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# Essential Oils of Three *Hypericum* Species from Colombia: Chemical Composition, Insecticidal and Repellent Activity Against *Sitophilus zeamais* Motsch. (Coleoptera: Curculionidae)

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**Abstract:** The maize weevil (*Sitophilus zeamais*) is one of the main insect responsible of significant losses in stored products, and to keep nutritional value of them to find effective and safe solutions are very important. The *Hypericum* genus might be a potential source of new bio-insecticides due to the chemical composition of essential oils. In this study, components of essential oils of three *Hypericum* species were investigated for first time by Gas Chromatography-Mass Spectrometry (GC-MS) and, fumigant and contact toxicities as well as the repellent activity of essential oils of them were evaluated against *S. zeamais* adults. While the main components in *H. mexicanum* oil were determined as *n*-nonane (53.08%) and α-pinene (25.28%), the major constituents were determined as α-pinene (45.52%) and β-caryophyllene (13.59%) in the essential oil of *H. myricariifolium*. Chemical composition of essential oil of *H. juniperinum* were found to be *n*-nonane (12.0%), α-pinene (8.25%), geranyl acetate (7.93%), and β-caryophyllene (13.60%). The results revealed that *H. mexicanum* and *H. myricariifolium* oils have fumigant toxicity ($LC_{50}$ < 500 µL/L air) and a potential action as repellents (RP > 70% at 6.2–22.7 µL/L air) for the control of the pest.

**Keywords:** *Sitophilus zeamais*; essential oil; repellent; *Hypericum mexicanum*; *Hypericum myricariifolium*; *Hypericum juniperinum*. 

## 1. Introduction

The maize weevil (*S. zeamais*), is one of the major pests of stored products that affect different commodities important for food security, included maize, rice, sorghum, wheat and among others. The negative impact attributed to this pest is principally due to their high reproduction rate and with the possibility of larvae and adults to damage the grains **[**1, 2**]**. This primary pest can damage shelled grains, creating holes and reducing them to powder. Besides, it can cause a loss in germination ability and nutritional quality of the grains **[**3, 4**]**. The control of this kind of insects is performed by use of synthetic pesticides such as methyl bromide and phosphine **[**5**]**. However, the indiscriminate application of synthetic products has led to serious problems such as toxic residues in the products, environment

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pollution and has led to the increased resistances of pests [6, 7]. Thus, the development of new chemical control strategies with less environmental impact and high effectivity is necessary.

The essential oils (EOs) are a promissory source of bioinsecticides due to the chemical diversity of their secondary metabolites, among which monoterpenes, sesquiterpenes, phenylpropanoids and hydrocarbons predominate [8, 9, 10]. This variety in terms of composition, added to lipophilicity and high volatility, allows EOs to present several entrance modes to the insect and, therefore, exert different modes of insecticide action [11, 12]. Most EOs are highly effective as repellents, and others are toxic by direct contact or penetration into the body by the respiratory route [13, 14]. The EOs have also shown insecticidal actions such as inhibition of molting, reduction in growth and fecundity, cuticle disruption, and effects on the invertebrate octopamine pathway [15, 16]. Other EOs affect the nutritional physiology of insects, either by modifying their behaviour or by producing toxic effects after ingestion [17, 18].

*Hypericum* genus is composed of shrubs or herbs that usually possess secretory structures present in both the vegetative and reproductive organs; among them are translucent glands containing considerable amounts of EOs [43, 44]. Many species are native to high mountain regions of Andes in Central and South America, where a complex mixture of habitats occurs in Paramo. Due to the particular zones where *Hypericum* species grow, they possess the ability to biosynthesize a wide variety of defensive secondary metabolites. Even though many species of the genus highlighted their medicinal properties like anti-oxidant, anti-inflammatory, anti-depressant and anti-nociceptive [18, 45, 46], several studies has been reported on their effectiveness as insecticides [19,18,20]. Lipophilic extract obtained from the aerial parts of *H. polyanthemum* showed larvicidal activity and inhibited the pupae formation of *Aedes aegypti* [19]. Regarding to those reports against stored-product pests, *H. scabrum* oil was found to be toxic by fumigation on adults of *Bruchus dentipes* [18]; meanwhile, EO from *H. hyssopifolium* showed promissory fumigant toxicity against *Sitophilus oryzae* and *Tribolium confusum* [20].

In Colombia, studies of the bioactivity and secondary metobolite profile of few alcoholic extracts of *Hypericum* species have been reported. Methanol extract and butanol fractions of *H. juniperinum* showed antidepressant effects [21], and ethanol extracts of *H. mexicanum, H. myricariifolium* and *H. juniperinum* exhibited high inhibitory activity against *Staphylococcus aureus* and *Staphylococcus epidermidis,* and those extracts are mainly composed by phenolics such as flavonoids, tannins and quinones, as well as saponins [21, 22]. Even though the species in current study have been subjected to preliminary investigations, none of them has focused on the study of the chemical composition of their essential oils and insecticidal activities. Therefore, this study was designed with the objective to determine the chemical composition of the EOs extracted from these three *Hypericum* species and evaluate the insecticidal activity of the oils against *S. zeamais* adults.

## 2. Materials and Methods

### *2.1. Plant Material*

The aerial parts of *H. mexicanum* L., *H. juniperinum* Kunth and *H. myricariifolium* Hieron, were collected at 3542 masl on the Usme-Sumapaz road, Cundinamarca, Colombia. The voucher specimens rest in the herbarium of the "Jardín Botánico José Celestino Mutis" with the numbers JBB10659, JBB00348 and JBB00350, respectively.

### *2.2. Extraction of Essential Oils*

The aerial parts (fresh leaves and branches) of the three plants collected were subjected to steam extraction for 2 hours. The EOs were recovered by condensation using a Clevenger-type apparatus and after decantation they were dried with anhydrous sodium sulfate and stored in amber sealed glass bottles at 4 °C until use.

### *2.3. Chemical Composition of Essential Oils*

#### *2.3.1. Sample Preparation*

A volume of 25 µL of each EO was taken and brought to a final volume of 1 mL with n-hexane or dichloromethane. The standard hydrocarbon solution was prepared by dissolving 25 µL of a homologous hydrocarbon solution ($C_8$ - $C_{26}$) to a final volume of 1 mL with *n*-hexane.

#### *2.3.2. Analysis by GC-MS*

The chromatographic analysis was performed using an Agilent Tecnologies 6850 II series gas chromatograph with selective mass detector Agilent Technologies MSD5975B, which was operated at 70 eV, using a quadrupole analyzer, in full scan mode at 4.57 scan $s^{-1}$. Mass spectra were acquired between 40 and 400 *m/z*. The analysis was performed with two orthogonal polarity columns (DB-5MS and HP-INNOWax).

In the first analysis, a DB-5MS column ((5%-phenyl)-methylpolysiloxane, 60 m x 0.25 mm x 0.25 µm) was used with injection in Split mode (20:1) for 1.5 min. The temperature ramp started at 40 °C for 2 min, then it was increased to 123 °C (4 °C/min) and remained constant for 2 min. Afterward increased to 160 °C (4° C/ min) remained constant 5 min, subsequently increased to 220 °C (5 °C/min) and kept constant for 8 min. Finally, it was increased to 280 °C (5 °C/min) keeping it constant 4 min, for a total run time of 75 min. In the second analysis a HP-INNOWax column (polyethylene glycol (PEG), 60 m x 0.25 mm x 0.25 µm) was used with injection in Split mode (20: 1) for 1.5 min. The temperature ramp started at 45 °C for 4 min, then it was increased to 120 °C (3 °C/min) remained constant for 2 min. Finally, it was increased to 250 °C (4 °C/ min) keeping it constant 8 min, for a total time of 71.5 min. The injection volume used in each analysis was 1 µL.

#### *2.3.3. Determination of Chemical Composition of Essential Oil*

The chemical constituents were determined by comparing the mass spectra and retention indices obtained for each compound with those reported in NIST 14.L, Wiley 8.1 and Pherobase databases, as well as those published in the literature [23-25]. The Relative Retention Index (RRI) were calculated using a homologous series of hydrocarbons from $C_8$ to $C_{26}$, eluted under the same operational conditions described for EOs [24].

### *2.4. Bioassays*

#### *2.4.1. Insects*

*S. zeamais* adults were obtained from a colony maintained in the research group Química de Productos Naturales Vegetales Bioctivos (QuiProNaB) of the Chemistry Department of the Universidad Nacional de Colombia - Bogotá. The adults were kept in corn mixtures of ICA variety 508 and yellow corn ICA variety, arranged in a culture chamber under conditions of darkness, humidity (65 ± 5% RH) and temperature controlled (27 ± 1 °C) [26]. Adult insects between 6-10 days after emergence were used in the different activity tests.

#### *2.4.2. Preliminary Insecticidal Activity*

The preliminary insecticidal activity of the EOs was determined by the "vial in vial" method reported in the literature [27]. A volume of 11 µL of EOs was applied to a 2 cm diameter Wathman® No. 1 filter paper placed on top of a 1.5 mL glass vial. Subsequently, the vial was introduced into a 22 mL vial with screw-type closure containing 10 insects without sexing, leaving a final concentration of essential oil of 500 µL/L air. As positive controls, Nuvan 50 ® containing dichlorvox as active ingredient (100 µL/L air) and Fosfamin ® with phosphine as active ingredient (150 µL/L air) were used. The negative control was applied out in the same way, but without the addition of any substance. All tests were performed in triplicate under controlled temperature and humidity conditions (27 ± 1 °C y 65 ± 5

% HR). Insect mortality was determined at 24 hours. The insects were considered dead when no observed movement after stimulation for 15 s with an entomological pin. The percentage of mortality was calculated using the Abbott's [28] correction formula: Mortality (%) = [(%Mt - %Mc)/100 - %Mc] *100, were Mt = mortality on treatment and Mc = mortality of control.

*2.4.3. Fumigant Activity Test*

The fumigant activity test was carried out similarly to the test described above, except that insect contact with the EOs was avoided. To avoid contact, the vial in which the paper impregnated with EO was placed, was covered with sheer curtain. The same conditions of the previous trial were reproduced to evaluate the EOs: 11 µL (500 µL/L air) of EO and 24-hour mortality reading. The percentage of mortality was calculated using the Abbott's correction formula. To obtain the results that allowed estimating the LC50, different quantities of EOs were used (oils quantities between 1.1 - 18 µL for obtain concentrations between 50 - 818 µL/L air). All treatments were performed in quintupled under the same temperature and humidity conditions [29].

*2.4.4. Topical Contact Toxicity Test*

The contact toxicity was determined by the topical contact method, which consists of applying different amounts of EOs (0.10, 0.15 and 0.20 µL) on the insect's prothorax [30]. Untreated insects were used as negative control and commercial product Nuvan 50 ® was used as positive control at a volume of 0.10 µL. The treated insects were transferred to 22 mL glass vials, leaving 10 insects per vial. The vials were kept in the culture chamber under controlled temperature and humidity conditions (27 ± 1 °C and 65 ± 5% RH). All treatments were performed in triplicate and insect mortality was determined at 24 hours. Mortality percentages were calculated using the Abbott's correction formula.

*2.4.5. Repellent Activity Test*

The repellent action was tested using an olfactometer, consisting of two 290 mL bottles connected by a tube with a container located in the central part of the duct [31]. In one of the bottles, corresponding to the treatment, was placed a 1.5 mL vial that had a 2 cm diameter Whatman® No. 1 paper disc impregnated with different volumes of EO, corresponding to concentrations between 6.2 - 22.7 µL/L of air. In the other bottle, was placed a 1.5 mL vial with the paper without EO, and this acted as a control. Adult *S. zeamais* insects (20 per assembly) were incorporated through the central container of the connecting tube. The activity reading was done at 2, 6 and 24 hours after the application and the number of insects present in both containers (treated and untreated) were recorded. All treatments were performed in triplicate and the repellency percentage (RP) was calculated as RP= [(N–C)/(N+C)]*100, were N = number of insects present in the untreated area and C = number of insects in the treated area.

*2.5. Statistical Analysis*

The results of the tests are presented as mean ± standard error. Statistical significance was determined by the Tukey tests and an analysis of variance (ANOVA) was performed to determine whether results obtained for insecticidal activity assays were statistically different. Statistical significance was set at $P < 0.05$. For EOs with fumigant potential $LC_{50}$ was estimated using the fumigant method and the Probit model.

## 3. Results and Discussion

*3.1. Chemical Composition*

The GC–MS analysis with orthogonal polarity columns of the three EOs allowed identifying 51 compounds corresponding to 65-95% of the total composition **(**Table 1). The EOs presented in their chemical composition mainly monoterpenes (30.9–54.7%), sesquiterpenes (27.8–33.7%) and aliphatic hydrocarbons (23.11–57.6%).

**Table 1.** Chemical composition of EOs from the three *Hypericum* species.

| N° | Components | RRI | | | | Relative % | | |
|---|---|---|---|---|---|---|---|---|
| | | Non-polar DB-5MS | | Polar (HP-INNOWax) | | HME | HMY | HJU |
| | | Exp. | Range(Ref) | Exp. | Range(Ref) | | | |
| 1 | octane | 797 | 800 | - | - | 0.36 | - | 0.18 |
| 2 | 2-methyloctane | 866 | 858-872 | - | - | - | 0.54 | 3.82 |
| 3 | nonane | 904 | 900 | - | - | **53.08** | 1.59 | **12.00** |
| 4 | α-thujene | 928 | 931 | 1026 | 1012-1039 | 0.08 | 0.05 | - |
| 5 | α-pinene | 939 | 910-944 | 1023 | 1000-1040 | **25.28** | **45.52** | **8.25** |
| 6 | α-fenchene | 955 | 943-951 | 1055 | 1045-1054 | - | 0.05 | - |
| 7 | canphene | 956 | 929-968 | 1064 | 1040-1083 | - | 0.28 | - |
| 8 | 3-methylnonane | 971 | 970-977 | 976 | 966-976 | 1.24 | 0.49 | - |
| 9 | sabinene | 976 | 973-976 | 1119 | 1123-1147 | 0.32 | - | - |
| 10 | β-pinene | 983 | 960-990 | 1105 | 1096-1120 | 3.60 | 2.86 | 0.92 |
| 11 | myrcene | 990 | 969-993 | 1172 | 1150-1176 | 1.11 | 1.67 | 3.94 |
| 12 | decane | 1000 | 1000 | 1000 | 1000 | 0.13 | - | 0.12 |
| 13 | α-terpinene | 1020 | 1012-1020 | 1184 | 1178-1223 | - | 0.07 | - |
| 14 | *p*-cymene | 1028 | 1014-1034 | 1279 | 1261-1290 | 0.14 | 0.55 | - |
| 15 | limonene | 1033 | 1031-1039 | 1205 | 1198-1234 | 0.28 | 1.90 | 0.79 |
| 16 | cis β-*o*cimene | 1035 | 1023-1050 | 1242 | 1242-1252 | - | 1.12 | - |
| 17 | β-phellandrene | 1036 | 1017-1043 | 1215 | 1195-1222 | 0.05 | - | - |
| 18 | *trans*-β-*o*cimene | 1046 | 1039-1061 | 1259 | 1242-1261 | - | 0.22 | - |
| 19 | γ-terpinene | 1060 | 1030-1078 | 1253 | 1221-1262 | - | 0.23 | 0.27 |
| 20 | 2-methyldecane | 1062 | 1062-1077 | 1051 | 1053-1057 | 0.07 | - | - |
| 21 | α-terpinolene | 1087 | 1063-1104 | 1291 | 1275-1297 | - | 0.21 | 0.09 |
| 22 | undecane | 1097 | 1099 | 1094 | 1099-1100 | 2.72 | 0.65 | 0.44 |
| 23 | nonanal | 1099 | 1082-1108 | 1402 | 1382-1415 | - | - | 2.25 |
| 24 | γ-terpineol | 1199 | 1188-1207 | 1696 | 1684-1695 | - | - | 0.15 |
| 25 | decanal | 1207 | 1186-1207 | 1508 | 1495-1517 | - | 0.54 | 3.27 |
| 26 | anethole | 1289 | 1284-1301 | 1846 | 1819-1847 | - | - | 0.31 |
| 27 | 2-undecanone | 1291 | 1291-1298 | - | - | - | - | 1.03 |
| 28 | geranyl acetate | 1381 | 1363-1383 | 1768 | 1755-1778 | - | - | **7.93** |
| 29 | cyclosativene | 1371 | 1367-1371 | 1489 | 1479-1492 | 0.37 | - | - |
| 30 | α-copaene | 1385 | 1365-1394 | 1500 | 1485-1509 | 0.41 | - | 0.16 |
| 31 | β-cubebene | 1396 | 1389-1393 | 1548 | 1542-1558 | 0.22 | - | - |
| 32 | α-santalene | 1424 | 1405-1435 | 1581 | 1555-1601 | 0.40 | 0.38 | - |
| 33 | β-caryophyllene | 1430 | 1418-1451 | 1610 | 1589-1617 | 2.01 | **13.59** | **13.60** |
| 34 | *trans*-α-bergamotene | 1436 | 1422-1452 | 1594 | 1536-1595 | - | 0.86 | - |
| 35 | *trans*-β-farnesene | 1450 | 1442-1457 | 1679 | 1646-1674 | - | 0.26 | - |
| 36 | α-caryophyllene | 1465 | 1444-1465 | 1687 | 1672-1702 | 0.46 | **4.69** | **6.06** |
| 37 | γ-selinene | 1481 | 1438-1484 | 1692 | 1682-1697 | - | 0.64 | - |
| 38 | α-curcumene | 1485 | 1469-1500 | 1786 | 1772-1798 | - | 1.46 | - |
| 39 | eremophilane | 1498 | 1486-1493 | - | - | 0.06 | - | - |
| 40 | α-zingiberene | 1499 | 1448-1495 | 1734 | 1728 | - | 1.34 | - |
| 41 | β-selinene | 1501 | 1492-1511 | 1749 | 1715-1749 | 0.32 | 3.09 | - |
| 42 | α-Farnesene | 1504 | 1495-1509 | 1731 | 1695-1748 | 0.10 | - | - |
| 43 | *cis*-α-bisabolene | 1505 | 1500-1511 | 1741 | 1719-1759 | - | 2.40 | - |
| 44 | α-selinene | 1508 | 1463-1510 | 1750 | 1701-1750 | 0.51 | 2.50 | - |
| 45 | β-bisabolene | 1514 | 1503-1517 | 1740 | 1724-1748 | - | 0.85 | - |
| 46 | γ-bisabolene | 1519 | 1515-1530 | 1769 | 1758-1773 | - | 0.24 | - |
| 47 | δ-cadinene | 1527 | 1523-1530 | 1771 | 1760-1786 | 0.46 | 0.07 | - |
| 48 | calamenene | 1532 | 1510-1532 | 1849 | 1826-1839 | 0.14 | - | - |
| 49 | β-sesquiphellandrene | 1532 | 1516-1531 | 1781 | 1748-1783 | - | 0.37 | - |
| 50 | 7-epi-α-selinene | 1534 | 1526-1540 | 1779 | 1775-1789 | - | 0.94 | - |
| 51 | cembrene A | 1834 | 1916-1929 | 2207 | 2207-2180 | 1.38 | 1.13 | - |
| | Total monoterpenes (%) | | | | | **30.86** | **54.73** | 14.41 |
| | Total sesquiterpenes (%) | | | | | 5.46 | **33.68** | **27.75** |
| | Diterpenes (%) | | | | | 1.38 | 1.13 | - |
| | Phenylpropanes (%) | | | | | - | - | 0.31 |
| | Total hydrocarbons (%) | | | | | **57.60** | 3.81 | **23.11** |
| | **Total identified (%)** | | | | | 95.30 | 93.35 | 65.58 |
| | Density (20 °C) (g/mL) | | | | | 0.775 | 0.852 | 0.864 |

**RRI:** Relative retention indices calculated against n-alkanes**; Ref:** the NIST WebBook; Pherobase Kovats Index [23,25]**;** Relative %: calculated from MS data. **HME**: *H. mexicanum*; **HMY**: *H. myricariifolium*; **HJU**: *H. juniperinum*

The major constituents of *H. mexicanum* oil were n-nonane (53.08%) and α-pinene (25.28%), meanwhile for *H. myricariifolium* oil were α-pinene (45.52%) and β-caryophyllene (13.59%). In the case of *H. juniperinum*, the majority components were n-nonane (12.00%), α-pinene (8.25%), geranyl acetate (7.93%), β-caryophyllene (13.60%), and α-caryophyllene (6.06%). The chemical composition of the OEs from aerial parts of *H. mexicanum*, *H. myricarifolium* and *H. juniperinum* were reported for the first time in this study.

The results of the essential oil composition of the studied *Hypericum* species are in agreement with previously reported data. Chemotaxonomic evaluation of the genus reveals that the main chemical constituents of the genus are aliphatic hydrocarbons, monoterpenes and sesquiterpenes. Hydrocarbons tend to be of the important metabolites in essential oils from species of the genus *Hypericum* and that makes them different from EOs obtained from other aromatic species [32, 33, 34].

### *3.2. Insecticidal and Repellent Activity Against S. zeamais*

Firstly, screening of fumigant toxicities of the species were performed at the maximum concentration of 500 µL/L air (Figure 1) in order to determine the insecticidal potential of them against *S. zeamais* adults. Essential oils of *H. mexicanum* and *H. myricariifolium* were found promissory with higher mortality values (45%). Meanwhile *H. juniperinum* oil does not have insecticidal activity against *S. zeamais* since it caused a mortality percentage lower than 10%.

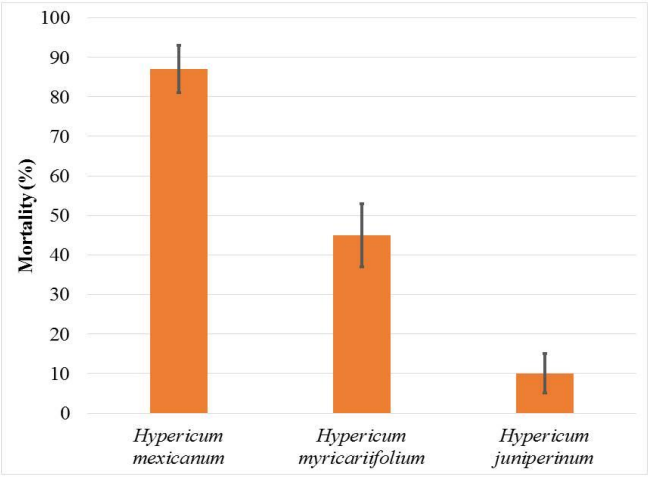


**Figure 1.** Results of preliminary screening of insecticidal activity of EOs from three species of the *Hypericum* genus

Taking into account that *S. zeamais* can climb the walls of the vial and come into contact with the paper impregnated with the treatment, a modified fumigant test and a topical contact assay were carried out with the two active EOs. This, in order to verify if the observed effect was only due to the fumigant action or had influence by contact. The fumigant toxicity results against *S. zeamais* adults are shown in Figure 2. The *H. mexicanum* oil produced very strong fumigant toxicity (the mortality reach to 94% at 500 µL/L air), whilst *H. myricariifolium* oil showed a low level of 56.0% (500 µL/L air) (See supporting information for details). These results may be attributed to the high content of volatile metabolites such as n-nonane and α-pinene, which can enter on the body of the insect through the spiracles generating mortality by fumigance [29]. Some reports indicate that linear and branched alkanes have insecticidal effects on the insects of Diptera, Lepidoptera, and Coleoptera orders [35, 36, 37]. On the other hand, the α-pinene has been reported as a potential fumigant against *S. zeamais* with $LC_{50}$ of 6.41 mg/L [38], allowing attributed a part of the fumigant toxicity of EOs to this monoterpene. Table 2 shows the fumigant toxicity of the oils, in terms of their $LC_{50}$, as well as the slope, intercept, and significance values (P-value). Between the two oils, the one obtained from *H. mexicanum* is the most promising, since it had a moderate lethal concentration (223.5 µL/L air) and the highest "slope" value,

a fact that indicates that do not require large variations in their concentration to significantly increase insect mortality.

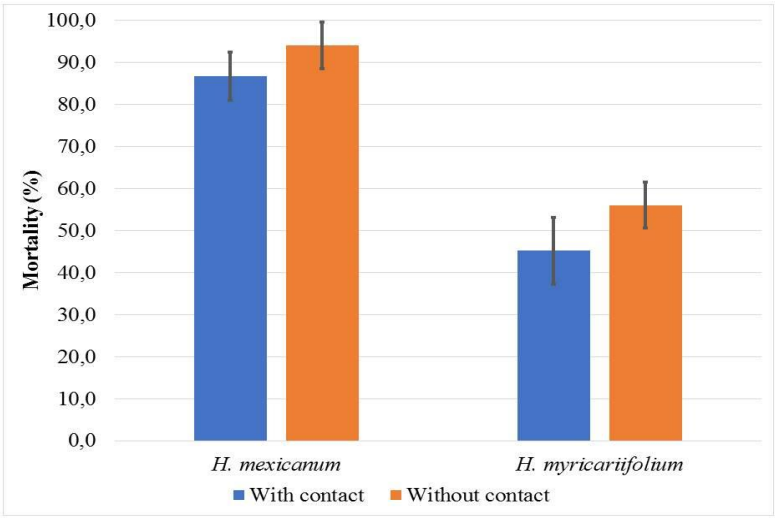


**Figure 2.** Fumigant activity results of "vial in vial" methods with and without contact

**Table 2.** Lethal concentrations and linear parameters

| Species | $LC_{50}$ (µL/L) (95% Confidence limit) | Slope | Intercept | *P*-value |
|---|---|---|---|---|
| *H. mexicanum* | 223.5 (173.6 – 262.0) | 0.005 | -1.14 | $1.60x10^{-13}$ |
| *H. myricariifolium* | 463.1 (338.3 – 559.9) | 0.002 | -0.779 | $2.10\ x10^{-13}$ |

Regarding to contact toxicity data, with doses between 0.10 to 0.20 µL/insect, mortalities of 0, 33.33 and 36.67 % were obtained for *H. myricariifolium* oil, while no response was observed with *H. mexicanum* oil (Figure 3). Since contact toxicity occurs when the insecticide, due to its lipophilic nature, penetrates the cuticle of the insect until reaching the white site or creates an impermeable film causing death by suffocation [39], just the less volatile metabolites can generate this effect. The oil from *H. myricariifolium* has a considerable amount of β-caryophyllene (13.59%), sesquiterpene that has been evaluated by contact against *S. zeamais* with promising results [1, 38], so the activity observed could be associated with this compound.

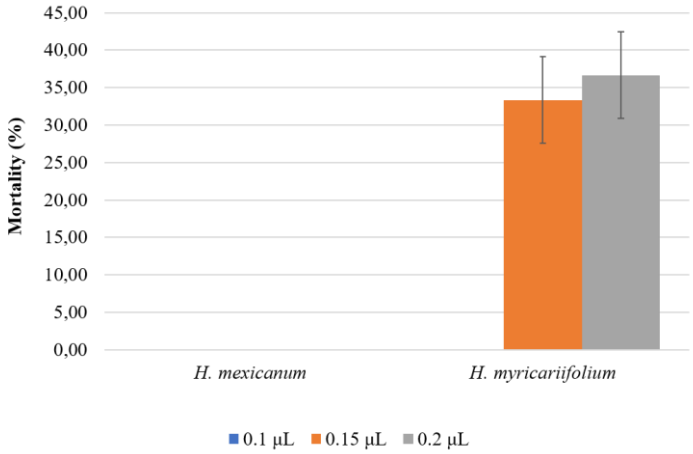


**Figure 3.** Contact toxicity results against *S. zeamais* of EO from active species of the *Hypericum* genus

To evaluate the repellent potential of the *H. mexicanum* and *H. myricariifolium* oils an olfactometer method was used. According to the scale reported by Kosini and collaborators [40], at the evaluated concentrations, in the three tested times, the oils behave like strong repellents, with a repellency rate >70% and follow a constant dose-response relationship with a relative preservation of the effect over time (Figure 4). Some constituents that are observed as majority in these EOs and which have been reported repellent action against *S. zeamais* are α-pinene, and β-caryophyllene [14, 41]. It is important to note that these oils cause repellence at concentrations up to 1000 times lower than the fumigation $LC_{50}$, so their potential use could be focused on grain protection. The repellent effect of EOs is useful in the management of stored grain pests since it contributes to removing insects from the storage zones, resulting in the decrease of the number of eggs and insects and consequent reduction of the losses caused by insects [42].

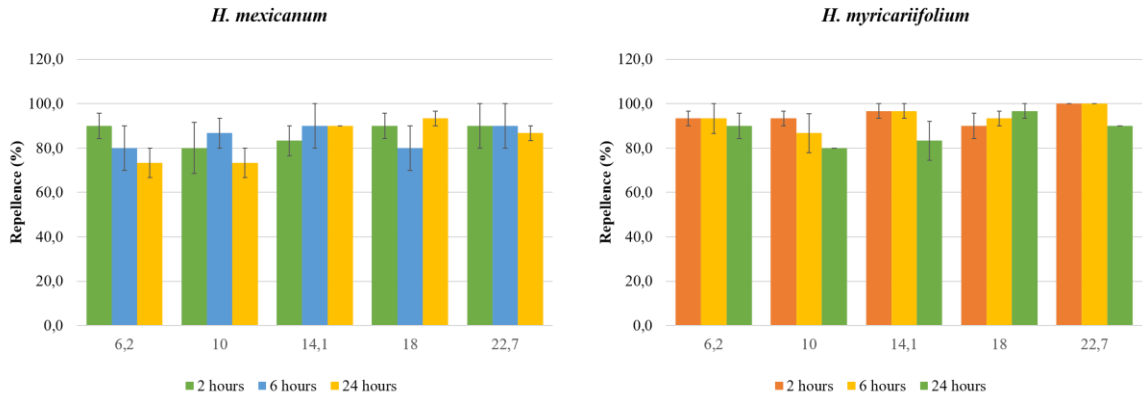


**Figure 4**. Repellent activity of EOs from species of the *Hypericum* genus against *S. zeamais*

In conclusion, the present research reported for the first time the chemical composition and insecticidal activity against *S. zeamais* of EOs from *H. mexicanum*, *H. myricariifolium* and *H. juniperinum*. The results indicated that oils were found to be rich in monoterpenes (30.9–54.7%), sesquiterpenes (27.8–33.7%), and aliphatic hydrocarbons (23.11–57.6%). EOs from *H. mexicanum* and *H. myricariifolium* showed potential to control *S. zeamais* adults, due these exhibit fumigant toxicity and strong repellence against the insect.

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## Supporting Information

Supporting information accompanies this paper on http://www.acgpubs.org/journal/records-of-natural-products

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