 2020). These have different modes of action on insects, in terms of promoting toxicity, mortality, anti-feeding activity, growth inhibition, the suppression of reproductive behavior and a reduction in fecundity and fertility, among others (Isman, 2006; Zarrad, Hamouda, Chaieb, Laarif, & Jemâa, 2015).

On a global basis, Colombia is considered a country with wide biodiversity in terms of its flora and, particularly, in the department of Chocó, some 9,000 species of endemic vascular plants claim a quarter of that figure. These have generated special interest given their potential and richness in natural substances, such as volatile compounds, especially in aromatic plants, from which essential oils can be extracted (Rangel-Ch & Rivera-Díaz, 2004; Pino-Benítez, 2009).

Such flora from the Choco region, nonetheless, is still unexplored and only some of the species of Piperaceae, have been studied and have demonstrated their antibacterial, antifungal, repellent, anti-food and healing activities, among others (Pino-Benítez, 2008; Jaramillo-Colorado, Julio-Torres, Duarte-Retrepo, González-Coloma, & Julio-Torres, 2015a). The genus Piper contains approximately 2,000 species, which are widely distributed worldwide and are characterized, for the most part, by their large number of medicinal (analgesic, anti-inflammatory, anti-asthma, anti-cancer, etc.) and biological (antifungal, fumigant, antioxidant, repellent and antibacterial, etc.) properties, all of which make Piperaceae gain great economic, commercial and medicinal value due to their chemical composition, rich in flavonoids, esters, unsaturated amides, steroids, alkaloids, polyphenols, terpenes, prenylated benzoic acids, epoxides, and piperidine, among others (Vanegas, Suaza, Naranjo, & Trujillo, 2012; Galeano et al., 2013; Silva et al., 2014).

There are several papers on the bioactivity of Piperaceae, which highlight the properties described so far, i.e. Piper daniel-gonzalezii Trel. and its leishmanicidal and reducing activities (Galeano et al., 2013), Piper peltatum L, as an anti-inflammatory, diuretic and antipyretic agent, Piper aduncum L and its medicinal properties in infusions capable of neutralizing viruses and infections and Piper sancti-felicis, due to its inhibitory activity against the enzyme acetylcholinesterase (Pino-Benítez, Espinosa, & Nagles, 2005; Silva et al., 2014; Jaramillo-Colorado, Pino-Benítez, & González-Coloma, 2019b).

Therefore, this research project an assessment of the fumigant activity of the essential oil from P. sancti-felicis Trel and five of its components on the T. castaneum biological model.

Material and methods

Reagents and chemical products

In this study, different chemical products were used. Anhydrous Na₂SO₄ and tetradecane standard for chromatography were obtained from Merck (Darmstadt, Germany); dichloromethane, acetone, and hexane from AppliChem Panreac (Darmstadt, Germany); limonene, 3-carene, p-cymene, α-terpinolene, and α-pinene compounds were bought from Sigma-Aldrich (St. Louis, MO, USA). Other materials, such as filter paper, were purchased from GE Healthcare (Hangzhou, China).

Vegetal material

Piper sancti-felicis plants were collected in the rural area of Quibdó, department of Chocó, Colombia (latitude 5.6918802 and longitude -76.6583481, northern hemisphere) (See Figure 1). The species was identified in the Colombian National Herbarium, with Voucher number COL No-519969, the image of exsiccate from P. sancti-felicis can be seen in the Figure 2.
Biocidal action of *Piper sancti-felicis* Trel against *Tribolium castaneum* (Herbst)

Figure 1. Geographical location of the collection point for plant material (Source: Instituto Geográfico Agustin Codazzi and QGIS version 2.18).

Figure 2. Image of exsiccate *Piper sancti-felicis*.

**Extraction of essential oil (EO)**

The oil was isolated at the laboratory of the Natural Products Group, *Universidad Tecnológica del Chocó*, Quibdó, based in the department of Chocó, Colombia. It was obtained through the hydrodistillation method by using a Clevenger type distillation equipment (Jaramillo-Colorado, Martelo, & Duarte-Restrepo, 2012). A total of 500 g of fresh leaves and stems, finely chopped, were immersed in water and, subsequently, hydrodistillation was carried out for two hours. The essential oil was separated from the water by decantation with the addition of anhydrous Na$_2$SO$_4$. An aliquot of the oil (30 µL) was diluted in 1 mL of dichloromethane for subsequent chromatographic analysis. This EO was stored under refrigeration temperature (± 4°C) prior to its use.

**Gas chromatography analysis**

For the identification of volatile and semi-volatile secondary metabolites of essential oils, the gas chromatography technique was used in Agilent GC-7890B coupled to Agilent MSD-5977A mass spectrometry, with an electron impact at 70 eV equipped with an HP-5MS column (30 m x 0.25 mm x 0.25 µm, methylpolysiloxane) in a 1: 100 split ratio, an injection of 1 µL, with helium as carrier gas (flow rate of 1.00 mL min.$^{-1}$ and constant linear speed of 36.8 cm s$^{-1}$), with temperature of the injector, detector and of the transfer line at 250, 150 and 280°C, respectively. The oven temperature programming started off at 70°C with a heating ramp of 4°C min.$^{-1}$ up to 180°C, followed by a ramp of 10°C min.$^{-1}$ up to 250°C. Compound identification was carried out by comparison with retention rates (Adams, 2007), and fragmentation patterns of mass spectra with the NIST database, Version 2.0 from 2008.

1 Retrieved from http://data.huh.harvard.edu/81ad83be-5a5a-442d-981e-279e9249161b
Culture of *Tribolium castaneum* (Herbst)

For the bioassays, the *T. castaneum* species was used, which was obtained from a food mix infested by this weevil in wholesale locations located in the city of Cartagena, Bolívar, Colombia, and subjected to screening. The weevils obtained were cultivated in the Agrochemical Research Laboratory of the School of Exact Sciences at Universidad de Cartagena, Colombia, at room temperature (26 ± 2°C), at a relative humidity of 70 to 85%, and a photoperiod of 12 hours (light/dark). *Tribolium castaneum* was classified and deposited in different watertight vessels containing flour without infestation and supplemented with yeast at a 1:10 ratio. Subsequently, they were separated into their different states (larvae and adults) for later use.

Bioassay of fumigant activity with *Tribolium castaneum* (Herbst)

A total of 10 *T. castaneum* weevils were deposited in each vial, at the different concentrations used. A 2 cm diameter filter paper disc was inserted into each, which was placed on a hook firmly attached to the bottom of the cap of a 22 mL glass vial (the filter paper did not contact the insect), and then impregnated with acetone as a negative control; five replicates were made, then the pier’s EO was added and was studied at concentrations of 500, 350, 250, 150, 50 μL of oils L⁻¹ of air, respectively. The vials were stored in the dark and the number of dead weevils was read 24, 48 and 72 hours after the start of the bioassay. Similarly, the control was carried out with the commercial insecticide ‘PIRLAN 50CE’, with the active ingredient of an organophosphate pesticide, methyl-pyrimiphos. In the Figure 3 can be seen the test of the fumigant activity of the EO from *P. sancti-felicis*.

Mortality percentages were calculated and analyzed by ANOVA and Student t tests. Mortality rates were calculated using the statistical formulas of Abbott and Probit to determine the LC50, chi-square values and related parameters (Jaramillo-Colorado, Martínez-Cáceres, & Duarte-Restrepo, 2016; Jaramillo-Colorado, Suarez-López, & Marrugo-Santander, 2019a). All data were processed through the Statgraphics Centurion XVI statistical software version 16.1.03.

![Image](image-url)

**Figure 3.** Test of the fumigant activity of the EO from *P. sancti-felicis* (Author’s own source).

Results and discussion

Chemical composition analysis

The EO extracted from the leaves and stems of *P. sancti-felicis* through the hydrodistillation method, reached a yield of 0.18% (% w w⁻¹). On the other hand, the volatile EO compounds of *P. sancti-felicis*, separated and identified by gas chromatography coupled to the mass spectrometry (MS) detector, are listed in Table 1. Most of the compounds found were: β-nerolidol (15.4%), 3-carene (14.9%), p-cymene (9.1%), spatulenol (8.2%), α-cubebe (6.2%) and calamenene (5.2%).

Fumigant activity

The fumigant activity of EO from *P. sancti-felicis* and of the six pure terpenes against adult *T. castaneum* was determined. The results of the probit data analysis, based on the lack of overlap at 95% fiducial limits, showed that methyl-pyrimiphos (positive control, CL₅₀ = 87.4 μg mL⁻¹ air) was significantly more toxic than *P. sancti-felicis* (CL₅₀ = 108.5 μg mL⁻¹ air) and other individual monoterpenes tested such as α-terpinolene (CL₅₀ =110.1 μg mL⁻¹ air), p-cymene (CL₅₀ =120.3 μg mL⁻¹ air), 3-carene (138.9 μg mL⁻¹ air), (R)-limonene (CL₅₀ = 189.6 μg mL⁻¹ air), and α-pinene (CL₅₀ = 215.1 μg mL⁻¹ air; Table 2).
environmentally regulated, such as geographical location, weather conditions, time of year, soil, (LCair) [F (6.00) = 36.01; p < 0.001]; 3

Biocidal action of

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α-Pinene
3,7,7-trimethylcyclohepta-1,3,5-triene
β-Pinene
(+)-3-Carene
p-Cymene
p-Cymene
D-Limonene
α-Terpinolene
Linalool
p-Cymen-8-ol
Eucarvone
α-Cubebe
α-Copaene
trans-Caryophyllene
β-Copaene
Aromadendrene
Allo-aromadendrene
g-Murolene
Bicyclosquiphellandrene
Calamenene oxide
4-epi-Cubebol
Calamenene
α-Calacorene
β-Nerolidol
Spathulenol
Caryophyllene Oxide
tau-Cadinol
α-Cadinol
Cadalone
cis-Nerolidol acetate
Aromadendrene Epoxide

Table 1. Chemical composition of essential oil from leaves of *Piper sancti-felicis* obtained by hydro-distillation.

<table>
<thead>
<tr>
<th>No</th>
<th>Compounds*</th>
<th>IR (teoretical) HP-5</th>
<th>IR (experimental) HP-5</th>
<th>Relative area#, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>α-Pinene</td>
<td>939</td>
<td>941</td>
<td>1.6±0.2</td>
</tr>
<tr>
<td>2</td>
<td>3,7,7-trimethylcyclohepta-1,3,5-triene</td>
<td>970</td>
<td>964</td>
<td>4.7±0.5</td>
</tr>
<tr>
<td>5</td>
<td>β-Pinene</td>
<td>980</td>
<td>978</td>
<td>1.0±0.1</td>
</tr>
<tr>
<td>4</td>
<td>(+)-3-Carene</td>
<td>1011</td>
<td>1012</td>
<td>14.9±0.8</td>
</tr>
<tr>
<td>2</td>
<td>p-Cymene</td>
<td>1022</td>
<td>1020</td>
<td>1.0±0.2</td>
</tr>
<tr>
<td>6</td>
<td>p-Cymene</td>
<td>1026</td>
<td>1028</td>
<td>9.1±0.5</td>
</tr>
<tr>
<td>7</td>
<td>D-Limonene</td>
<td>1031</td>
<td>1050</td>
<td>2.6±0.5</td>
</tr>
<tr>
<td>8</td>
<td>α-Terpinolene</td>
<td>1088</td>
<td>1080</td>
<td>1.0±0.2</td>
</tr>
<tr>
<td>9</td>
<td>Linalool</td>
<td>1098</td>
<td>1096</td>
<td>1.1±0.2</td>
</tr>
<tr>
<td>10</td>
<td>p-Cymen-8-ol</td>
<td>1183</td>
<td>1180</td>
<td>2.5±0.5</td>
</tr>
<tr>
<td>11</td>
<td>Eucarvone</td>
<td>1248</td>
<td>1250</td>
<td>1.6±0.4</td>
</tr>
<tr>
<td>12</td>
<td>α-Cubebe</td>
<td>1351</td>
<td>1346</td>
<td>6.2±0.5</td>
</tr>
<tr>
<td>13</td>
<td>α-Copaene</td>
<td>1376</td>
<td>1380</td>
<td>1.8±0.2</td>
</tr>
<tr>
<td>14</td>
<td>trans-Caryophyllene</td>
<td>1418</td>
<td>1410</td>
<td>1.4±0.2</td>
</tr>
<tr>
<td>15</td>
<td>β-Copaene</td>
<td>1422</td>
<td>1416</td>
<td>0.9±0.3</td>
</tr>
<tr>
<td>16</td>
<td>Aromadendrene</td>
<td>1439</td>
<td>1452</td>
<td>1.0±0.2</td>
</tr>
<tr>
<td>17</td>
<td>Allo-aromadendrene</td>
<td>1461</td>
<td>1455</td>
<td>1.6±0.2</td>
</tr>
<tr>
<td>18</td>
<td>g-Murolene</td>
<td>1477</td>
<td>1472</td>
<td>2.6±0.4</td>
</tr>
<tr>
<td>19</td>
<td>Bicyclosquiphellandrene</td>
<td>1488</td>
<td>1480</td>
<td>1.0±0.2</td>
</tr>
<tr>
<td>20</td>
<td>Calamenene oxide</td>
<td>1489</td>
<td>1490</td>
<td>3.6±0.4</td>
</tr>
<tr>
<td>21</td>
<td>4-epi-Cubebol</td>
<td>1495</td>
<td>1498</td>
<td>1.5±0.1</td>
</tr>
<tr>
<td>22</td>
<td>Calamenene</td>
<td>1521</td>
<td>1510</td>
<td>5.2±0.5</td>
</tr>
<tr>
<td>23</td>
<td>α-Calacorene</td>
<td>1542</td>
<td>1536</td>
<td>1.4±0.2</td>
</tr>
<tr>
<td>24</td>
<td>β-Nerolidol</td>
<td>1564</td>
<td>1550</td>
<td>15.4±1.2</td>
</tr>
<tr>
<td>25</td>
<td>Spathulenol</td>
<td>1576</td>
<td>1566</td>
<td>8.2±0.5</td>
</tr>
<tr>
<td>26</td>
<td>Caryophyllene Oxide</td>
<td>1581</td>
<td>1572</td>
<td>1.0±0.2</td>
</tr>
<tr>
<td>27</td>
<td>tau-Cadinol</td>
<td>1640</td>
<td>1633</td>
<td>1.0±0.1</td>
</tr>
<tr>
<td>28</td>
<td>α-Cadinol</td>
<td>1653</td>
<td>1642</td>
<td>1.1±0.5</td>
</tr>
<tr>
<td>29</td>
<td>Cadalone</td>
<td>1674</td>
<td>1668</td>
<td>2.4±0.6</td>
</tr>
<tr>
<td>30</td>
<td>cis-Nerolidolacetate</td>
<td>1675</td>
<td>1670</td>
<td>1.0±0.2</td>
</tr>
<tr>
<td>31</td>
<td>Aromadendrene Epoxide</td>
<td>1745</td>
<td>1760</td>
<td>1.0±0.1</td>
</tr>
</tbody>
</table>

*Identification made by mass spectrum (EI: electron impact ionization, 70 eV; peak matching > 90%, database wiley, NIST08); Literature retention indices (Adams, 2007).

#Experimental retention indices on HP-5 column; %Averages of three independent extractions.

Table 2. Fumigant toxicity from *Piper sancti-felicis* Trel. essential oil and its constituents against *Tribolium castaneum*.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>95% FL</th>
<th>$\chi^2(df)$</th>
<th>CL50 (µg mL$^{-1}$ of air)</th>
<th>Slope±SE</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>P. sancti-felicis</em></td>
<td>[87,212 - 119,700]</td>
<td>0.35</td>
<td>108.5</td>
<td>0.0022±0.0006</td>
</tr>
<tr>
<td>α-Terpinolene</td>
<td>[97,426 - 112,215]</td>
<td>0.85</td>
<td>110.1</td>
<td>0.0040±0.0021</td>
</tr>
<tr>
<td>p-Cymene</td>
<td>[99,263 - 139,698]</td>
<td>1.72</td>
<td>120.3</td>
<td>0.0145±0.0012</td>
</tr>
<tr>
<td>3-Carene</td>
<td>[110,533 - 120,789]</td>
<td>1.63</td>
<td>130.6</td>
<td>0.0053±0.0012</td>
</tr>
<tr>
<td>R-Limonene</td>
<td>[170,428 - 208,754]</td>
<td>1.85</td>
<td>189.6</td>
<td>0.0017±0.0014</td>
</tr>
<tr>
<td>α-Pinene</td>
<td>[192,751 - 233,492]</td>
<td>1.01</td>
<td>213.1</td>
<td>0.0015±0.002</td>
</tr>
<tr>
<td>Commercial insecticide (methyl pyrimiphos)</td>
<td>[78,072 - 96,718]</td>
<td>0.183</td>
<td>87.4</td>
<td>0.0019±0.0005</td>
</tr>
</tbody>
</table>

*95% lower and upper fiducial limits are shown in parenthesis. SE: Standard deviation.

*Piper sancti-felicis* EO, α-terpinolene, p-cymene, 3-carene, and R-limonene exhibited high fumigant activity (> 85%) at 500 µg mL$^{-1}$ air, after two hours of exposure, as shown in Figure 4.

The differences vanished in the number of dead *T. castaneum* after treatment with *P. sancti-felicis* EO (LC$_{50}$ = 108.5 µg mL$^{-1}$ air), [F (11.15) = 124.2; p < 0.001] for all doses tested compared to the pyrimiphos control group (LC$_{50}$ = 87.4 µg mL$^{-1}$ air), [F (6.60) = 12.66; p < 0.001] (Figure 4). The same was observed for treatments with α-Terpinolene (LC$_{50}$ = 110.1 µg mL$^{-1}$ air) [F (5.579) = 28.93; p < 0.001]; p-Cymene (LC$_{50}$ = 120.3 µg mL$^{-1}$ air) [F (6.00) = 56.01; p < 0.001]; 3-Carene (LC$_{50}$ = 130.6 µg mL$^{-1}$ air) [F (8.00) = 64.15; p < 0.001]; R-Limonene (LC$_{50}$ = 189.6 µg mL$^{-1}$ air) [F (5.988) = 55.85; p < 0.001]; α-Pinene (LC$_{50}$ = 213.1 µg mL$^{-1}$ air) [F (6.329) = 40.06; p < 0.001].

The yield and chemical composition of an essential oil can be affected by factors exogenous or environmentally regulated, such as geographical location, weather conditions, time of year, soil, precipitation, light, growing site, and might modify the quantitative/qualitative amount of the compounds in the oils. And the endogenous factors that are strictly correlated to the physiological and anatomical characteristics of the plants associated to chemical variation between different plant parts, and from genetically linked elements (Barra, 2009). The aforementioned is reiterated by the notable differences

Acta Scientiarum. Biological Sciences, v. 43, e53534, 2021
between the yields of the *P. sancti-felicis* EO, which registered a yield of 0.18% (pp⁻¹), which is much lower than that reported on the same species by Jaramillo-Colorado et al. (2019b), with a percentage of 0.32%.

**Figure 4.** Fumigant activity of EO from *Piper sancti-felicis* Trel., and their constituents α-terpinolene, *p*-cymene, 3-carene, R-limonene, and α-pinene against *Tribolium castaneum* at 24 hours after exposure.
However, variations have been observed in other species of the genus *Piper* spp. such as *Piper cernuum*, collected in Blumenau, Brazil, with reports in various seasons such as winter (1.49%), spring (1.66%) and summer (2.07%). Whereas, in studies carried out using the essential oil from *Piper ananifolium* out of Paraúapebas, Brazil, a yield of 0.6% was provided (Gasparetto et al., 2017), which is similar to what was obtained by Santos et al. (2015) in *Piper Regnellii* from Dourados, state Mato Grosso do Sul, Brazil, with a yield of 0.5% from in leaves and 0.2% from stems. The main compounds detected in the essential oil of *P. sanctifelcis* from Chocó were monoterpenes such as: β-nerolidol (15.4%), 3-carene (14.9%), p-cymene (9.1%) and sesquiterpenes: spathulenol (8.2%), and α-cubebene (6.2%). In a previous study on the volatile composition from *P. sanctifelcis* Chocoan essential oil, it was found that the main compounds were: d-3-carene (55.3%), limonene (27.7%) and β-pinene (6.9%) (Jaramillo-Colorado et al., 2015b). The considerable variability in the composition of the EO probably refers to the differences in certain ecological conditions, which are related to the production of secondary metabolites (Benyelles et al., 2017). Much research indicates the existence of the morphological and chemical variability of plant chemotypes, and their wide geographic range, suggesting that species have adapted to new combinations of environmental factors through permanent changes in the genotype, as well as the plasticity of the phenotype (Andrade et al., 2016; Paucar et al., 2018).

When reviewing other species such as *P. auritum* (Havana, Cuba), compounds such as b-caryophyllene (4.65%), germacrene (3.11%), cis-nerolidol (2.8%), linalol (2.29%), γ-terpinene (2.19%), terpinolene (1.87%), α-terpinene + p-cymene (1.79%), β-pinene (1.45%) and bicyclogermagrene (1.26%), were studied by (Sánchez, Pino-Benítez, Correa, Naranjo, & Iglesia, 2009). On the other hand, for *P. tuberculatum* (Sucre, Venezuela), spatulenol (11.37%), α-farnesene (6.22%), fumelene epoxide II (6.04%), β-eudesmol (4.36%), 2-tridecanone (4.27%), 2-pentadecanone (4.06%), ledeano (3.62%), (E, E)-farnesilactone (3.55%), β-cedrenoxide (2.96%), α-cadinol (2.86%), dibutylphthalate (2.84%), (1RS, 2SR)-2-hydroxy-2,4,4-trimethyl-3-(3-methyl-5-buteryliden) cyclopentyl methyl ketone (2.68%), 4-norpyridoxol (2.26%), epiglobulol (2.14%) and 8-acetyl-3, 3-epoxyxemane-6,6,7-trimethylbicyclo[5,1,0]octan-2-one (2.11%) were present in (Ordaz, D'Armas, Yáñez, & Moreno, 2011). Other data in *P. hispidinervum* (Porto Alegre, state Rio Grande do Sul, Brazil), found safrole (85.08%), terpinolene (5.40%), bicyclogermacrene (1.43%), (E)-β-ocimeno (1.59%), (Z)-β-ocimeno (0.64%), δ-3-carene and spatunol (0.55%) (Andrés et al., 2017; Sauter et al., 2012). Likewise, in *P. aduncum* (state of Minas Gerais, Brazil), α-terpinol (5.9%), trans-ocimen (4.8%), β-pinene (4.7%) and α-pinene (4.5%) were present. These five monoterpenes comprise 75.7% of the mixture. Bicyclogermacrine (4.4%) was assigned as the most representative sesquiterpene (Oliveira et al., 2014). The foregoing probably explains how the volatile chemical composition varies remarkably, depending on its geographical location and according to genus and species, accounting for very few similarities in its chemical composition.

In this study, the fumigant activity could be attributable to the compounds belonging to the group of terpenes. Studies show that the repellent properties of essential oils are associated with the presence of mono and/or sesquiterpene compounds. Particularly, the repellent or fumigant properties of essential oils are associated with the presence of monoterpenes and sesquiterpenes in their volatile chemical composition (Khani & Heydarian, 2014; Ukeh & Umoetok, 2011). However, depending on the type of components present, these may or may not enhance activity. It is recognized that β-myrcene, caryone, α-pinene, cineol, eugenol, limonene, terpinolene, citronellol, citronellal, camphor, thymol, dilapil, linalool, terpinen-4-ol; α-terpinene, nerolidol, α-humulene and β-caryophyllene, among others, have repellent and/or fumigant activity against *Tribolium* (Stamopoulos, Damos, & Karagianidou, 2007; Saad, El-Deeb, & Abdelgaleil, 2019). On the other hand, in the case of the fumigant action of some terpenes, this is similar to that of some organophosphate compounds and carbamates present in some conventional insecticides, inhibitors of the enzyme acetylcholinesterase, which is attributed to rapid death due to respiratory failure in certain stored grain insects (Saad et al., 2019).

It should be noted that some monoterpenes have been recognized as useful pharmacological ingredients due to their ability to treat numerous diseases. For example, limonene and its metabolites (perlic acid and methyl ester) perform bioactivity as antitumor, antiviral, anti-inflammatory and antibacterial agents. Such therapeutic properties, have been well documented (Vieira, Beserra, Souza, Totti, & Rozza, 2018), while biological properties, such as chemoprotective agents, are being tested in some studies (Miller et al., 2015; Mukhtar, Adu-Frimpong, Xu, & Yu, 2018). p-Cymene is another monoterpene found in *P. sanctifelcis* EO, which has been reported as a palliative treatment of pain from cancer through its participation in inhibitory pathways and modulation of calcium current (Saad et al., 2019).
Interestingly, some studies evaluate the activities of all the compounds present in the extracts, as the majority components are not always responsible for the active results. Revised publications confirm that the main components are not the only ones responsible for the activities, since the responses sometimes depend on the interactions between the compounds that are found in a smaller proportion (Couto et al., 2019).

Taking the above into account, the components found in essential oils possess biological actions, and in some cases, they are more effective than synthetic insecticides. However, some do not have such capacity when standing alone, but they do with the help of other terpenes or sesquiterpenes, on a synergistic basis. Some researches expose that the reciprocal action of the components can be additive or subtractive depending on the type of activity and the compounds (Couto et al., 2019). On the other hand, there is evidence, that by developing natural plant extracts and essential oils in the future the negative effects of synthetic chemicals will reduce in the control of insects that harm agricultural products and/or stored food. As reported by Zhang et al. (2017), who demonstrated the fumigant activity of 42 pure monoterpenes against Musca domestica L. revealed that the compounds p-cymene and terpinolene were strong in their fumigant activity against M. domestica. On the other hand, limonene enantiomers also presented repellent and fumigant activity against Tribolium confusum in a study by Malacrinò, Campolo, Laudani, and Palmeri (2016).

Conclusion

This research contributes to the knowledge of essential oils as natural sources of biocides and will be of help in both the environmental and health fields, especially the essential oil extracted from P. sancti-felicis which, thanks to its chemical composition rich in terpenes makes it an oil with great potential to develop as insecticides and/or natural repellents to control Tribolium castaneum.

Acknowledgements

Universidad Tecnológica del Chocó, Natural Products Group, Young Researchers Program at Universidad Tecnológica del Chocó. The authors thank funding from Ministerio de Ciencia, Tecnología e Innovación, Ministerio de Educación Nacional, Ministerio de Industria, Comercio y Turismo, ICETEX - Colombia Científica, Fondo José de Caldas; Grant RC-FP44842-212-2018. To Research Groups Support Program - Research Vicepresidency at Universidad de Cartagena (2015-2019).

References


Acta Scientiarum. Biological Sciences, v. 43, e53534, 2021


Biocidal action of *Piper sancti-felicis* Trel against *Tribolium castaneum* (Herbst)


