UNIVERSIDADE FEDERAL DO PARANÁ

GREISSI TENTE GIRALDI

# BIOATIVIDADE DE ÓLEOS ESSENCIAIS COMO ESTRATÉGIA NO CONTROLE PARA *Spodoptera frugiperda* (LEPIDOPTERA: NOCTUIDAE)

CURITIBA

2024

GREISSI TENTE GIRALDI

# BIOATIVIDADE DE ÓLEOS ESSENCIAIS COMO ESTRATÉGIA NO CONTROLE PARA *Spodoptera frugiperda* (LEPIDOPTERA: NOCTUIDAE)

Tese apresentada ao Programa de Pós-Graduação em Agronomia, Área de Concentração em Produção Vegetal, Departamento de Fitotecnia e Fitossanitarismo, Setor de Ciências Agrárias, Universidade Federal do Paraná, como parte das exigências para obtenção do título de Doutora em Agronomia.

ORIENTADOR: Prof. Dr. Luís Amilton Foerster
CO-ORIENTADOR: Dr. Wanderlei do Amaral

CURITIBA
2024

FICHA CATALOGRÁFICA

DADOS INTERNACIONAIS DE CATALOGAÇÃO NA PUBLICAÇÃO (CIP)
UNIVERSIDADE FEDERAL DO PARANÁ
SISTEMA DE BIBLIOTECAS – BIBLIOTECA DE CIÊNCIAS AGRÁRIAS

Giraldi, Greissi Tente
Bioatividade de óleos essenciais como estratégia no controle para *Spodoptera frugiperda* (Lepidoptera: Noctuidae) / Greissi Tente Giraldi. – Curitiba, 2024.
1 recurso online: PDF.

Tese (Doutorado) – Universidade Federal do Paraná, Setor de Ciências Agrárias, Programa de Pós-Graduação em Agronomia (Produção Vegetal).
Orientador: Prof. Dr. Luís Amilton Foerster
Coorientador: Dr. Wanderlei do Amaral

1. Praga de planta. 2. Spodoptera Frugiperda. 3. Óleo essencial. I. Foerster, Luís Amilton. II. Amaral, Wanderlei do. III. Universidade Federal do Paraná. Programa de Pós-Graduação em Agronomia (Produção Vegetal). IV. Título.

Bibliotecária: Ana Camila Quaresma Moura CRB-9/2212

MINISTÉRIO DA EDUCAÇÃO
SETOR DE CIÊNCIAS AGRÁRIAS
UNIVERSIDADE FEDERAL DO PARANÁ
PRÓ-REITORIA DE PESQUISA E PÓS-GRADUAÇÃO
PROGRAMA DE PÓS-GRADUAÇÃO AGRONOMIA
(PRODUÇÃO VEGETAL) – 40001016031P6

# TERMO DE APROVAÇÃO

Os membros da Banca Examinadora designada pelo Colegiado do Programa de Pós-Graduação AGRONOMIA (PRODUÇÃO VEGETAL) da Universidade Federal do Paraná foram convocados para realizar a arguição da tese de Doutorado de **GREISSI TENTE GIRALDI** intitulada: **BIOATIVIDADE DE ÓLEOS ESSENCIAIS COMO ESTRATÉGIA NO CONTROLE PARA *Spodoptera frugiperda* (LEPIDOPTERA: NOCTUIDAE)**, sob orientação do Prof. Dr. LUÍS AMILTON FOERSTER, que após terem inquirido a aluna e realizada a avaliação do trabalho, são de parecer pela sua APROVAÇÃO no rito de defesa.

A outorga do título de doutora está sujeita à homologação pelo colegiado, ao atendimento de todas as indicações e correções solicitadas pela banca e ao pleno atendimento das demandas regimentais do Programa de Pós-Graduação.

CURITIBA, 13 de Dezembro de 2024.

Assinatura Eletrônica
20/12/2024 08:37:04.0
LUÍS AMILTON FOERSTER
Presidente da Banca Examinadora

Assinatura Eletrônica
19/12/2024 08:49:00.0
WANDERLEI DO AMARAL
Coorientador(a)

Assinatura Eletrônica
16/12/2024 12:11:35.0
GLAUBER RENATO STÜRMER
Avaliador Externo (COOPERATIVA CENTRAL GAUCHA)

Assinatura Eletrônica
16/12/2024 15:45:02.0
ALESSANDRA BENATTO
Avaliador Externo (UNIVERSIDADE FEDERAL DO PARANÁ)

*Dedicatória*

À Deus, por que até aqui
o Senhor tem me sustentado.

## AGRADECIMENTOS

À Deus, por tudo e por tanto.

À minha mãe Sueli, ao meu irmão Flávio e a Safira, pelo amor genuíno e apoio incondicional.

À Universidade Federal do Paraná e ao CNPQ, pela oportunidade do crescimento profissional por meio desse curso e pela concessão da bolsa de estudos.

Ao Professor Dr. Luís Amilton Foerster pela acolhida no laboratório para desenvolvimento da pesquisa e orientação neste trabalho.

Ao Dr. Wanderlei do Amaral pela coorientação, amizade e paciência.

À minha família por entender a distância e a ausência em momentos importantes.

Aos colegas do Laboratório de Controle Integrado de Insetos, Fábio Sampaio e Alisson Gerber, pela amizade e auxílio na pesquisa.

Aos amigos Rubens Zimmermann e Ana Marta Schafaschek pela amizade, apoio e pelas contribuições na pesquisa e na coleta de dados.

Ao Professor Mário Navarro pela acolhida no Laboratório de Morfologia e Fisiologia de Culicidae e Chironomidae, pelo valioso auxílio para a coleta de dados e pela amizade que construímos.

À Professora Beatriz Maia pela colaboração na análise dos óleos essenciais e aos Professores Carlos Eduardo Nogueira Martins e Edson José Mazarotto pela colaboração na análise estatística dos dados.

À família que Curitiba me deu, André Luiz e Maria de Fátima Corradini e Cláudia Jankowski, pela amizade, companheirismo, paciência e por serem luz na minha vida.

À Família Jedyn, pela acolhida, especialmente ao Adrian, que ressignificou a minha vida, trazendo amor, companheirismo e alegria para os meus dias.

Aos queridos amigos Amaral, Júlio César Guerreiro, Priscila Suane, Larissa Bongiorno, Lázaro Menegon, Gabriel Medina, Evandro e Marines Wahl, Isabel Petry, Luís Eduardo Curioletti, Keli Souza da Silva, Carla Arns, Sebastião Netto e aos Colegas da República John Beer pelos momentos compartilhados, pelo apoio quando as situações se fizeram adversas e por acreditarem em mim e na minha pesquisa.

A todos que direta ou indiretamente estiveram presente na minha formação acadêmica e contribuíram para que esse momento fosse possível.

**“***Pouco conhecimento torna as pessoas orgulhosas. Muito conhecimento faz com que se sintam humildes.*

*Assim, como as espigas de trigo sem grãos erguem a cabeça soberba para o céu, as cheias, inclinam suas cabeças para a terra, sua mãe”*

(Leonardo da Vinci)

**RESUMO**

Várias famílias botânicas produzem óleos essenciais (OEs) com atividades biológicas para fins agrícolas. *Spodoptera frugiperda* J.E. Smith, 1797 (Lepidoptera: Noctuidae) é uma praga importante em culturas de milho, por causar perdas significativas de produtividade quando manejada de forma inadequada, por algumas populações do inseto apresentarem alta resistência a inseticidas sintéticos. Os OEs são substâncias naturais conhecidas por sua atividade inseticida contra várias pragas agrícolas. Diante do exposto, o objetivo da pesquisa foi analisar e avaliar a eficiência dos OEs de *Drimys brasiliensis* (Canellales: Winteraceae), *Elionurus muticus* (Poales: Poaceae), *Baccharis articulata, Baccharis calvescens, Baccharis dracunculifolia, Baccharis milleflora* e *Baccharis uncinella* (Asterales: Asteraceae) no manejo de *S. frugiperda*. Os OEs foram extraídos pelo método de arraste a vapor em dorna, e analisados por cromatografia gasosa acoplado a espectrometria de massas. No Capítulo 01, foi avaliada a composição química do OE de *D. brasiliensis*, a atividade inseticida do OE pelo método de contato, para determinar a concentração letal ($CL_{50}$ e $CL_{90}$) e o efeito em marcadores bioquímicos de lagartas de terceiro instar de *S. frugiperda*. Foram identificados 29 compostos por CG-MS. O OE de *D. brasiliensis* resultou em 100% de mortalidade na concentração de 2.5%, com valores de $CL_{50}$ e $CL_{90}$ de 0.90% e 1.40%, respectivamente. Ambas as CLs aumentaram a atividade enzimática de AChE e LPO, enquanto apenas a $CL_{90}$ afetou as enzimas de EST-α e EST-β. No Capítulo 02, foi avaliada a composição química do OE de *E. muticus*, a atividade inseticida do OE pelo método de contato, para determinar a concentração letal ($CL_{50}$ e $CL_{90}$) e o efeito em marcadores bioquímicos de lagartas de terceiro instar de *S. frugiperda*. Foram identificados 14 compostos por CG-MS. O OE de *E. muticus* resultou em 99.3% de mortalidade na concentração de 2.5%, com valores de $CL_{50}$ e $CL_{90}$ de 1.26% e 2.25%, respectivamente. Ambas as CLs causaram um aumento na LPO, diferindo do controle e a $CL_{90}$ provocou a redução de importantes enzimas de desintoxicação. O Capítulo 03 objetivou avaliar a composição química do OE de 5 espécies de plantas do gênero *Baccharis*, a atividade inseticida desses óleos sobre lagartas de terceiro instar de *S. frugiperda* pelos métodos de contato e ingestão, a toxicidade dos OEs sobre os marcadores bioquímicos e o efeito dos OEs em diferentes fases de desenvolvimento do parasitoide de ovos *Telenomus remus* (Hymenoptera: Scelionidae). O número de compostos identificados nos OEs avaliados variou entre 7 para *B. articulata* e 27 para *B. milleflora*. Houve variação na toxicidade dos OEs de *Baccharis* em *S. frugiperda*, com efeito neurotóxico e danos por peroxidação lipídica. As espécies *B. calvescens e B. milleflora* não causaram mortalidade em ovos e pupas de *T.*

*remus*, mas demonstraram repelência variando entre 40 a 55%. Nossos resultados demonstram que os OEs estudados nessa pesquisa apresentam potencial inseticida, demonstrando ser um possível método de controle no manejo de *S. frugiperda*, visando modelos de produção agrícola sustentáveis.

**Palavras-chave:** Produtos Naturais. Biopesticidas. *Spodoptera*. Parasitoides.

**ABSTRACT**

Several botanical families produce essential oils (EOs) with biological activities for agricultural purposes. *Spodoptera frugiperda* J.E. Smith, 1797 (Lepidoptera: Noctuidae) is a major pest in corn crops, causing significant yield losses and exhibiting high resistance to synthetic insecticides. EOs are natural substances known for their insecticidal activity against several agricultural pests. Thus, the objective of this research was to analyze and evaluate the efficiency of EOs from *Drimys brasiliensis* (Canellales: Winteraceae), *Elionurus muticus* (Poales: Poaceae), *Baccharis articulata, Baccharis calvescens, Baccharis dracunculifolia, Baccharis milleflora* and *Baccharis uncinella* (Asterales: Asteraceae) in the management of *S. frugiperda*. The EOs were extracted by the steam distillation method in a vat, and analyzed by gas chromatography coupled with mass spectrometry. In Chapter 01, the chemical composition of *D. brasiliensis* EO and its insecticidal activity by the contact method were evaluated to determine the lethal concentration ($LC_{50}$ and $LC_{90}$) and the effect on biochemical markers of third-instar caterpillars of *S. frugiperda*. Twenty-nine compounds were identified by GC-MS. The EO of *D. brasiliensis* resulted in 100% mortality at a concentration of 2.5%, with $LC_{50}$ and $LC_{90}$ values of 0.90% and 1.40%, respectively. Both LCs increased the enzymatic activity of AChE and LPO, while only $LC_{90}$ affected the EST-α and EST-β enzymes. In Chapter 02, the chemical composition of *E. muticus* EO and its insecticidal activity by the contact method were evaluated to determine the lethal concentration ($LC_{50}$ and $LC_{90}$) and the effect on biochemical markers of third-instar caterpillars of *S. frugiperda*. Fourteen compounds were identified by GC-MS. *E. muticus* EO resulted in 99.3% mortality at a concentration of 2.5%, with $LC_{50}$ and $LC_{90}$ values of 1.26% and 2.25%, respectively. Both LCs caused an increase in LPO, differing from the control, and $LC_{90}$ caused a reduction in important detoxification enzymes. Chapter 03 aimed to evaluate the chemical composition of EOs from 5 species of plants of the genus *Baccharis*, the insecticidal activity of these oils on third-instar caterpillars of *S. frugiperda* by contact and ingestion, the toxicity of EOs on biochemical markers and the effect of EOs on different stages of development of the egg parasitoid *Telenomus remus*. The number of compounds identified in the evaluated EOs ranged from 7 for *B. articulata* to 27 for *B. milleflora*. There was variation in the toxicity of *Baccharis* oils on *S. frugiperda*, with neurotoxic effect and damage by lipid peroxidation. The species *B. calvescens* and *B. milleflora* did not cause mortality in eggs and pupae of *T. remus*, but had a repelente effect ranging from 40 to 55%. Our results demonstrate that the EOs studied in this research have insecticidal potential, proving to be a possible control method in the management of *S. frugiperda*, aiming at sustainable agricultural production models.

**Keywords:** Natural Products. Biopesticides. *Spodoptera*. Parasitoids.

**LISTA DE FIGURAS**

# LISTA DE TABELAS

# SUMÁRIO

## INTRODUÇÃO GERAL

A Mata Atlântica é um dos seis biomas brasileiros (GUERRA et al., 2020; MAKSIC et al., 2022), localizado na costa leste do Brasil, abrangendo também parte dos territórios do Paraguai e da Argentina (SANCHA; BOYLE; MCLNTYRE, 2021). Esse bioma é conhecido mundialmente por sua abundante diversidade biológica, sendo uma das regiões mais ricas em biodiversidade do mundo (RIBEIRO et al., 2009; LIMA et al., 2020).

No período histórico pré-colonial, a Mata Atlântica ocupava um vasto espaço em território nacional, no entanto, após a colonização iniciaram-se no Brasil vários ciclos econômicos, os quais impactaram de forma direta na preservação da floresta, além dos ciclos extrativistas de madeira e de minérios, e da expansão das fronteiras agrícolas (TABARELLI et al., 2010; BARLOW et al., 2016; ERB et al., 2018). A urbanização foi outro aspecto que contribuiu significativamente para a redução do bioma Mata Atlântica (Ferreira et al., 2019; CASTELO BRANCO et al., 2021). No entanto, apesar da redução florestal e da biodiversidade, consequência da extinção de diversas espécies vegetais e animais que viviam no bioma, as áreas remanescentes tornaram-se foco de preservação (REZENDE et al., 2018), uma vez que, observou-se a importância desse bioma para a preservação de diversas espécies endêmicas, a regulação do fluxo dos mananciais hídricos e diversos outros aspectos, como a preservação de espécies nativas do bioma (FERREIRA et al., 2023).

A abrangência da diversidade botânica que está presente na Mata Atlântica conta com uma multiplicidade de famílias e gêneros, que contribuem na estruturação do bioma e do ecossistema como um todo (OLIVEIRA; GASPER; VIBRANS, 2021), fornecendo abrigo e alimento para várias espécies animais que habitam o local (VALE et al., 2018, BATISTA et al., 2021, DINIZ et al., 2023). Entre as famílias botânicas que tem significativa ocorrência no bioma estão a Asteraceae, Myrtaceae, Lauraceae, Canellaceae, Winteraceae, Poaceae, entre muitas outras que possuem importância econômica e medicinal (REGNAULT-ROGER et al., 2012, OLIVEIRA; GASPER; VIBRANS, 2021).

Muitos gêneros que pertencem à essas famílias botânicas produzem metabólitos secundários (BHATTACHARYA, 2016), que estão relacionados com funções ecológicas de defesa e atração de polinizadores, proteção contra radiação e temperatura (TAIZ; ZEIGER, 2013, BHATTACHARYA, 2016), e sofrem variação quantitativa e qualitativa em resposta ao ambiente (TAIZ; ZEIGER, 2013). Diferentemente dos produtos do metabolismo primário, que são responsáveis por diversas funções vitais das plantas como fotossíntese, respiração, síntese de proteínas, assimilação de nutrientes, entre outras funções básicas para o crescimento e desenvolvimento das plantas (CROTEAU et al., 2000, TAIZ; ZEIGER, 2013).

Os metabólitos secundários também diferem dos metabólitos primários por apresentarem distribuição restrita no reino vegetal (TAIZ; ZEIGER, 2013), isto significa que certos metabólitos secundários específicos são restritos a uma espécie vegetal, ou a um grupo de espécies relacionadas, enquanto os metabólitos primários são encontrados em todo o reino vegetal (TAIZ; ZEIGER, 2013, KREIS, MUNKERT, PÁDUA, 2017).

Os metabólitos secundários são divididos em três grupos distintos, devido a sua constituição química: terpenos, substâncias fenólicas e compostos nitrogenados (TAIZ; ZEIGER, 2013, BORGES; AMORIM, 2020), no entanto, a origem de todos os metabólitos secundários parte do metabolismo da glicose, através de dois intermediários principais, o ácido chiquímico e o acetato (KREIS, MUNKERT, PÁDUA, 2017, BORGES; AMORIM, 2020).

No grupo dos terpenos, encontram-se produtos do metabolismo secundário, conhecidos como óleos essenciais (HEINZMANN; SPITZER; SIMÕES, 2017), que podem ser definidos como misturas complexas de compostos voláteis, lipofílicas, geralmente odoríferas e líquidas (TAIZ; ZEIGER, 2013, RÍOS, 2016, BORGES; AMORIM, 2020). Os óleos essenciais estão presentes em diversos órgãos dos vegetais, como nas flores, folhas, cascas, raízes e frutos, sendo armazenados em estruturas secretoras internas, como as células parenquemáticas, idioblastos, bolsas esquizógenas ou lisígenas e canais oleíferos (TAIZ; ZEIGER, 2013, FRANCO; ALBIERO, 2018), ou ainda em estruturas externas, como os tricomas glandulares (TAIZ; ZEIGER, 2013). Estes últimos se projetam da epiderme e atuam como sinal de advertência sobre a toxicidade do vegetal, repelindo potenciais herbívoros, mesmo antes que ataquem as plantas (PARK; TAK, 2016).

A extração dos óleos essenciais das estruturas de armazenamento pode ser feita por meio de diversos métodos (FLAMINI et al., 2007; STRATAKOS; KOIDIS, 2016), como pela prensagem do material vegetal, maceração, extração por solvente, hidrodestilação (CASSEL et al., 2009), entre outras. Dentre esses, o método de maior aplicação é o de hidrodestilação, utilizando a técnica de arraste a vapor, que consiste em um método de separação de misturas que utiliza o vapor de água para volatilizar as substâncias presentes nas plantas (SANTOS et al., 2004).

Os óleos essenciais são amplamente utilizados para conferir aroma e sabores especiais a produtos alimentícios, perfumaria, produtos de limpeza (ISMAN, 2020), além de serem fontes de princípios ativos para a indústria farmacêutica (SOARES; FARIAS, 2017) e, são crescentes as pesquisas e o uso de óleos essenciais na agricultura (BENELLI et al., 2018, KUMAR et al., 2022), por apresentarem reconhecidas propriedades como repelentes de insetos e propriedades inseticidas, uma vez que as substâncias naturais são utilizadas para controle de insetos desde a Antiguidade (THEIS; LERDAU, 2015, GIUNTI et al., 2023).

O modelo de agricultura moderna busca, cada vez mais produzir alimentos utilizando produtos que sejam menos tóxicos ao meio ambiente, ao operador e aos inimigos naturais que ocorrem no sistema agrícola (ISMAN, 2006, HIKAL et al., 2017, HANS; SAXENA, 2021), o que leva a pesquisa a buscar respostas na natureza para encontrar o equilíbrio entre manter a produtividade das culturas, utilizando recursos para o controle de insetos que sejam eficientes e que atendam os requisitos de baixa toxicidade e baixa persistência no ambiente (JAHANIAN et al., 2022).

Nesse sentido, uma das possibilidades que está figurando no cenário das pesquisas agrícolas é o uso de óleos essenciais com propriedades inseticidas (MARANGONI et al., 2012, ISMAN, 2020, KUMAR et al., 2022), com a finalidade de integrá-la como estratégia usual em programas de manejo integrado de pragas.

Diversas culturas agrícolas têm programas de manejo integrado de pragas consolidados e funcionais, como é o caso dos cereais (HURLEY; SUN, 2019, HURLEY; MITCHELL, 2020). O milho, por exemplo, é uma cultura que movimenta a economia mundial e brasileira, figurando entre as principais culturas agrícolas nacionais produzidas para exportação (SANCHES; SALES, 2022), uma vez que o Brasil é o primeiro exportador de milho no ranking, seguido dos Estados Unidos e da Argentina (USDA, 2023).

Dada a relevância da cultura e a extensão de área ocupada para produzi-la, é natural que na dinâmica populacional de insetos que ocorre, vez ou outra ocorra insetos que adquirem o *status* de praga, como é o caso de *Spodoptera frugiperda* (J. E. Smith) (Lepidoptera: Noctuidae) (GARCIA et al., 2018, WARBURTON et al., 2023).

A lagarta do cartucho do milho, como é popularmente conhecida a fase imatura de*S. frugiperda* é um dos principais insetos-praga que ocorrem na cultura do milho no Brasil (BARROS et al., 2010, PORTO et al., 2023), causando sérios prejuízos à produtividade da cultura quando não manejada adequadamente. Uma das principais formas de controlar a população dessa lagarta é por meio de inseticidas sintéticos (BURTET et al., 2017, LIRA et al., 2020, VAN den BERG; PLESSIS, 2022), no entanto, devido ao uso frequente e muitas vezes inadequado dos produtos, a espécie adquiriu resistência a diversos ingredientes ativos (BOLZAN et al., 2019, CHEN et al., 2023, OMUUT et al., 2023).

Diante desse cenário de resistência da lagarta do cartucho aos inseticidas sintéticos, os programas de manejo buscaram se alicerçar em outras estratégias de controle, como o uso de plantas geneticamente modificadas (expressando proteínas Bt) (SILVA et al., 2019, MOSCARDINI et at., 2020), uso de inimigos naturais, via controle biológico, como parasitoides (QUEIROZ et al., 2019), fungos (RUSSO et al., 2021) e vírus entomopatogênicos (SILVA et al., 2018, MACIEL et al., 2024).

Embora sejam diversos os casos de sucesso no controle da lagarta do cartucho utilizando as estratégias citadas, ainda há lacunas a serem preenchidas para melhorar a eficiência na redução das populações quando estas ultrapassam o nível de dano. Nesse sentido, buscando outras estratégias de controlar a lagarta de *S. frugiperda,* essa pesquisa se propôs a estudar o efeito inseticida de óleos essenciais provenientes de três famílias botânicas nativas da Mata Atlântica, dos gêneros *Baccharis (*Asteraceae)*, Drimys* (Winteraceae) e *Elionurus* (Poaceae).

# 2 REVISÃO BIBLIOGRÁFICA

## 2.1 BIOMA MATA ATLÂNTICA

O domínio da Floresta Atlântica é um complexo ecossistema de grande importância, nacional e mundial, pois abriga uma parcela significativa da diversidade biológica do Brasil e do mundo, sendo considerada uma das grandes prioridades para a conservação da biodiversidade (BATISTA et al., 2021).

Aproximadamente 95% da Floresta Atlântica encontra-se em território brasileiro e o restante na Argentina e no Paraguai (STEHMANN et al. 2009). A região nuclear do Domínio corresponde a uma série de ecossistemas quase contínuos ao longo da costa brasileira, ocorrendo desde o Rio Grande do Norte ao Rio Grande do Sul, contemplando áreas florestais mais continentais e outras disjuntas inseridas como encraves no Cerrado, Pantanal, Caatinga e Pampa também são consideradas como pertencentes à Floresta Atlântica. Como exemplos podemos citar os brejos de altitude localizados na região da Caatinga, as florestas decíduas ao longo do médio rio São Francisco e ao sul do Piauí, e as florestas decíduas e semidecíduas isoladas ao longo da Serra da Bodoquena no Mato Grosso do Sul (IBGE, 2008).

Diferentemente da maioria das florestas tropicais, a Floresta Atlântica possui um conjunto de variáveis geográficas e climáticas que a tornam singular (CÂMARA 2005; SIQUEIRA-FILHO e LEME, 2006), promovendo elevados níveis de riqueza e endemismo.

A riqueza da Floresta Atlântica se traduz de diversas formas, cores e tamanhos, mas é notório destacar a interdependência entre as espécies da flora e da fauna, Myers et al. (2000) estimaram a flora da Floresta Atlântica em 20 mil espécies de plantas vasculares, sendo oito mil (40%) endêmicas. Essas estimativas, juntamente com a da vegetação remanescente, foram utilizadas para nortear estratégias de conservação em nível global, como a delimitação de *hotspots* (MYERS et al. 2000; MITTERMEYER et al. 2004). Como as angiospermas representam 95% das plantas vasculares, a riqueza e a endemicidade para a Floresta Atlântica pode ser projetada para 19.000 e 7.600 espécies, respectivamente.

Esses números constituíram o marco referencial da diversidade vegetal encontrada nessa floresta, pois permitiram a comparação da riqueza e endemismo em uma escala planetária (STEHMANN et al. 2009). A abrangência da diversidade botânica que está presente na Floresta Atlântica conta com uma multiplicidade de famílias e gêneros, que contribuem na estruturação do bioma e do ecossistema como um todo (OLIVEIRA; GASPER; VIBRANS, 2021), fornecendo abrigo e alimento para várias espécies animais que habitam o local (VALE et al., 2018, BATISTA et al., 2021, DINIZ et al., 2023). Entre as famílias botânicas que tem significativa ocorrência no bioma estão a Asteraceae, Myrtaceae, Lauraceae, Canellaceae, Winteraceae, Poaceae, entre muitas outras que possuem importância econômica e medicinal (REGNAULT-ROGER et al., 2012, OLIVEIRA; GASPER; VIBRANS, 2021).

Algumas dessas espécies ocorrentes no bioma Floresta Atlântica vêm sendo estudadas devido à produção de metabólitos secundários bioativos, que exercem diferentes funções nos organismos (ADORJAN e BUCHBAUER, 2010). Pagare et al. (2015) demostraram em um estudo que 28% das plantas superiores são usadas medicinalmente e que 74% dos componentes farmacologicamente ativos derivados de plantas foram descobertos após o acompanhamento etnomedicinal das plantas. O uso de produtos oriundos do metabolismo secundário, como os óleos essenciais, também é amplamente utilizado na área de cosméticos e perfumaria (RÍOS, 2016, IVANO et al, 2023), na preservação de alimentos (RÍOS, 2016) e na agricultura (OOTANI et al., 2013).

## 2.2 METABÓLITOS SECUNDÁRIOS

Os metabólitos secundários ou produtos do metabolismo secundário das plantas são compostos orgânicos que, aparentemente, não tem função direta no seu crescimento e desenvolvimento (TAIZ e ZEIGER, 2013). Diferentemente dos produtos do metabolismo primário, que são essenciais para os processos de crescimento e desenvolvimento das plantas, os produtos do metabolismo secundário são derivados do metabolismo basal e responsáveis pela defesa das plantas (PAGARE et al., 2015).

Os compostos oriundos do metabolismo secundário apresentam, muitas vezes, uma grande variabilidade química estrutural, de modo que substâncias com estruturas semelhantes não possuem necessariamente propriedades biológicas idênticas (HARTMANN, 1996). Outra característica dos produtos do metabolismo secundário é que alguns compostos são formados, muitas vezes, apenas durante fases muito específicas do desenvolvimento das plantas, como consequência, ocorrem alterações nos teores de metabólitos secundários específicos durante o processo de desenvolvimento das plantas (TAIZ e ZEIGER, 2013), essa variação pode ser atribuída a fatores intrínsecos (genética da planta) e extrínsecos (disponibilidade de água, luz, temperatura, sazonalidade). Além disso, os produtos do metabolismo secundário costumam ser depositados e armazenados em estruturas específicas, variando de metabólito para metabólito (SEMMAR, 2024).

Os metabólitos secundários são divididos em três grupos distintos, devido a sua constituição química: terpenos, substâncias fenólicas e compostos nitrogenados (TAIZ e

ZEIGER, 2013, BORGES e AMORIM, 2020), no entanto, a origem de todos os metabólitos secundários parte do metabolismo da glicose, através de dois intermediários principais, o ácido chiquímico e o acetato (KREIS, MUNKERT, PÁDUA, 2017, BORGES E AMORIM, 2020) (Figura 1).

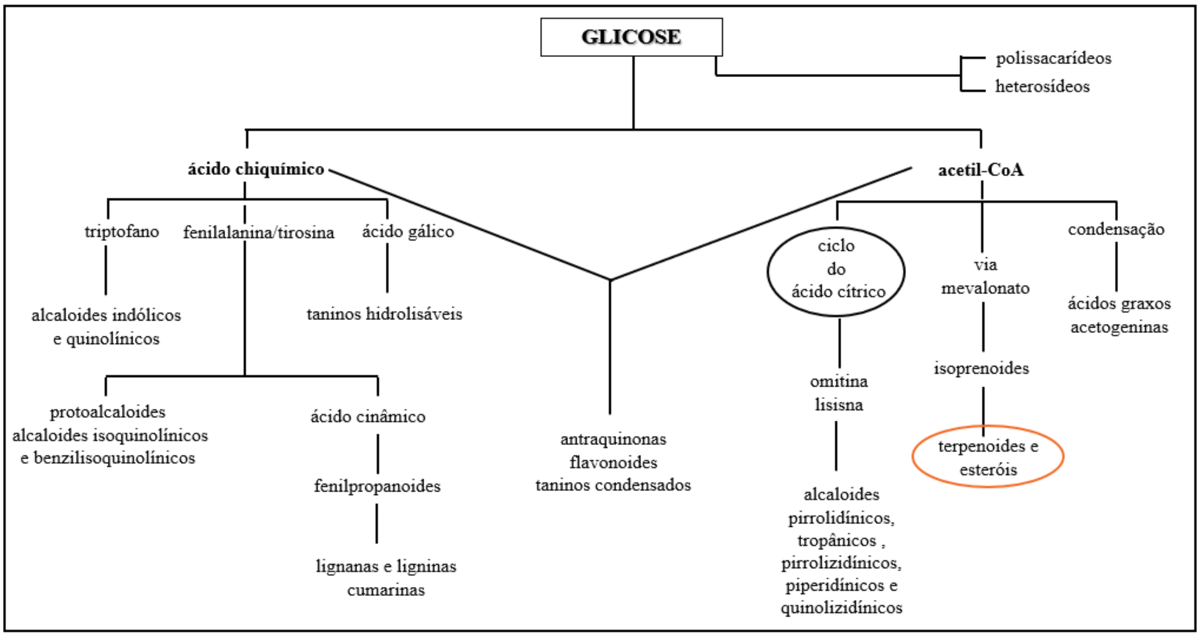


Figura 1: Ciclo biossintético de metabólitos secundários. Adaptado de Simões et al. (2007).

Os terpenoides formados a partir da justaposição sucessiva de unidades de cinco carbonos são denominados isopentilpirofosfato (IPP). O IPP é derivado do ácido mevalônico ou mevalonato e dá origem a todos os outros terpenos. Sendo que os monoterpenos (C10), sesquiterpenos (C15) e diterpenos (C20) são formados por adição de duas unidades de C10, os triterpenos (C30) são resultado da junção de duas unidades C15 (Farnesilpirofosfato) e os tetraterpenos de duas unidades C20 (Geranilgeranilpirofosfato) (CASTRO et al., 2005).

### 2.2.1 Óleos essenciais

No grupo dos terpenos, encontra-se um produto do metabolismo secundário que é conhecido como óleos essenciais (HEINZMANN; SPITZER; SIMÕES, 2017), que podem ser definidos como misturas complexas de compostos voláteis, lipofílicas, geralmente odoríferas e líquidas (TAIZ e ZEIGER, 2013, RÍOS 2016, BORGES e AMORIM, 2020).

Por serem solúveis em solventes orgânicos, como éter, recebe a denominação de óleos etéreos e, devido ao aroma agradável e intenso da maioria dos óleos voláteis, também são chamados de essências. Quimicamente, são constituídos geralmente por compostos terpênicos e fenilpropanóides (SIMÕES et al., 2007; BIASI e DESCHAMPS, 2009).

Os óleos essenciais estão presentes em diversos órgãos dos vegetais, como nas flores, folhas, cascas, raízes e frutos (HYLDGAARD et al., 2012) (Figura 2), sendo armazenados em estruturas secretoras internas, como as células parenquemáticas, idioblastos, bolsas esquizógenas ou lisígenas e canais oleíferos (TAIZ e ZEIGER, 2013, FRANCO e ALBIERO, 2018), ou ainda em estruturas externas, como os tricomas glandulares (TAIZ e ZEIGER, 2013). Estes últimos se projetam da epiderme e atuam como sinal de advertência sobre a toxicidade do vegetal, repelindo potenciais herbívoros, mesmo antes que ataquem as plantas (PARK e TAK, 2016).

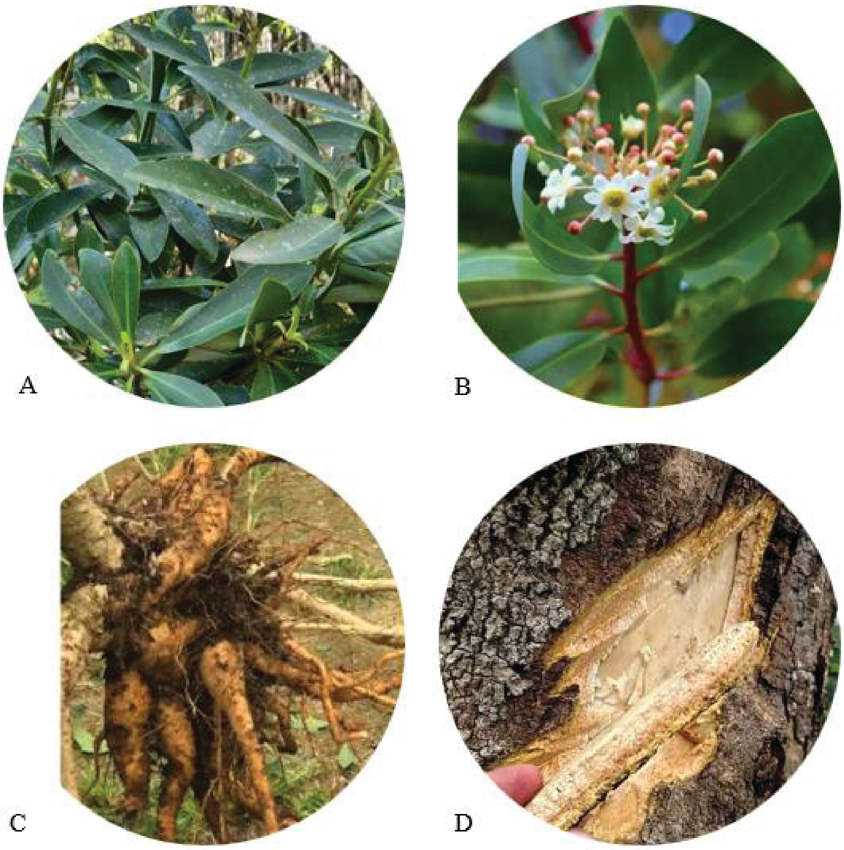


Figura 2: Estruturas de armazenamento de óleo essencial de *Drimys brasiliensis:* A) folhas; B) flores; C) raízes; D) cascas. Adaptado de Carvalho, 2008.

A extração dos óleos essenciais das estruturas de armazenamento pode ser feita por meio de diversos métodos (FLAMINI et al., 2007; STRATAKOS e KOIDIS, 2016), como pela prensagem do material vegetal, maceração, extração por solvente, hidrodestilação, destilação por arraste a vapor (CASSEL et al., 2009), entre outras. Dentre esses, o método de maior aplicação é o de destilação, utilizando a técnica de arraste a vapor, que consiste em um método de separação de misturas que utiliza o vapor de água para volatilizar as substâncias presentes nas plantas (SANTOS et al., 2004), e é utilizado em larga escala industrialmente.

## 2.3 FAMÍLIAS BOTÂNICAS E OS GÊNEROS QUE PRODUZEM ÓLEOS ESSENCIAIS

Dentro da classificação botânica das plantas, existem muitas plantas ricas em óleos voláteis, e estas são abundantes no grupo das Angiospermas, e nas Dicotiledôneas, pertencentes principalmente às famílias botânicas Asteraceae, Apiaceae, Lauraceae, Myrtaceae, Myristicaceae, Piperaceae, Rutaceae, entre outros, com grande abrangência em espécies nativas na América tropical e subtropical (CHIZZOLA, 2013).

### 2.3.1 Asteraceae

A família Asteraceae possui distribuição cosmopolita, sendo a maior família de Eudicotiledôneas, classe Euasterídeas II, ordem Asterales, com aproximadamente 1600 gêneros e 23000 espécies. No Brasil a família também está bem representada, ocorrendo aproximadamente 300 gêneros e 2000 espécies. São particularmente comuns em formações abertas , como cerrado e campos. As espécies desta família são representadas por ervas ou subarbustos, menos frequentemente arbustos, pequenas árvores ou lianas, látex às vezes presentes, espinhos presentes em algumas espécies, com folhas alternas, menos frequentemente opostas, raramente verticiladas, simples (pinatissectas e terminadas em gavinha em algumas espécies), sem estípulas, margem inteira ou mais frequentemente serreada. Inflorescência do tipo capítulo, o qual é envolvido por brácteas que formam um invólucro e flores dispostas sobre um receptáculo geralmente discoide, as flores são todas iguais entre si ou diferenciadas em flores do raio (as mais externas) e flores do disco (as mais internas), as primeiras, em geral, altamente modificadas, podendo ser estéreis e possuir corola hipertrofiada, flores do disco bissexuadas ou raramente unissexuadas, geralmente actinomorfas, diclamídeas ou sem cálice, cálice frequentemente transformado em papilho cerdoso ou plumoso, corola geralmente valvar, 5 estames, sinanteros, epipétalos, anteras rimosas, ovário ínfero, bicarpelar, unilocular, com um único óvulo de placentação ereta. Fruto geralmente do tipo aquênio, com papilho geralmente persistente, auxiliando na dispersão do fruto (SOUZA e LORENZI, 2008).

Muitas Asteraceae são cultivadas como ornamentais, destacando-se a margarida (*Leucanthemum vulgare*), os crisântemos (*Chrysanthemum* spp.), a dália (*Dahlia x hybrida*), entre outras, como alimentícia pode-se citar a alface (*Lactuca sativa*) (SOUZA e LORENZI, 2008). Diversas espécies estão incluídas como medicinais e aromáticas produtoras de óleos essenciais como, por exemplo, *Calendula officinalis*, *Baccharis uncinella*, *Baccharis dracunculifolia*, *Matricharia recutita*, *Artemisia absinthium*, *Cynara scolymus* (Figura 3).


Figura 3: Exemplares de plantas do gênero *Baccharis*. A) *Baccharis calvescens;* B) *Baccharis dracunculifolia*; C) *Baccharis articulata*; D) *Baccharis milleflora*; E) *Baccharis uncinella*. Amaral (2024).

Um dos maiores gêneros da família é o *Baccharis* (Figura 2-3) com diversas espécies com propriedades farmacêuticas (GRECCO et al., 2010a; GRECCO et al., 2010b; PASSERO et al., 2011; GRECCO et al., 2012; KURDELAS et al., 2012; OLIVEIRA et al., 2014) e ecológicas (SCHRIPSEMA et al., 2019).

### 2.3.2 Winteraceae

Esta família pertence a classe das Magnoliídeas, ordem Canelales, é composta por árvores ou arbustos, com folhas alternas, simples, sem estípulas, com margem inteira. Suas inflorescências são cimosa, flores vistosas, geralmente actinomorfas e bissexuais, diclamídeas, com cálice 2-4(-6)-mero, geralmente dialissépalo, corola com 2 a muitas pétalas, geralmente dispostas em 2 ou mais verticilos, dialipétala, prefloração imbricada, estames 3-numerosos, geralmente livre entre si, anteras rimosas, gineceu dialicarpelar, uni a pluricarpelar, o ovário súpero, uni a pluriovulado, estigma às vezes pouco diferenciado, disposto ao longo da sutura do carpelo. Fruto composto, frutículos geralmente bacáceos.

Anatomicamente a família destaca-se por não possuir elementos de vaso em seu sistema vascular, mas apenas traqueídes, à semelhança das Gimnospermas. Possui distribuição predominantemente pan-tropical, com 4 gêneros e cerca de 60 espécies, sendo o gênero *Drimys* (Figura 4) o único nativo do Brasil (SOUZA e LORENZI, 2008).

Figura 4: Exemplar de *Drimys brasiliensis*. Amaral (2024).

Algumas espécies do gênero *Drimys* possuem óleo essencial (LAGO, 2010; SANTOS et al., 2013), *Drimys brasiliensis* possui como componente majoritário no óleo essencial o germacreno D, com atividade antibacteriana e insetífuga (FRANCESCATO et al., 2007).

2.3.3 Poaceae

A família Poaceae (Gramineae) pertence à classe Liliopsida, ordem Poales e é composta por plantas monocotiledôneas caracterizadas por um conjunto de características morfológicas e anatômicas próprias (JUDD et al., 2009). A principal característica que define as monocotiledôneas é a presença de apenas um cotilédone (primeira folha embrionária) na semente, além disso, apresentam o sistema radicular fasciculado e as folhas apresentam venação paralela, ou seja, as nervuras correm paralelamente ao longo da folha, sem ramificações evidentes (CHASE, 1991). O caule das monocotiledôneas não apresenta crescimento secundário, de modo que o tecido vascular está disperso ao longo do caule em feixes vasculares e as flores, podem ser divididas em partes florais (pétalas, sépalas e estames) dispostas em múltiplos de três, por isso são chamadas trímeras.

Estima-se que a família Poaceae tenha cerca de 12.000 espécies distribuídas em aproximadamente 780 gêneros. Essa família é uma das mais diversificadas e ecologicamente importantes, com espécies adaptadas a diversos ambientes ao redor do mundo, desde regiões tropicais até áreas temperadas e áridas (CHASE, 1991).

Apesar de ser uma família botânica conhecida por suas gramíneas alimentícias, como arroz, trigo, milho e cana-de-açúcar, além de outras espécies importantes para a forragicultura (ALCÂNTARA e BUFARAH, 1982), essa família botânica abriga gêneros como o *Elionurus*, encontrado principalmente em regiões tropicais e subtropicais, incluindo a América do Sul, África e partes da Ásia, com potencial considerável para a produção de óleos essenciais (CELAYA et al., 2023). *Elionurus muticus* (Figura 5) produz óleo essencial com aroma cítrico, rico em compostos como citronelal, citronelol e outros terpenos.

Figura 5: Exemplares de *Elionurus muticus*. Amaral (2024).

Devido à sua composição química, que apresenta diversas propriedades biológicas (CACCIABUE et al., 2005; SABINI et al., 2006; HESS et al., 2007), *E. muticus* tem despertado interesse econômico significativo, especialmente para a indústria farmacêutica (FÜLLER et al., 2010).

## 2.4 IMPORTÂNCIA ECONÔMICA DO MILHO (Z*ea mays)*

O milho (*Zea mays* L.) enquanto cultivo agrícola e fonte alimentar teve seu potencial reconhecido pelos povos da Mesoamérica, na região que hoje corresponde ao sul do México, há cerca de 9 mil anos (PIPERNO et al., 2009). À medida em que o milho se tornou mais domesticado e produtivo, se espalhou para outras regiões das Américas, sendo um dos alimentos centrais no desenvolvimento de sociedades complexas e nas práticas agrícolas de toda a América pré-colombiana.

O cultivo de milho nessa região era favorecido por sua adaptabilidade a diferentes tipos de clima e de solo, e pela sua capacidade de ser armazenado por longos períodos após a colheita. O processo de expansão agrícola do milho envolveu a disseminação gradual para o norte (FRITZ, 2007), onde foi adotado pelas sociedades nativas norte-americanas, e também para o sul, para as regiões andinas (IRIARTE, 2007).

Na Europa, o milho foi inicialmente visto como uma curiosidade, mas logo se tornou um alimento importante para comunidades rurais em países como a Espanha, Itália e França (REBOURG et al., 2003). Na África, ele se tornou uma cultura agrícola fundamental, especialmente nas regiões subsaarianas, onde substituiu diversos cereais nativos (FAKOREDE et al., 2001), isso se deu, principalmente, devido à alta densidade energética e ao rendimento do milho, fatores que contribuíram para a sua popularidade crescente.

Com o passar do tempo, o milho passou a desempenhar um papel crucial não apenas na alimentação humana, mas também na alimentação animal e na produção de combustíveis, particularmente na forma de etanol (SHIFERAW et al., 2011; THOMPSON, 2012).

Atualmente, o milho é o cereal mais produzido no mundo, superando trigo e arroz em volume total. No ano de 2023, a produção global de milho foi estimada em cerca de 1,2 bilhão de toneladas, sendo os Estados Unidos o maior produtor mundial , seguido da China, Brasil e Argentina (ERENSTEIN et al., 2022). A produção estadunidense é destinada ao consumo animal, produção de etanol e outros derivados industriais (SHIFERAW et al., 2011; ERENSTEIN et al., 2022), já a China tem sua produção voltada principalmente para a alimentação animal e o consumo humano (PICKSON et al, 2022). O Brasil é um dos maiores exportadores de milho, desempenhando um papel importante no comércio mundial de grãos, assim como a Argentina (ANEC, 2023).

Segundo a Companhia Nacional de Abastecimento (CONAB), na safra brasileira 23/24 a produção de milho foi de 112,7 milhões de tonelada, com grande parte sendo destinada à exportação. Os estados de Mato Grosso, Paraná, Mato Grosso do Sul, Goiás e Minas Gerais são os maiores produtores do cereal no país, respondendo por uma parte significativa da produção nacional (COÊLHO, 2024), a qual é destinada à alimentação de animais, particularmente no setor de aves e suínos, e também como matéria-prima para a indústria de biocombustíveis (COÊLHO, 2024).

A alta produtividade do milho pode ser atribuída a diversos fatores, bióticos e abióticos, entre os quais estão a disponibilidade adequada de água e nutrientes, manejo adequado do solo e a sanidade da lavoura (RUSSO et al., 2021; DAWAR et al., 2022; WANG et al., 2022; IQBAL et al., 2024). No que diz respeito a sanidade da lavoura de milho, diversas são as doenças e insetos, caracterizados como pragas, que podem comprometer a produtividade do cereal se não forem bem manejadas.

Na diversidade de insetos que podem acometer a sanidade das plantas de milho, a lagarta *Spodoptera frugiperda* (J. E. Smith, 1797) (Lepidoptera: Noctuidae) ganha destaque, pois ela figura entre as principais pragas da cultura do milho. Também conhecida como lagarta-do-cartucho, *S. frugiperda* é de ocorrência frequente e voracidade, no entanto, a importância da lagarta-do-cartucho deve-se não somente aos danos provocados, mas também à dificuldade de controle devido à resistência que apresenta, aos principais inseticidas utilizados como estratégia de controle (KAUR et al., 2024).

## 2.5 IMPORTÂNCIA AGRONÔMICA DA LAGARTA DO CARTUCHO – *Spodoptera frugiperda*

A lagarta do cartucho do milho *Spodoptera frugiperda* (J. E. Smith, 1797) (Lepidoptera: Noctuidae) é uma praga holometábola, polífaga e com característica migratória (RUSSO et al., 2020), esses fatores aliados à voracidade das lagartas, a alta taxa de dispersão das mariposas e a capacidade destas de gerar grandes populações de descendentes, fazem de *S. frugiperda* um dos noctuídeos mais importantes do milho na América do Sul (CASTRO et al., 2009; OVERTON et al., 2021).

Levantamentos apontam que a lagarta do cartucho ataca aproximadamente 353 espécies de plantas hospedeiras de 76 famílias botânicas (MONTEZANO et al., 2018), mas o maior dano é comumente registrado em gramíneas cultivadas, como o milho (Figura 6) e o sorgo, tanto na fase vegetativa, quanto na fase reprodutiva das culturas.

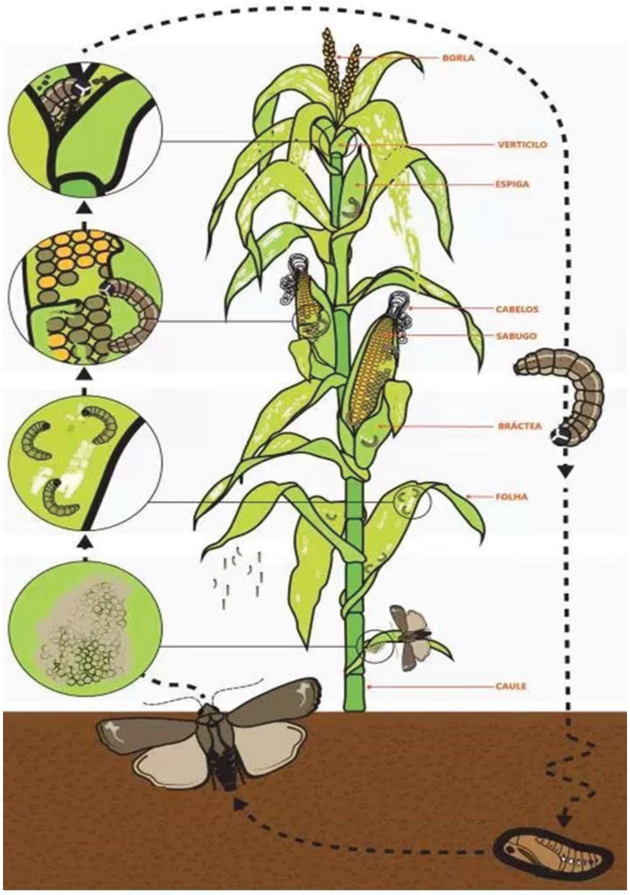


Figura 6: Ilustração do ataque de *S. frugiperda* na fase reprodutiva do milho. CABI, 2024.

Nativa dos neotrópicos, na América, *S. frugiperda* foi relatada como uma praga invasora na África (NIASSY et al., 2021) e na Ásia (SUN et al., 2021) e atualmente impõe uma séria ameaça à segurança alimentar e à produtividade sustentável das culturas devido à falta de manejo eficaz (BHUSAL e CHAPAGAIN, 2020), visto que as medidas de controle atuais concentram-se amplamente na aplicação pesada e indiscriminada de inseticidas de amplo espectro, que não só afetam negativamente a saúde humana e o ambiente, mas frequentemente resultam em um controle inconsistente da lagarta (STOKSTAD, 2017; HARRISON et al., 2019).

Em populações nativas de *S. frugiperda*, a resistência a piretróides, carbamatos e organofosforados foi relatada desde a década de 1970 (CARVALHO et al., 2013; PITRE, 1988; YOUNG e McMILLAN, 1979), e, mais recentemente, foi relatada a resistência de populações de *S. frugiperda* às novas classes de compostos inseticidas (toxinas de Bt e espinosade), no Brasil (FARIAS et al., 2014; OKUMA et al., 2017) e em Porto Rico (STORER et al., 2010; GUTIÉRREZ-MORENO et al., 2019).

Por apresentar um ciclo de desenvolvimento holometábolo, *S. frugiperda* vive aproximadamente 40 dias (Figura 7), em condições de desenvolvimento favoráveis (ROSA et al., 2012).

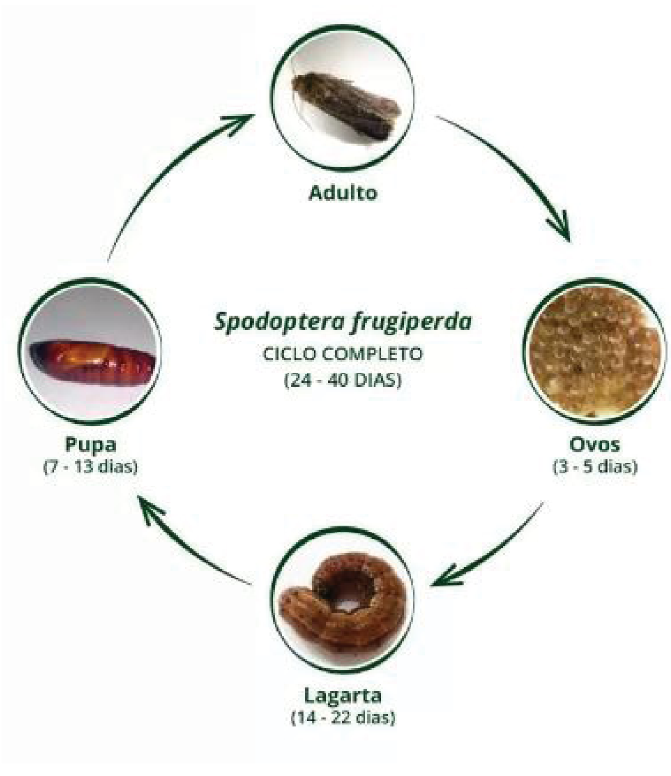


Figura 7: Metamorfose e estimativa do período de desenvolvimento de *Spodoptera frugiperda*.

No entanto, ao longo do período embrionário e pós-embrionário, *S. frugiperda* pode ser atacada por um grande número de patógenos (bactérias, fungos e vírus), parasitoides (Diptera e Hymenoptera) e predadores (Coleoptera, Dermaptera, Hemiptera e Hymenoptera) (TAY et al., 2023). Pesquisas apontam, dentro do contexto de manejo integrado de pragas, que utilizar estratégias como o controle biológico pode ser bastante interessante para o controle da lagarta do cartucho e que para liberações aumentativas, os parasitoides de ovos são os inimigos naturais mais fáceis de criar em grandes números (SAMPAIO et al., 2024).

No Brasil, uma série de estudos mostrou que a liberação dos parasitoides de ovos *Telenomus remus* Nixon e *Trichogramma pretiosum* Riley tem o potencial de reduzir populações de campo, e informações suficientes foram coletadas sobre o número de indivíduos liberados (FIGUEIREDO et al., 2002; POMARI-FERNANDES et al., 2013), capacidade de dispersão (POMARI-FERNANDES et al., 2018) e custos (VIEIRA et al., 2017) para permitir o desenvolvimento de um programa de liberação de *T. remus*. Um programa de liberação de *T. pretiosum* no milho também foi desenvolvido usando dados sobre o número de machos de *S. frugiperda* capturados em armadilhas de feromônios (FIGUEIREDO et al., 2015).

Diferentes tipos de vírus também foram identificados e explorados como potenciais agentes de controle biológico (HUSSAIN et al., 2021) e os candidatos virais mais promissores são o *S. frugiperda* nucleopolyhedrovirus (SfNPV) (POPHAM et al., 2021) e granulovirus (CUARTAS et al., 2014).

## 2.6 ÓLEOS ESSENCIAS E SUA UTILIZAÇÃO NO MANEJO INTEGRADO DE PRAGAS

O uso de óleos essenciais (OEs) como alternativa no manejo de pragas agrícolas tem ganhado destaque devido às suas propriedades inseticidas (ISMAN, 2020) e pesquisas tem demostrado um grande potencial de controle de diversas espécies vegetais contra insetos-praga (BENELLI et al., 2019).

O uso de OEs no controle da lagarta do cartucho está emergindo como uma alternativa promissora para complementar o controle biológico tradicional (BABENDREIER et al., 2020), e justamente por isso, essa abordagem tem atraído a atenção dos pesquisadores, devido à necessidade de reduzir o uso de inseticidas sintéticos, aos quais já é conhecido o desenvolvimento de resistência de *S. frugiperda* (TAY et al., 2023).

Óleos essenciais como os das famílias botânicas Asteraceae, Rutaceae, Lamiaceae e Apiaceae possuem compostos voláteis com atividade inseticida e repelente (CANTÓ-TEJERO et al., 2022; AL-GHANIM et al., 2023), devido à presença de compostos, como terpenos, aldeídos e fenóis, que atuam de maneira direta, afetando o sistema nervoso dos insetos, e indireta, repelindo-os ou inibindo a sua alimentação (CASTILLO-MORALES et al., 2019; DUQUE et al., 2023).

Estudos demonstraram que OEs extraídos de espécies como *Thymus vulgaris*, *Rosmarinus officinalis, Melaleuca alterifolia* e *Mentha spicata* apresentaram boa eficácia no controle da população de lepidópteros (PLATA-RUEDA et al., 2021; SANTOS et al., 2021), por meio de altas taxas de mortalidade de lagartas e efeito de antixenose (PAVELA et al., 2016).

A integração de OEs com inimigos naturais de *S. frugiperda*, como parasitoides do gênero *Trichogramma* (PARREIRA et al., 2017; CRUZ et al., 2021) ou predadores (CAMPOLO et al., 2020), potencializa o controle de insetos-praga, apontando que o uso combinado desses recursos é vantajoso e promissor (ISMAN, 2020).

## 2.7 MARCADORES ENZIMÁTICOS PARA ENTENDIMENTO DO MECANISMO DE AÇÃO DOS ÓLEOS ESSENCIAIS SOBRE *Spodoptera frugirperda*

Os insetos são um dos organismos mais bem-sucedidos que sobreviveram em seus habitats, isso graças a sua adaptabilidade a mudanças climáticas, e principalmente aos vários sistemas que eles desenvolveram para neutralizar ou aliviar os efeitos causados por discrepâncias alimentares e compostos químicos (SHAHRIARI et al., 2018), que poderiam ser fatais.

Além da adaptabilidade digestiva e do sistema imunológico, os insetos recrutaram alguns componentes altamente eficazes na estrutura do sistema antioxidante, para proteger seus tecidos contra alguns componentes químicos, como os radicais livres (AHMAD E PARDINI, 1990). Espécies reativas de oxigênio (ROS), incluindo ânion superóxido, peróxido de hidrogênio e radical hidroxila, são consideradas geradas durante processos oxidativos normais em todos os organismos aeróbicos (MENG et al., 2009). Acredita-se que baixos níveis de ROS não são prejudiciais às células e desempenham papel importante na sinalização celular e na indução de defesa do hospedeiro (WANG et al., 2001).

No entanto, sob vários tipos de estresse ambiental, por exemplo, radiação ultravioleta (UV) ou exposição a compostos químicos, o nível de ROS pode aumentar drasticamente e resultar em estresse oxidativo (LUKASIK et al., 2007; LOPEZ-MARTINES et al., 2008; MENG et al., 2009; KIRAN e PRAKASH, 2015). O excesso de ROS causa peroxidação lipídica, que rompe a estrutura da membrana, levando a morte celular (HALLIWELL e GUTTERIDGE, 2015). Danos oxidativos às proteínas podem variar de modificações específicas de aminoácidos e cisão de peptídeos até a perda da atividade enzimática (STADTMAN, 1986; STADTMAN e LEVINE, 2003), além de alterações irreversíveis no DNA (IMLAY e LINN, 1988).

Em um organismo, níveis aumentados de peroxidação lipídica e carbonilas de proteínas são considerados geradores de estresse oxidativo (WANG et al., 2001; LOPEZ-MARTINEZ et al., 2008), para neutralizar a toxicidade de ROS, os insetos desenvolveram um conjunto de enzimas antioxidantes, como outros eucariotos, para lidar com o estresse oxidativo.

Nos insetos, entre as principais enzimas responsáveis pela desintoxicação estão as esterases, glutationa – S – transferase (GST), superóxido dismutase (SOD) e catalase, que atuam biotransformando compostos químicos e combatendo espécies reativas de oxigênio (ROS) (MENG et al., 2009; SHAHRIARI et al., 2018). Essas enzimas previnem o estresse oxidativo, bloqueando a formação de radicais livres e agindo na homeostase celular. Isso indica que o papel dessas enzimas é degradar e transformar moléculas tóxicas em substâncias inativas mais hidrossolúveis, que serão excretadas, permitindo que o inseto sobreviva após a exposição a compostos químicos, sejam naturais ou sintéticos, como é o caso dos inseticidas (HALLIWELL e GUTTERIDGE, 2015; BAI et al., 2024).

Os OEs são usados em todo o mundo e tem mostrado efeitos negativos significativos na sobrevivência, reprodução, desenvolvimento, comportamento e vias metabólicas dos insetos (TRIPATHI et al., 2003; ISMAN, 2006; SENTHIL-NATHAN, 2013; TAK e ISMAN, 2016).

As reações de desintoxicação geralmente são parte de um sistema multi-enzimático, que pode ser dividido em enzima de Fase I e II. Entre as enzimas que atuam na Fase I estão as oxidases de função múltipla, que reconhecem o composto exógeno, e atuam sobre ele, provocando a oxidação, e as esterases (PARKINSON e OGILVIE, 2008).

As esterases estão entre os grupos de enzimas que desempenham diferentes funções fisiológicas vitais para os insetos, e estudos mostraram que as enzimas esterase $\alpha$ e esterase $\beta$ atuam no processo de desintoxicação de moléculas químicas de óleos essenciais, incluindo inseticidas sintéticos (GUENGERICH et al., 2008).

Baixas concentrações de óleos essenciais provocam um aumento na síntese dessas enzimas e, consequentemente, os insetos podem realizar a biotransformação desses compostos por meio da hidrólise das cadeias de ésteres de compostos químicos, presentes nos óleos essenciais, em moléculas que serão excretadas pelo organismo (REGNAULT-ROGER et al. 2012).

A GST é importante na Fase II da biotransformação de compostos orgânicos, catalisando a conjugação do tripeptídeo glutationa, com grupos eletrofílicos de compostos xenobióticos, visando torná-los menos tóxicos. Tal como acontece com as esterases, o aumento da atividade da enzima GST está associado à capacidade do inseto de desintoxicar e sobreviver (LILLIG e BERNDT, 2013).

As GSTs atuam na Fase II catalisando a redução peróxido, mediada pela glutationa (GSH), com uma variedade de eletrófitos reativos, mais comumente gerados pelo metabolismo do citocromo P450. As GSTs compreendem duas super-famílias distintas: a microsomal, ligadas à membrana e as cistólicas solúveis. Devido a polimorfismos, duplicação de genes e recombinação genética, as GSTs têm múltiplas isoenzimas com sobreposição de especificidade de substrato e diversidade, dessa forma, as GSTs biotransformam compostos orgânicos, catalisando a conjugação do tripeptídeo GSH com grupos eletrofílicos de compostos xenobióticos, com o objetivo de torná-los menos tóxicos e predispostos para modificação posterior e excreção pela célula (FELTON e SUMMERS, 1995; FORMAN et al., 2009).

As GSTs também estão envolvidas no transporte de xenobióticos através do citoplasma para serem novamente metabolizados através de enzimas da Fase I, fundamental para biotransformação intracelular. Por outro lado, a redução na atividade enzimática da GST pode afetar a capacidade de neutralizar os efeitos dos peróxidos lipídicos, podendo ocasionar o acúmulo de metabólitos da Fase I e o desequilíbrio do estado redox celular (HAYES e McLELLAN, 1999; SHEEHAN et al., 2001).

As enzimas antioxidantes SOD são importantes mecanismos de defesa dos insetos contra a toxicidade do estresse oxidativo causado por ROS, nas vias enzimáticas de eliminação de ROS, a SOD decompõe o superóxido de hidrogênio em peróxido de hidrogênio, que é então eliminado pela catalase (BARBEHENN, 2002; FELTON e SUMMERS, 2005).

Além de alterar a síntese enzimática, os OEs também podem atuar desregulando a homeostase celular, por meio da formação e liberação de radicais livres, aumentando o nível de ROS nas células resultando na peroxidação lipídica (ISMAN, 2000). Dessa forma, pode-se entender que a peroxidação lipídica é o dano direto, causado na membrana plasmática celular, o qual aumenta a permeabilidade da membrana e, favorece a liberação de conteúdo intracelular, aumentando o estresse oxidativo, o que resulta em apoptose celular (BAKKALI et al., 2008).

Os diferentes compostos presentes nos OEs como fenilpropanoides e monotepenoides, com propriedades inseticidas, além de atuar gerando compostos oxidativos que levam ao vazamento iônico das células e à degeneração de mitocôndrias e proteínas (LUKASIK et al., 2007; MONAGHAM et al., 2009; RAHIMI et al., 2018), também podem atuar na inibição da acetilcolinesterase (AChE) (KIM et al., 2013; SEO et al., 2014).

A AChE é uma das mais importantes enzimas hidrolíticas do sistema nervoso dos insetos, que equilibram a transdução do sinal neural pela hidrólise rápida do sinal de acetilcolina na fenda sináptica (JACOB e MASON, 2005). Além de inseticidas químicos como organofosforados e carbamatos, a AChE tem se mostrado um alvo significativo de OEs (PHILIPPOU et al., 2010; KIM et al., 2013; LI et al., 2013; SEO et al., 2014), isso pode ser atribuído, principalmente pela presença de monoterpenos, com propriedades inibitórias da AChE, que são ligadas a diferença na lipofilicidade e volatilidade, bem como a inibição de monoxigenases P450 (De OLIVEIRA et al., 1997; LEE et al., 2001).

## REFERÊNCIAS

ADORJAN, B., BUCHBAUER, G. Biological properties of essential oils: an updated review. **Flavour Fragr. J**. 25, 2010. DOI: https://doi.org/10.1002/ffj.2024

AHMAD, S., PARDINI, R.S., 1990. Mechanisms for regulating oxygen toxicity in phytopha gous insects. **Free Radic. Biol. Med**. 8, 401–413.

ALCÂNTARA, P.B. & BUFARAH, G. 1982. Plantas forrageiras: gramíneas & leguminosas. 1 ed., Nobel, São Paulo.

AL-GHANIM, K. A., KRISHNAPPA, K., PANDIYAN, J., NICOLETTI, M. et al. Insecticidal Potential of *Matricaria chamomilla's* Essential Oil and Its Components (E)--Farnesene, Germacrene D, and-Bisabolol Oxide A against Agricultural Pests, Malaria, and Zika Virus Vectors. **Agriculture** 2023, 13, 779. https://doi.org/10.3390/agriculture13040779

ANEC - Associação Nacional dos Exportadores de Cereais – Brasil em destaque: Rumo ao recorde para as exportações de soja e milho. Disponível em: https://periodicos.fgv.br/agroanalysis/article/view/90110/84578 Acesso em: 18 set. 2024.

BABENDREIER, D., AGBOYI, L. K., BESEH, P., OSAE, M. et al. The E cacyofAlternative, Environmentally Friendly Plant Protection Measures for Control of Fall Armyworm, *Spodoptera frugiperda*, in Maize. **Insects**, 11, 2020. DOI: https://doi.org/10.3390/insects11040240

BAI, Y., LIU, X., BALDWIN, I. T. Using Synthetic Biology to Understand the Function of Plant Specialized Metabolites. **Annual Review of Plant Biology**, 75, 2024. https://doi.org/10.1146/annurev-arplant-060223-013842

BAKKALI, F., AVERBECK, S., AVERBECK, D., IDAOMAR, M. Biological effects of essential oils – a review. **Food Chem Toxicol**., 46, 2008. DOI: https://doi.org/10.1016/j.fct.2007.09.106.

BARBEHENN, R. V. Gut-based antioxidant enzymes in a polyphagous and a graminivorous grasshopper. **J Chem Ecol**. 28, 2002. DOI: https://doi.org/10.1023/a:1016288201110

BARROS, E.M.; TORRES, J.B.; BUENO, A.F. Oviposition, Development and Reproduction of *Spodoptera frugiperda* (J.E.Smith) (Lepidoptera: Noctuidae) Fedo n Differents Hosts of Economic Importance. **Neotropical Entomology**, v. 39, 2010. DOI: https://doi.org/10.1590/S1519-566X2010000600023

BARLOW, J. et al. Anthropogenic disturbance in tropical forests can double biodiversity loss from deforestation. **Nature**, 535, 2016. DOI: https://doi.org/10.1038/nature18326

BATISTA, C. B.; DE LIMA, I. P.; ARRUDA, R.; LIMA, M. R. Downscaling the Atlantic Forest biodiversity hotspot: Using the distribution of bats to find smaller hotspots with conservation priority. **Biological Conservation**, 263, 2021. DOI: https://doi.org/10.1016/j.biocon.2021.109331

BENELLI, G., PAVELA, R., MAGGI, F., WANDJOU, J. G. N. et al. Insecticidal activity of the essential oil and polar extracts from *Ocimum gratissimum* grown in Ivory Coast: Efficacy on insect pests and vectors and impact on non-target species. **Industrial Crops and Products**, 132, 2019. DOI: https://doi.org/10.1016/j.indcrop.2019.02.047

BHATTACHARYA, S. Cultivation of Essential Oils (2016). In: **Essential Oils in Food Preservation, Flavor and Safety**, Ed: Preedy, V.R. Elsevier, 2016.

BHUSAL, S., CHAPAGAIN, E. Threats of fall armyworm (*Spodoptera frugiperda*) incidence in Nepal and it's integrated management-A review. **Journal of Agriculture and Natural Resources**, 3, 2020. DOI: https://doi.org/10.3126/janr.v3i1.27186

BOLZAN, A.; PADOVEZ, F.O.E.; NASCIMENTO, A.R.B.; KAISER, I.S. et al. Selection and characterization of the inheritance of resistance of *Spodoptera frugiperda* (Lepidoptera: Noctuidae) to chlorantraniliprole and cross-resistance to Other diamide insecticides. **Pest Management Science**, v. 75, 2019. DOI: https://doi.org/10.1002/ps.5376

BORGES, L.P.; AMORIM, V.A. Secondary Plant Metabolites. **Revista Agrotecnologia**, v.11, 2020.

BURTET, L. M.; BERNARDI, O.; MELO, A.A.; PES, M.P. et al. Managing fall armyworm, *Spodoptera frugiperda* (Lepidoptera: Noctuidae), with Bt maize and insecticides in Southern Brazil. **Pest Management Science**, v. 73, 2017. DOI: https://doi.org/10.1002/ps.4660

CACCIABUE, M. et al. *Elionurus muticus* from north of Argentina: evaluation of the antibacterial activity of three essencial oil chemotypes. **Biocell**, 29 2005.

CÂMARA, I. G. **Breve história da conservação da Mata Atlântica**. In: Galindo-Leal, C.; Câmara, I.G. (eds.). Mata Atlântica: biodiversidade, ameaças e perspectivas. Fundação SOS Mata Atlântica/Conservação Internacional, São Paulo/Belo Horizonte. p. 31-42, 2005.

CAMPOLO, O., PUGLISI, I., BARBAGALLO, R. N., CHERIF, A. et al. Side effects of two citrus essential oil formulations on a generalist insect predator, plant and soil enzymatic activities. **Chemosphere**, 257, 2020. DOI: https://doi.org/10.1016/j.chemosphere.2020.127252

CANTÓ-TEJERO, M., CASAS, J. L., MARCOS-GARCÍA, M. A., PASCUAL-VILLALOBOS, M. J. et al. Essential oils-based repellents for the management of *Myzus persicae* and *Macrosiphum euphorbiae*. **Journal of Pest Science**, 95, 2022. https://doi.org/10.1007/s10340-021-01380-5

CARVALHO, R. A., OMOTO, C., FIELD, L. M., WILLIAMSON, M. S., BASS, C. Investigating the molecular mechanisms of organophosphate and pyrethroid resistance in the fall armyworm *Spodoptera frugiperda*. PLOS ONE, 8, 2013. DOI: https://doi.org/10.1371/journal.pone.0062268

CASSEL, E., VARGAS, R.M.F., MARTINEZ, N., LORENZO, D., DELLACASS, E. Steam distillation modeling for essential oil extraction process. **Industrial and Crops Products**, 29, 2009. DOI: https://doi.org/10.1016/j.indcrop.2008.04.017

CASTELO BRANCO, A.F.V.; LIMA, P.V.P.S.; MEDEIROS FILHO, E.S. et al. Avaliação da perda da biodiversidade na Mata Atlântica. **Ciência Florestal**, v. 31, 2021. DOI: https://doi.org/10.5902/1980509853310

CASTRO, P. R. C.; KLUGE, R. A.; PERES, L. E. P. **Manual de fisiologia vegetal** (teoria e prática). Ed. Agronomica Ceres, Piracicaba, 2005. 650p.

CASTRO, Y. C., ROJAS, C. G., CEDEÑO, C. V., VELÁSQUEZ, V. V. Development of a laboratory rearing methodology for the corn worm *Spodoptera frugiperda* (Smith) (Lepidoptera: Noc tuidae) as a possible host for bio-controller insects of agricultural interest. **Tecnología en marcha**, 22, 2009.

CHASE, M.A. 1991. Primeiro livro de gramíneas: noções sobre a estrutura com exemplos da flora brasileira. 1 ed., Instituto de Botânica, São Paulo

CHEN, Y.; NGUYEN, D.T.; SPAFFORD, H.; HERRON, G.A. A high-throughput multilocus-amplicon sequencing panel to monitor insecticide resistance in fall armyworm (FAW) *Spodoptera frugiperda* (Lepidoptera:Noctuidae). **Pest Management Science**, v. 80, 2024. DOI: https://doi.org/10.1002/ps.7883

CHIZZOLA, R. **Regular Monoterpenes and Sesquiterpenes (Essential Oils)**. In: Ramawat, K., Mérillon, JM. (eds) Natural Products. Springer, Berlin, Heidelberg. 2013. https://doi.org/10.1007/978-3-642-22144-6_130

COÊLHO, Jackson Dantas. MILHO: v. 9, n. 342, junho, 2024. **Caderno Setorial ETENE**, Fortaleza, v. 9, n. 343, 2024. Disponível em: https://www.bnb.gov.br/revista/cse/article/view/2728. Acesso em: 5 ago. 2024.

CONAB - COMPANHIA NACIONAL DE ABASTECIMENTO. Acompanhamento da safra brasileira de grãos 2023/2024. 6º. Levantamento. Disponível em: https://www.conab.gov.br/info-agro/safras/graos Acesso em: 18/09/2024.

CROTEAU, R.; KUTCHAN, T. M.; LEWIS, N.G. Natural Products – Secondary Metabolites. In: **Biochemistry & Molecular Biology of Plants**, B. Buchanan, W. Gruissem, R. Jones, Eds. 2000, American Society of Plant Physiologists.

CRUZ, R. A., PARREIRA, D. S., DIMATÉ, F. A. R., BATISTA, L. D. et al. Effects of essential oils on biological attributes of *Trichogramma galloi* adults. **Journal of Asia-Pacific Entomology**, 24, 2021. DOI: https://doi.org/10.1016/j.aspen.2021.04.002

CUARTAS, P., BARRERA, G., BARRETO, E., VILLAMIZAR, L. Characterisation of a Colombian granulovirus (Baculoviridae: Betabaculovirus) isolated from *Spodoptera frugiperda* (Lepidoptera: Noctuidae) larvae. **Biocontrol Sci. Technol**. 24, 2014. DOI: https://doi.org/10.1080/09583157.2014.933312

DAWAR, K., KHAN, A., MIAN, I. A., KHAN, B. et al. Maize productivity and soil nutrients variations by the application of vermicompost and biochar. **Plos One**, 2022. DOI: https://doi.org/10.1371/journal.pone.0267483

De-OLIVEIRA, A.C., Ribeiro-Pinto, L.F., Paumgartten, F.J. In vitro inhibition of CYP2B1 monooxygenase by β-myrcene and other monoterpenoid compounds. **Toxicol. Lett**. 92, 1997. DOI: https://doi.org/10.1016/s0378-4274(97)00034-9

DINIZ, M. F.; ANDRADE-NÚÑES, M.J.; DALLMEIER, F.; SÁNCHES-CUERVO, A.M. Habitat assessment for threatened species in the cross-border region of the Atlantic Forest. **Landsc Ecol**, 38, 2023. DOI: https://doi.org/10.1007/s10980-023-01689-9

DUQUE, J. E., URBINA, D. L., VESGA, L. C., ORTIZ-RODRÍGUEZ, L. A. et al. Insecticidal activity of essential oils from American native plants against *Aedes aegypti* (Diptera: Culicidae): an introduction to their possible mechanism of action. **Scientific Reports**, 2023. https://doi.org/10.1038/s41598-023-30046-8

ERB, K. et al. Unexpectedly large impact of forest management and grazing on global vegetation biomass. **Nature** 553, 2018. DOI: https://doi.org/10.1038/nature25138

ERENSTEIN, O., JALETA, M., SONDER, K. *et al.* Global maize production, consumption and trade: trends and R&D implications. **Food Sec**. 14, 2022. https://doi.org/10.1007/s12571-022-01288-7

FAKOREDE, M. A. B., BADU-APRAKU, B., KAMARA, A. Y., MENKIR, A. et al. Maize revolution in West and Central Africa: An overview. In *Maize revolution in West and Central Africa*, ed. B. Badu-Apraku, M.A.B. Fakorede, M. Ouédraogo, R.J. Carsky, and A. Menkir, 3–15. Proceedings of a Regional Maize Workshop, IITA-Cotonou, 14–18 May 2001.

FARIAS, J. R., ANDOW, D. A, HORIKOSHI, R. J., SORGATTO, R, J. et al. Field-evolved resistance to Cry1F maize by *Spodoptera frugiperda* (Lepidoptera: Noctuidae) in Brazil. Crop Prot. 64:150–58, 2014. https://doi.org/10.1016/j.cropro.2014.06.019

FELTON, G. W., SUMMERS, C. B. Antioxidant system in insects. **Arch Insect Biochem Physiol**. 29, 1995 DOI: https://doi.org/10.1002/arch.940290208.

FERREIRA, I.J.M.; CAMPANHARO, W.A.; FONSECA, M.G. et al. Potential aboveground biomass increase in Brasilian Atlantic Forest fragments with climate change. **Global Change Biology**, v. 29, 2023. DOI: https://doi-org.ez22.periodicos.capes.gov.br/10.1111/gcb.16670

FIGUEIREDO MLC, DELLA LUCIA TMC, CRUZ I. Effect of *Telenomus remus* Nixon (Hymenoptera: Scelionidae) density on control of Spodoptera frugiperda (Smith) (Lepidoptera: Noctuidae) egg masses upon release in a maize field. **Rev. Bras. Milho Sorgo** 1, 2002. DOI: https://doi.org/10.18512/1980-6477/rbms.v1n02p%25p

FIGUEIREDO, M. L. C., CRUZ, I., DA SILVA, R. B., FOSTER, J.E. Biological control with *Trichogramma pretiosum* increases organic maize productivity by 19.4%. **Agron. Sustain. Dev.** 35, 2015. DOI: https://doi.org/10.1007/s13593-015-0312-3

FLAMINI, G., TEBANO, M., CIONI, P.L., CECCARINI, L., RICCI, A.S., LONGO, I. Comparison between the conventional method of extraction of essential oil of *Laurus nobilis* L. and a novel method which uses microwaves applied in situ, without resorting to an oven. **Journal of Chromatography A**, 2007. DOI: https://doi.org/10.1016/j.chroma.2007.01.031

FORMAN, H.J.; ZHANG, H.; RINNA, A. Glutathione: Overview of its protective roles, measurement, and biosynthesis. **Mol. Asp. Med**. 2009, 30, 1–12. DOI: https://doi.org/10.1016/j.mam.2008.08.006

FRANCESCATO, L. N.; DEUSCHLE, R. A. N.; MALLMANN, C. A.; ALVES, S. H.; HEIZMANN, B. M. Atividade antimicrobiana de *Senecio heterotrichius* DC (Asteraceae). **Revista Brasileira de Ciências Farmacêuticas**, 43, 2007.

FRANCO, M.J.V; ALBIERO, A.L.M. Estruturas secretoras em folha e caule de *Esenbeckia febrifuga* (A.St.-Hil.) A. Juss. ex Mart. e *Esenbeckia grandiflora* Mart. (Rutaceae). **Hoehnea** 45, 2018. DOI: http://dx.doi.org/10.1590/2236-8906-75/2017

FRITZ, G.J. **Keepers of Louisiana's levees: Early mound builders and forest managers**. In Rethinking agriculture: Archaeological and ethnoarchaeological perspectives, ed. T.P. Denham, J. Iriarte, and L. Vrydaghs, 189–209, 2007.

FÜLLER, T.N., TESSELE, C., BARROS, I.B.I., BARBOSA NETO, J.F.

Phenotypical, phytochemical and molecular characterization of “capim-carona” [*Elionurus muticus* (Spreng.) Kuntze] populations. **Rev. Bras. Plantas Med**. 12, 2010. DOI: https://doi.org/10.1590/S1516-05722010000300003

GARCIA, A.G.; FERREIRA, C.P.; GODOY, W.A. et al. A computational model to predict the population dynamics of *Spodoptera frugiperda*. **Journal of Pest Science**, v. 92, 2019. https://doi.org/10.1007/s10340-018-1051-4

GIUNTI, G.; CAMPOLO, O.; LAUDANI, F.; PALMERI, V. et al. Essential oil-based nanoinsecticides: ecological costs and commercial potential. In: **Development and Commercialization of Biopesticides** – Cost and Benefits. Ed: Opender Koul, 2023. DOI: https://doi.org/10.1016/B978-0-323-95290-3.00002-9

GRECCO, S.S., GIMENES, L., FERREIRA, M.J.P., ROMOFF, P., FAVERO, O.A., ZALEWSKI, C.A., LAGO, J.H.G. Triterpenoids and phenolic derivatives from *Baccharis uncinella* DC. (Asteraceae). **Biochem. Syst. Ecol.** 38, 1234–1237, 2010a. DOI: https://doi.org/10.1016/j.bse.2010.12.005

GRECCO, S.S., REIMÃO, J.Q., TEMPONE, A.G., SARTORELLI, P., ROMOFF, P., FERREIRA, M.J.P., FÁVERO, O.A., LAGO, J.H.G. Isolation of an antileishmanial and antitrypanosomal flavanone from the leaves of *Baccharis retusa* DC. (Asteraceae). **Parasitol. Res.** 106, 1245–1248, 2010b. DOI: https://doi.org/10.1007/s00436-010-1771-8

GRECCO S.S., REIMÃO J.Q., TEMPONE A.G., SARTORELLI P., CUNHA R.L.O.R., ROMOFF P., FERREIRA M.J.P., FÁVERO O.A., LAGO J.H.G. In vitro antileishmanial and antitrypanosomal activities of flavanones from *Baccharis retusa* DC. (Asteraceae). **Experimental Parasitology**. 130, 141–145, 2012. DOI: https://doi.org/10.1016/j.exppara.2011.11.002

GUENGERICH, F.P. Cytochrome P450 and chemical toxicology. **Chem Res Toxicol**. 21, 2008. DOI: https://doi.org/10.1021/tx700079z.

GUERRA, A.; REIS, L. K.; BORGES, F. L. G. et al. Ecological restoration in Brazilian biomes: Identifying advances and gaps. **Forest Ecology and Management**, v. 458, 2020. DOI: https://doi.org/10.1016/j.foreco.2019.117802

GUTIÉRREZ-MORENO R, MOTA-SANCHEZ D, BLANCO CA, WHALON ME, TERÁN-SANTOFIMIO H, et al. Field-evolved resistance of the fall armyworm (Lepidoptera: Noctuidae) to synthetic insecticides in Puerto Rico and Mexico. **J. Econ. Entomol**. 112, 2019. DOI: https://doi.org/ 10.1093/jee/toy372

HALLIWELL, B., GUTTERIDGE, J. M. C. **Free Radicals in Biology and Medicine**, 5th edn (Oxford, 2015; online edn, Oxford Academic, 22 Oct. 2015. DOI: https://doi.org/10.1093/acprof:oso/9780198717478.001.0001

HANS, A.L.; SAXENA, S. Plant Bioprospecting for Biopesticides and Bioinsecticides. In: **Bioprospecting of Plant Biodiversity for Industrial Molecules**. Ed: Santosh Kumar Upadhyay, Sudhir P. Singh, 2021. DOI: https://doi.org/10.1002/9781119718017

HARTMANN, T. **Diversity and variability of plant secondary metabolism: a mechanistic view**. In: Städler, E., Rowell-Rahier, M., Bauer, R. (eds) Proceedings of the 9th International Symposium on Insect-Plant Relationships. Series Entomologica, vol 53. Springer, Dordrecht. 1996. DOI: https://doi.org/10.1007/978-94-009-1720-0_42

HAYES, J. D., McLELLAN, L. I. Glutathione and Glutathione Dependent-Enzymes Represent a Co-Ordinately Regulated Defence against Oxidative Stress, **Free Radical Research**, 31, 1999. DOI: http://dx.doi.org/10.1080/10715769900300851

HESS, S.C. et al. Evaluation of seasonal changes in chemical composition and antibacterial activity of *Elyonurus muticus* (Sprengel) O. Kuntze (Gramineae). **Química Nova**, v.30, n.2, p.370-3, 2007.

HEINZMANN, B.M.; SPITZER, V.; SIMÕES, C.M.O. **Óleos voláteis**. In: Simões, C. M. O.; Schenkel, E. P.; Mello, J. C. P.; Mentz, L. A.; Petrovick, P. R. Farmacognosia: da planta ao medicamento. Simões C. M. O et al. Porto Alegre: Artmed, 2017.

HIKAL et al. Botanical insecticide as simple extractives for pest control. **Cogent Biology** (2017), 3: 1404274 DOI: https://doi.org/10.1080/23312025.2017.1404274

HURLEY, T.M.; MITCHELL, P.D. The value of insect management to US maize, soybean and cotton farms. **Pest Management Science**, v. 76, 2020. DOI: https://doi.org/10.1002/ps.5974

HUSSAIN, A. G., WENNMANN, J. T., GOERGEN, G., BRYON, A. et al. Viruses of the fall armyworm *Spodoptera frugiperda*: a review with prospects for biological control. **Viruses**, 13, 2021. DOI: https://doi.org/10.3390/v13112220

HYLDGAARD M, MYGIND T, MEYER RL. Essential oils in food preservation: mode of action, synergies, and interactions with food matrix components. **Front Microbiol**. 2012. DOI: 10.3389/fmicb.2012.00012. PMID: 22291693; PMCID: PMC3265747.I

IBGE – Instituto Brasileiro de Geografia e Estatística. Mapa da área de aplicação da Lei nº 11.428 de 2006, 2008.

IMLAY, J.A., LINN, S. DNA damage and oxygen radical toxicity. **Science**, 240, 1988. DOI: https://doi.org/10.1126/science.3287616

IQBAL, W., KHAN, A., JAMAL, A., RADICETTI, E. et al. Optimizing Maize Productivity and Soil Fertility: Insights from Tillage, Nitrogen Management, and Hydrochar Applications. **Land**, 13, 2024. DOI: https://doi.org/10.3390/land13081329

IRIARTE, J. **New perspectives on plant domestication and the development of agriculture in the New World**. In: Rethinking agriculture: Archaeological and ethnoarchaeological perspectives, ed. T.P. Denham, J. Iriarte, and L. Vrydaghs, 167–188, 2007.

ISMAN, M. B. Plant essential oils for pest and disease management. **Crop Protection**, 19, 2000. DOI: https://doi.org/10.1016/S0261-2194(00)00079-X

ISMAN, M.B. Botanical Insecticides, Deterrents, and Repellents in Modern Agriculture and an Increasingly Regulated World. **Annual Review Entomology**, v. 51, 2006. DOI: https://doi.org/10.1146/annurev.ento.51.110104.151146

ISMAN, M.B. Bioinsecticides based on plant essential oils: a short overview. **Z. Naturforsch**, 75, 2020.

IVANO, L.R.P.F.M.; FREITAS, J.F.; NETTO, M.F. Óleos essenciais na indústria cosmética e medicina alternativa: benefícios e desafios para uso responsável. **Revista Contemporânea**, 3, 2023. DOI: https://doi.org/10.56083/RCV3N10-084

JACOB, R.F., MASON, R.P. Lipid peroxidation induces cholesterol domain formation in model membranes. **J. Biol. Chem**. 280, 2005. https://doi.org/10.1074/jbc.M507587200

JAHANIAN, H.; KAHKESHANI, N.; SANEI-DEHKORDI, A.; ISMAN, M.B. et al. *Rosmarinus officinalis* as natural insecticide: a review. **International Journal of Pest Management**, 2022. DOI: https://doi.org/10.1080/09670874.2022.2046889

JUDD, W.S., CAMPBELL, C.S., KELLOGG, E.A., STEVENS, P.F. & DONOGHUE, M.J. Sistemática vegetal: um enfoque filogenético. 3 ed., Artmed, Porto Alegre. 2009.

KAUR, K., CHEEMA, H. K., JINDA, J., GARG, T. et al. Categorization of resistance against the fall armyworm, *Spodoptera frugiperda* (J.E. Smith) in select maize inbred lines. **Crop Protection**, 178, 2024. DOI: https://doi.org/10.1016/j.cropro.2024.106581

KIM, S.W., KANG, J., PARK, I.K. Fumigant toxicity of Apiaceae essential oils and their constituents against Sitophilus oryzae and their acetylcholinesterase inhibitory ac tivity. **J. Asia Pac. Entomol**. 16, 2013. DOI: https://doi.org/10.1016/j.aspen.2013.07.002

KIRAN, S., PRAKASH, B. Toxicity and biochemical efficacy of chemically characterized Rosmarinus officinalis essential oil against Sitophilus oryzae and Oryzaephilus surinamensis. **Ind. Crops Prod**. 74, 2015. https://doi.org/10.1016/j.indcrop.2015.05.073

KREIS, W.; MUNKERT, J.; PÁDUA, R.M. Biossíntese de metabólitos primários e secundários. In: Simões, C. M. O.; Schenkel, E. P.; Mello, J. C. P.; Mentz, L. A.; Petrovick, P. R. Farmacognosia: da planta ao medicamento. Simões C. M. O et al. Porto Alegre: Artmed, 2017.

KUMAR, S. et al. Essential oil as green pesticides: An overview. **Indian Journal of Agricultural Sciences** 92 (11): 1298–1305, 2022. DOI: https://doi.org/10.56093/ijas.v92i11.122746

KURDELAS R.R, LÓPEZ S, LIMA B, FERESIN G.E, ZYGADLO J, ZACCHINO S, LÓPEZ M.L, TAPIA A, FREILE M.L. Chemical composition, anti-insect and antimicrobial activity of *Baccharis darwinii* essential oil from Argentina, Patagonia. **Industrial Crop and Products**, 40, 2012. DOI: https://doi.org/10.1016/j.indcrop.2012.03.024L

LAGO, L. H. G.; ROMOFF P.; FÁVERO O. A. Chemical composition of the essential oils from leaves of six species of the genus *Baccharis* of São Paulo rainforest. **Química Nova**. 31, 2008.

LEE, S.E., LEE, B.H., CHO, W.S., PARK, B.S., KIM, J.G., CAMPBELL, B.C. Fumigant toxicity of volatile natural products from Korean species and medicinal plants to wards the rice weevil, Sitophilus oryzae (L). **Pest Manag. Sci.** 57, 2001. DOI: https://doi.org/10.1002/ps.322

LI, S.G., LI, M.Y., HUANG, Y.Z., HUA, R.M., et al. Fumigant activity of Illicium verum fruit extracts and their effects on the acet ylcholinesterase and glutathione S-transferase activities in adult Sitophilus zeamais. **J. Pest. Sci.** 86, 2013. DOI: https://doi.org/10.1007/s10340-013-0520-z

LILLIG, C.H.; BERNDT, C. Preface. Cellular functions of glutathione. **Biochim. Biophys. Acta**, 1830, 2013. DOI: https://doi.org/10.1016/j.bbagen.2013.02.019

LIMA, R. A. F.; OLIVEIRA, A.A.; PITTA, G.R. et al., The erosion of biodiversity and biomass in the Atlantic Forest biodiversity hotspot. **Nature Communications**, v. 11, 2020. DOI: https://doi.org/10.1038/s41467-020-20217-w

LIRA, E.C.; BOLZAN, A.; NASCIMENTO, A, R.B.; AMARAL, F.S.A.; KANNO, R.H. et al. Resistance of *Spodoptera frugiperda* (Lepidoptera:Noctuidae) to spinetoram: inheritance and cross-resistance to spinosad. **Pest Management Science**, v. 76, 2020. DOI: https://doi.org/10.1002/ps.5812

LOPEZ-MARTINEZ, G., ELNITSKY, M.A., BENOIT, J.B., LEE JR., R.E., DENLINGER, D.L. High resistance to oxidative damage in the Antarctic midge Belgica antarctica, and developmentally linked expression of genes encoding superoxide dismutase, catalase and heat shock proteins. **Insect Biochemistry and Molecular Biology** 38, 2008. DOI: https://doi.org/10.1016/j.ibmb.2008.05.006

LUKASIK, I., 2007. Changes in activity of superoxide dismutase and catalase within cereal aphids in response to plant o-dihydroxyphenols. **J. Appl. Entomol**. 131, 209–214. DOI: https://doi.org/10.1111/j.1439-0418.2006.01136.x

MACIEL, R.M.A.; LUSKI, P.G.G.; SUTIL, W.P.; GONÇALVEZ, J. et al. The use of baculovirus Spodoptera SfMNPV alone and combined with herbicides and adjuvant to control *Spodoptera frugiperda* (Smith, 1797) (Lepidoptera: Noctuidae). **Biological Control**, v.188, 2024. DOI: https://doi.org/10.1016/j.biocontrol.2023.105408

MAKSIC. J.; VENANCIO, I.M.; SHIMIZU, M.H. et al. Brazilian biomes distribution: Past and future. **Palaeogeography, Palaeoclimatology, Palaeoecology**, v. 585, 2022. DOI: https://doi.org/10.1016/j.palaeo.2021.110717

MARANGONI, C.; MOURA, N.F.; GARCIA, F.R.M. Utilização de Óleos Essenciais e Extratos de Plantas no Controle de Insetos. **Revista de Ciências Ambientais**, v. 6, n.2, p. 95 a 112, 2012.

MENG, J.Y., ZHANG, C.Y., ZHU, F., WANG, X.P., LEI, C.L. Ultraviolet light-induced oxidative stress: effects on antioxidant response of Helicoverpa armigera adults. J. **Insect Physiol**. 55, 2009. DOI: https://doi.org/10.1016/j.jinsphys.2009.03.003

MITTERMEIER, R. A.; GIL, P. R.; HOFFMANN, M.; PILGRIM, J.; BROOKS, T.; MITTERMEIER, C. G.; LAMOUREX, J. & FONSECA, G. A. B. **Hotspots revisited**. CEMEX, México City, 2004. 392p.

MONAGHAN, P., METCALFE, N.B., TORRES, R. Oxidative stress as a mediator of life history trade-offs: mechanisms, measurements, and interpretations. **Ecol. Lett**. 12, 2009. DOI: https://doi.org/10.1111/j.1461-0248.2008.01258.x

MONTEZANO, D. G., SPECHT, A., SOSA-GÓMEZ, D., ROQUE-SPECHT, V. F. et al. Host plants of *Spodoptera frugiperda* (Lepidoptera: Noctuidae) in the Americas. **African Entomology**, 26, 2018. DOI: https://doi.org/10.4001/003.026.0286

MOSCARDINI, V.F.; MARQUES, L.H.; SANTOS, A.C.; ROSSETO, J. et al. Efficacy of *Bacillus thuringiensis* (Bt) maize expressing Cry1F, Cry1A.105, Cry2Ab2 and Vip3Aa20 proteins to manage the fall armyworm (Lepidoptera: Noctuidae) in Brazil. **Crop Protection**, v. 137, 2020. DOI: https://doi.org/10.1016/j.cropro.2020.105269

MYERS, N., MITTERMEIER, R. A., MITTERMEIER, C.G., FONSECA, G. A. B. & KENT, J. Biodiversity hotspots for conservation priorities. **Nature**, 403, 2000. DOI: https://doi.org/10.1038/35002501

NIASSY S, AGBODZAVU MK, KIMATHI E, MUTUNE B, ABDEL-RAHMAN EFM, SALIFU D, et al. Bioecology of fall armyworm *Spodoptera frugiperda* (J. E. Smith), its management and potential patterns of seasonal spread in Africa. **Plos One**, 16, 2021. DOI: https://doi.org/ 10.1371/journal.pone.0249042

OKUMA, D. M., BERNARDI, D., HORIKOSHI, R. J., BERNARDI, O., SILVA, A. P., OMOTO, C. Inheritance and fitness costs of *Spodoptera frugiperda* (Lepidoptera: Noctuidae) resistance to spinosad in Brazil. **Pest Manag. Sci**. 74, 2017. DOI: https://doi.org/10.1002/ps.4829

OLIVEIRA R.N., REHDER V.L.G., OLIVEIRA A.S.S., MONTANARI JÚNIOR Í., CARVALHO J.E., RUIZ A.L.T.G., JERALDO V.L.S., LINHARES A.X., ALLEGRETTI S.M. Anthelmintic activity in vitro and in vivo of *Baccharis trimera* (Less) DC against immature and adult worms of *Schistosoma mansoni*. **Experimental Parasitology**. 139, 2014. DOI: https://doi.org/10.1016/j.exppara.2014.02.010

OLIVEIRA, L.Z.; GASPER, A. L.; VIBRANS, A. C. Potential new areas for conservation of key botanical families in the subtropical Atlantic Forest. **Biodiversity and Conservation**, 2021. DOI: https://doi.org/10.1007/s10531-021-02280-x

OLIVEIRA, L.Z.; GASPER, A.L.; VIBRANS, A.C. Potential new areas for conservation of key botanical families in the subtropical Atlantic Forest. **Biodiversity and Conservation**, v. 30, 2021. https://doi-org.ez22.periodicos.capes.gov.br/10.1007/s10531-021-02280-x

OMUUT, G.; MOLLEL, H.G.; KANYESIGYE, D.; AKOHOUE, F. et al. Genetic analyses and detection of point mutations in the acetylcholinesterase-1 gene associated with organophosphate insecticide resistance in fall armyworm (*Spodoptera frugiperda)* populations from Uganda. **BMC Genomics**, v. 24, 2023. DOI: https://doi-org.ez22.periodicos.capes.gov.br/10.1186/s12864-022-09093-4

OOTANI, M. A., AGUIAR, R. W., RAMOS, A. C. C., BRITO, D. R. et al. Use of Essential Oils in Agriculture. **Journal of Biotechnology and Biodiversity**, 4, 2013.

OVERTON, K., MAINO, J. L., DAY, R., UMINA, P. A. et al. Global crop impacts, yield losses and action thresholds for fall armyworm (*Spodoptera frugiperda*): A review. **Crop Protection**, 145, 2021. DOI: https://doi.org/10.1016/j.cropro.2021.105641

PAGARE, S., BHATIA, M., TRIPATHI, N., PAGARE, S. et al. Secondary Metabolites of Plants and their Role: Overview. **Current Trends in Biotechnology and Pharmacy**, 9, 2015.

PARREIRA, D. S., CRUZ, R. A., ZANUNCIO, J. C., LEMES, P. G. et al. Essential oils cause detrimental effects on biological parameters of *Trichogramma galloi* immatures. Journal of Pest Science, 2017. DOI: https://doi.org/10.1007/s10340-017-0945-x.

PARK, Y.L.; TAK, J.H. **Essential Oils for Arthropod Pest Management in Agricultural Production Systems**. In: Essential Oils in Food Preservation, Flavor and Safety, Ed: Preedy, V.R. Elsevier, 2016.

PARKINSON, A., OGILVIE, B. W. **Biotransformation of xenobiotics**. In C. D. Klaassen (Ed.), Casarett and Doull's Toxicology: The Basic Science of Poisons. 8th ed. 2008.

PASSERO, L.F.D., BONFIM-MELO, A., CORBETT, C.E.P., LAURENTI, M.D., TOYAMA, M.H., TOYAMA, D.O., ROMOFF, P., FÁVERO, O.A., GRECCO, S.S., ZALEWSKY, C.A., LAGO, J.H.G. Anti-leishmanial effects of purified compounds from aerial parts of *Baccharis uncinella* DC. (Asteraceae). **Parasitol. Res**. 108, 2011. DOI: https://doi.org/10.1007/s00436-010-2091-8

PAVELA, R. History, Presence and Perspective of Using Plant Extracts as Commercial Botanical Insecticides and Farm Products for Protection against Insects – a Review. **Plant Protect. Sci**. 52, 2016. DOI: https://doi.org/10.17221/31/2016-PPS

PHILIPPOU, D., FIELD, L., MOORES, G. Metabolic enzyme(s) confer imidacloprid resistance in a clone of *Myzus persicae* (Sulzer) (Hemiptera: Aphididae) from Greece. **Pest Manag. Sci**. 66, 2010. DOI: https://doi.org/10.1002/ps.1888

PIPERNO, D. R., RANERE, A. J., HOLST, I. IRIARTE, J. et al. Starch grain and phytolith evidence for early ninth millennium B.P. maize from the Central Balsas River Valley, Mexico. **PNAS**, 2009. DOI: 10.1073pnas.0812525106

PICKSON, R. B., GUI, P., CHEN, A., BOATENG, E. Empirical analysis of rice and maize production under climate change in China. **Environmental Science and Pollution Research**, 29, 2022. DOI: https://doi.org/10.1007/s11356-022-20722-z

PITRE, H. N. Relationship of fall armyworm (Lepidoptera: Noctuidae) from Florida, Honduras, Jamaica, and Mississippi: susceptibility to insecticides with reference to migration. **Fla. Entomol**, 71, 1988. DOI: https://doi.org/10.2307/3494893

PLATA-RUEDA, A., FIAZ, M., BRÜGGER, B. P., CAÑAS, V. et al. Lemongrass essential oil and its components cause effects on survival, locomotion, ingestion, and histological changes of the midgut in *Anticarsia gemmatalis* caterpillars. **Toxin Reviews**, DOI: https://doi.org/10.1080/15569543.2020.1861468

POMARI-FERNANDES A, DE FREITAS BUENO A, OLIVEIRA DE FREITAS BUENO R C, MENEZES A JR., PRADO FERNANDES FONSECA AC. Releasing number of *Telenomus remus* (Nixon) (Hymenoptera: Platygastridae) against *Spodoptera frugiperda* Smith (Lepidoptera: Noctuidae) in corn, cotton and soybean. **Cienc. Rural**, 43, 2013. DOI: https://doi.org/10.1590/S0103-84782013005000013

POMARI-FERNANDES A, DE FREITAS BUENO A, DE BORTOLI SA, FAVETTI BM. Dispersal capacity of the egg parasitoid *Telenomus remus* Nixon (Hymenoptera: Platygastridae) in maize and soybean crops. **Biol. Control**, 126, 2018. DOI: https://doi.org/10.1016/j.biocontrol.2018.08.009

POPHAM, H. J. R., ROWLEY, D. L., HARRISON, R. L. Differential insecticidal properties of *Spodoptera frugiperda* multiple nucleopolyhedrovirus isolates against corn-strain and rice-strain fall armyworm, and genomic analysis of three isolates. **J. Invertebr. Pathol**. 183, 2021. DOI: https://doi.org/10.1016/j.jip.2021.107561

PORTO, J.V.A.; REZENDE, F.P.C.; NUCCI, H.H.P.; ROEL, A.R. et al. Deep neural networks with attention mechanisms for *Spodoptera frugiperda* pupae sexing. **Smart Agricultural Technology**, v. 4, 2023. DOI: https://doi.org/10.1016/j.atech.2023.100200

QUEIROZ, A.P.; FAVETTI, B.M.; LUSKI, P.G.G.; GONÇALVEZ, J. et al. Telenomus remus (Hymenoptera: Platygastridae) parasitism on *Spodoptera frugiperda* (Lepidoptera: Noctuidae) eggs: different parasitoid and host egg ages. **Semina**: Ciências Agrárias, v. 40, 2019. DOI: https://doi.org/10.5433/1679-0359.2019v40n6Supl2p2933

RAHIMI, V., HAJIZADEH, J., ZIBAEE, A., SENDI, J.J. Effect of Polygonum persicaria (Polygonales: Polygonaceae) extracted agglutinin on life table and antioxidant re sponses in Helicoverpa armigera (Lepidoptera: Noctuidae) larvae. **J. Econ. Entomol**. 111, 2018. DOI: https://doi.org/10.1093/jee/toy006

REBOURG, .C., CHASTANET, .M., GOUESNARD, B. et al. Maize introduction into Europe: the history reviewed in the light of molecular data. **Theor Appl Genet**, 106, 2003. DOI: https://doi.org/10.1007/s00122-002-1140-9

REGNAULT-ROGER, C.; VINCENT, C.; THOR, J. Essential oils in insect control: low-risk products in a high-stakes world. **Annual Review Entomology**, 57, 2012. DOI: https://doi.org/10.1146/annurev-ento-120710-100554

REZENDE, C.L.; SCARANO, F.R.; ASSAD, E.D. et al. From hotspot to hopespot: An opportunity for the Brazilian Atlantic Forest. **Perspectives in Ecology and Conservation**, v. 16, 2018. DOI: https://doi.org/10.1016/j.pecon.2018.10.002

RIBEIRO, M.C.; METZGER, J.P.; MARTENSEN, A.C. et al. The Brazilian Atlantic Forest: Much is left, and how is the remaining forest distributed? Implications for conservation. **Biological Conservation**, v. 142, 2009. DOI: https://doi.org/10.1016/j.biocon.2009.02.021

RÍOS, J.L. Essential Oils: What They Are and How the Terms Are Used and Defined. In: Essential Oils in Food Preservation, Flavor and Safety, Ed: Preedy, V.R. Elsevier, 2016.

ROSA, A. P. A., TRECHA, C. O., ALVES, A. C., GARCIA, L. et al. biologia e tabela de vida de fertilidade de *Spodoptera frugiperda* (J.E. SMITH) em linhagens de milho. **Arq. Inst. Biol**., São Paulo, v.79, n.1, p.39-45, jan./mar., 2012

RUSSO, M.L.; JARBER, L.R.; SCORSETTI, A.C.; VIANNA, F. et al. Effect of entomopathogenic fungi introduced as corn endophytes on the development, reproduction, and food preference of the invasive fall armyworm *Spodoptera frugiperda*. **Journal of Pest Science**, v. 94, 2021. DOI: https://doi.org/10.1007/s10340-020-01302-x

SABINI, L.I. et al. Study of the cytotoxic and antifungal activity of the essencial oil of *Elyonurus muticus* against *Candida* spp. **Molecular Medicinal Chemistry**, v.11, p.31-3, 2006.

SAMPAIO, F. et al. A new biocontrol agent against old enemies: The potential of *Trichogramma foersteri* for the control of *Spodoptera frugiperda* and *Spodoptera eridania*. **Biological Control**, v. 192, p. 1-8, 2024. DOI: https://doi.org/10.1016/j.biocontrol.2024.105504.

SANCHES, A.; SALES, C. Expressivo aumento nas exportações brasileiras de milho impõe mudanças na dinâmica do mercado nacional. **Centro de Estudos Avançados em Economia Aplicada** (CEPEA-USP), set, 2022. Disponível em: < https://www.cepea.esalq.usp.br/br/opiniao-cepea/expressivo-aumento-nas-exportacoes-brasileiras-de-milho-impoe-mudancas-na-dinamica-do-mercado-nacional.aspx#:~:text=O%20maior%20excedente%20export%C3%A1vel%20em,milh%C3%B5es%20de%20toneladas%2C%20um%20recorde.> Acesso em: 18 fev. 2024

SANTOS, A.S.; ALVES, S.M., FIGUEIREDO, F.J.C.; ROCHA NETO, O.G. Descrição de sistema e de métodos de extração de óleos essenciais e determinação de umidade de biomassa em laboratório. Belém, PA: **Comunicado técnico, 99**. Embrapa Amazônia Oriental, 2004. Disponível em: http://www.infoteca.cnptia.embrapa.br/infoteca/handle/doc/402448 Acesso em: 25 fev. 2024

SANTOS, T. G.; DOGNINI, J.; BEGNINI, I. M.; REBELO, R. A.; VERDI, M.; GASPER, A. L. DALMARCOD, E. M. Chemical Characterization of Essential Oils from *Drimys angustifolia* Miers (Winteraceae) and Antibacterial Activity of their Major Compounds. **J. Braz. Chem. Soc**., 24, 2013. DOI: https://doi.org/10.1590/S0103-50532013000100020

SANTOS, A. A., WANDERLEY-TEIXEIRA, V., CRUZ, G. S., DUTRA, K. A. et al. Essential oil toxicity on biological and reproductive parameters of Alabama argillacea (Hübner) (Lepidoptera: Erebidae). **Acta Histochemica**, 123, 2021. DOI: https://doi.org/10.1016/j.acthis.2021.151714

SCHRIPSEMA, J., LEMOS, M.A., DAGNINO, D. *et al.* Carqueja (*Baccharis* sect. *Caulopterae*), a critical review of its history, phytochemistry and medicinal use: problems of ethnopharmacology in Latin America. **Phytochem Ver**, 18, 2019. https://doi.org/10.1007/s11101-019-09616-0

SEMMAR, N. **Variational Factors and Regulation Processes of Secondary Metabolites**. In: Secondary Metabolites in Plant Stress Adaptation. Signaling and Communication in Plants. Springer, Cham. 2024. https://doi.org/10.1007/978-3-031-52595-7_2

SENTHIL-NATHAN, S. Physiological and biochemical effect of neem and other Meliaceae plants secondary metabolites against lepidopteran insects. **Front. Physiol**. 4, 2013. DOI: https://doi.org/10.3389/fphys.2013.00359

SEO, S.M., KIM, J., KANG, J., KOH, S.H. et al. Fumigant toxicity and acetylcholinesterase inhibitory activity of 4 Asteraceae plant essential oils and their constituents against Japanese termite (Reticulitermes speratus Kolbe). Pestic. Biochem. Physiol. 113, 2014. DOI: https://doi.org/10.1016/j.pestbp.2014.06.001

SHAHRIARI, M., ZIBAEE, A., SAHEBZADEH, N., SHAMAKHI, L. Effects of α-pinene, trans-anethole, and thymol as the essential oil constituents on antioxidant system and acetylcholine esterase of *Ephestia kuehniella* Zeller (Lepidoptera: Pyralidae). Pestic. **Biochem. Phys.** 150, 2018. https://doi.org/10.1016/j.pestbp.2018.06.015

SHEEHAN, D., MEADE, G., FOLEY, V. M., DOWD, C. A. Structure, function and evolution of glutathione transferases: implications for classification of non-mammalian members of an ancient enzyme superfamily. Biochem J., 15, 2001. DOI: https://doi.org/10.1042/0264-6021:3600001.

SHIFERAW, B., et al. Crops that feed the world 6. Past successes and future challenges to the role played by maize in global food security. **Food Security**, 3, 2011. DOI: 10.1007/s12571-011-0140-5.

SILVA, C.L.T.; PAIVA, L. A.; CORREA, F.; SILVA, F.C.; PELOSI, A.P. et al. Interaction between Corn Genotypes with Bt Protein and Management Strategies for *Spodoptera frugiperda* (Lepidoptera: Noctuidae). **Florida Entomologist**, v. 12, 2019. DOI: https://doi.org/10.1653/024.102.0409

SILVA, I.H.S.; COSTA, V.H.D.; CURY, J.C.; VALICENTE, F. H. et al. The Infectivity of SfMNPV on fall armyworm is influenced by the host plant. **Revista Brasileira de Milho e Sorgo**, v. 17, 2018. https://doi.org/10.18512/1980-6477/rbms.v17n39369-379

SIQUEIRA-FILHO, J. A., LEME, E. M. C. **Fragmentos de Mata Atlântica do Nordeste**. Biodiversidade, conservação e suas bromélias. Andrea Jakobsson Estúdio, Rio de Janeiro, 2006. 415p.

SOARES, L.A.L.; FARIAS, M.R. Qualidade de insumos farmacêuticos ativos de origem natural. In: Simões, C. M. O.; Schenkel, E. P.; Mello, J. C. P.; Mentz, L. A.; Petrovick, P. R. **Farmacognosia**: da planta ao medicamento. Simões C. M. O et al. Porto Alegre: Artmed, 2017.

SOUZA, C.V; LORENZI, H. **Botânica Sistemática**: Guia ilustrado para identificação das famílias de fanerógamas nativas e exóticas no Brasil, baseado em APG II. 2ª edição, Editora Plantarum, Nova Odessa, SP, 2008.

STADTMAN, E.R. Oxidation of proteins by mixed-function oxidation systems: implication in protein turnover, aging and neutrophil function. **Trends in Biochemistry Sciences**, 11, 1986. DOI: https://doi.org/10.1016/0968-0004(86)90221-5

STADTMAN, E.R., LEVINE, R.L. Free radical-mediated oxidation of free amino acids and amino acid residues in proteins. **Amino Acids** 25, 2003. DOI: https://doi.org/10.1007/s00726-003-0011-2

STEHMANN et al. Plantas da Floresta Atlântica. – Rio de Janeiro: Jardim Botânico do Rio de Janeiro, 2009. 516 p. Disponível em: https://www.gov.br/jbrj/pt-br/centrais-de-conteudo/publicacoes/plantas_floresta_atlantica.pdf Acesso em: 23 mar. 2024.

STOKSTAD, E. New crop pest takes Africa at lightning speed. Science 356, 2017. DOI: https://doi.org/10.1126/science.356.6337.473

STORER, N. P., BABCOCK, J. M., SCHLENZ, M., MEADE, T., THOMPSON, G. D. et al. Discovery and characterization of field resistance to Bt maize: *Spodoptera frugiperda* (Lepidoptera: Noctuidae) in Puerto Rico. **J. Econ. Entomol**. 103, 2010. DOI: https://doi.org/10.1603/ec10040

STRATAKOS, A. C.; KOIDIS, A. **Methods for Extracting Essential Oils**. In: Essential Oils in Food Preservation, Flavor and Safety, Ed: Preedy, V.R. Elsevier, 2016.

SUN X-X, HU C-X, JIA H-R, WU Q-L, SHEN X-J, et al. Case study on the first immigration of fall armyworm, *Spodoptera frugiperda* invading into China. **J. Integr. Agric**. 20, 2021. DOI: https://doi.org/10.1016/S2095-3119(19)62839-X

TABARELLI, M.; AGUIAR, A.V.; RIBEIRO, M.C. Prospects for biodiversity consercation in the Atlantic Forest: Lesson from aging human-modified landscapes. **Biological Conservation**, v. 143, 2010. DOI: https://doi.org/10.1016/j.biocon.2010.02.005

TAIZ, L.; ZEIGER, E. Fisiologia Vegetal, trad. Armando Molina Divan Junior, et al. 5 ed. Porto Alegre: Artmed, 2013.

TAK, J.H., ISMAN, M.B. Metabolism of citral, the major constituent of lemongrass oil, in the cabbage looper, Trichoplusia ni, and effects of enzyme inhibitors on toxicity and metabolism. **Pestic. Biochem. Physiol**. 133, 2016. DOI: https://doi.org/10.1016/j.pestbp.2016.03.009

TAY, W. T., MEAGHER Jr, R. L., CZEPAK, C., GROOT, A. *Spodoptera frugiperda*: Ecology, Evolution, and Management Options of an Invasive Species. **Annu. Rev. Entomol**. 68, 2023. DOI: https://doi.org/10.1146/annurev-ento-120220 102548

THEIS, N.; LERDAU, M. The Evolution of Function in Plant Secondary Metabolites. **International Journal of Plant Science**, 2015. https://doi.org/10.1086/374190.

THOMPSON, P. B. The Agricultural Ethics of Biofuels: The Food vs. Fuel Debate. **Agriculture**. 2, 2012. DOI: https://doi.org/10.3390/agriculture2040339.

TRIPATHI, A.K., PRAJAPATI, V., KUMAR, S. Bioactivity of l-carvone, d-carvone and dihydrocarvone towards three stored product beetles. **J. Econ. Entomol**., 96, 2003. DOI: https://doi.org/10.1603/0022-0493-96.5.1594

UNITED STATES DEPARTAMENT OF AGRICULTURE – USDA – **Corn**: Production, Supply and Distribution, 2023. Disponível em: < https://apps.fas.usda.gov/newgainapi/api/Report/DownloadReportByFileName?fileName=Grain%20and%20Feed%20Annual_Brasilia_Brazil_BR2023-0008> Acesso em 18 fev. 2024

VALE, M. M., TOURINHO, L., LORINI, M. L.; RAJÃO, H. et al. Endemic birds of the Atlantic Forest: traits, conservation status, and patterns of biodiversity. **J. Field Ornithol**. 89, 2018. DOI: https://doi.org/10.1111/jofo.12256

VAN den BERG, J.; PLESSIS, H. Chemical Control and Inseticide Resistance in *Spodoptera frugiperda* (Lepidoptera: Noctuidae). **Entomological Society of America**, v. 115, 2022. DOI: https://doi.org/10.1093/jee/toac108

VIEIRA, N. F., POMARI-FERNANDES, A., LEMES, A. A. F., VACARI, A. M. et al. Cost of production of *Telenomus remus* (Hymenoptera: Platygastridae) grown in natural and alternative hosts. **J. Econ. Entomol**. 110, 2017. DOI: https://doi.org/10.1093/jee/tox271

WANG, Y., OBERLEY, L.W., MURHAMMER, D.W. Evidence of oxidative stress following the viral infection of two lepidopteran insect cell lines. **Free Radic. Biol. Med**., 31, 2001. DOI: https://doi.org/10.1016/S0891-5849(01)00728-6

WANG, F., XUE, J., XIE, R., MING, B. et al. Assessing Growth and Water Productivity for Drip-Irrigated Maize under High Plant Density in Arid to Semi-Humid Climates. **Agriculture**, 12, 2022. DOI: https://doi.org/10.3390/agriculture12010097

WARBURTON, M.L.; WOOLFOLK, S.W.; SMITH, J.S.; HAWKINS, L.K. Genes and genetic mechanisms contributing to fall armyworm resistance in maize. **The Plant Genome**, v. 16, 2023. DOI: https://doi.org/10.1002/tpg2.20311

YOUNG, J. R., McMILLAN, W. W. Differential feeding by two strains of fall armyworm larvae on carbaryl treated surfaces. **J. Econ. Entomol**. 72, 1979.

# CHAPTER 1: INSECTICIDAL ACTIVITY, TOXICITY AND BIOCHEMICAL ALTERATIONS OF *Drimys brasiliensis* ESSENTIAL OIL AGAINST *Spodoptera frugiperda*

* These results were published in Journal of Pest Science (https://doi.org/10.1007/s10340-024-01827-5)

**Abstract**

*Spodoptera frugiperda* is a major pest in corn crops, causing significant productivity losses and exhibiting high resistance to synthetic insecticides. Essential oils (EOs) are natural substances known for their insecticidal activity against various agricultural pests. This study describes the chemical composition and bioactivity of *Drimys brasiliensis* EO against *S. frugiperda* larvae. The EO was extracted using the steam distillation method in a vat, and its chemical composition was determined using gas chromatography coupled with mass spectrometry (GC-MS). The insecticidal activity of this EO was assessed by the contact method to estimate the lethal concentration ($LC_{50}$ and $LC_{90}$) and to evaluate the effects on biochemical markers, including glutathione S-transferase (GST), esterase-α (EST-α), esterase-β (EST-β), superoxide dismutase (SOD), acetylcholinesterase (AChE), and lipid peroxidation (LPO), in 3rd instar larvae of *S. frugiperda*. Twenty-nine compounds were identified by GC-MS, accounting for 81.32% of the total chemical composition *D. brasiliensis* EO resulted in 100% mortality of *S. frugiperda* larvae at a concentration of 2.5%, with $LC_{50}$ and $LC_{90}$ values of 0.90% and 1.40%, respectively. Both lethal concentrations increased AChE and LPO activity, while only $LC_{90}$ affected the EST-α and EST-β enzymes. *Drimys brasilien*sis EO exhibits insecticidal activity against *S. frugiperda* with neurotoxic effects, as well as cellular damage, demonstrating its potential as a control method in managing this pest in conventional and organic production methods.

**Keywords:** fall armyworm, enzymatic activities, Winteraceae, biochemical effects

## 1. Introduction

*Spodoptera frugiperda* (JE Smith, 1797) (Lepidoptera: Noctuidae), commonly known as the fall armyworm, is the most destructive pest of corn crops in Brazil and other South American countries (Pogue 2002; Cruz et al., 2012). In this country, the prevailing production systems promote high levels of insect infestations at all stages of corn growth (Barros et al., 2010).

Historically, the control of fall armyworms in corn has relied on synthetic insecticides. However, the efficacy of this control strategy is limited by the larval behavior of the species, as the caterpillars remain within the corn whorl, which complicates targeting with sprays from conventional insecticides (Carvalho et al., 2013; Kenis et al., 2023). Moreover, intensive corn cultivation in certain regions of Brazil has also accelerated the evolution of insecticide resistance in *S. frugiperda* populations. In these agricultural systems, the insect has developed resistance to several insecticides, including lambda-cyhalothrin, chlorpyrifos, spinosad, and lufenuron (Bolzan et al., 2019; Lira et al., 2019).

Low adherence to integrated pest management and insecticide resistance management strategies has negatively affected the control of *S. frugiperda* in Brazil (Moscardini et al., 2020). Given this scenario, developing new control tactics for *S. frugiperda* that are more effective and less harmful to the environment and non-target organisms, such as bioinsecticides, is necessary. Several botanical families produce a variety of bioactive secondary metabolites, including terpenes, flavonoids, and alkaloids (Erb and Kliebenstein, 2020; Ninkuu et al., 2021), which may exhibit insecticidal activity.

Among the products derived from plant secondary metabolism are essential oils (EOs) (Heinzmann et al., 2017), which are complex mixtures of volatile, lipophilic, generally odorous, and liquid compounds (Borges and Amorim 2020). These compounds are stored in various plant organs, such as bark, leaves, and fruits (Taiz and Zeiger 2013). EOs offer several advantages, including low toxicity to non-target organisms, minimal persistence in field conditions, reduced environmental and human health risks, and a lower likelihood of inducing pest resistance (Isman 2020). However, despite their potential as botanical insecticides for agricultural use, there is a scarcity of studies investigating their mechanisms of action on agricultural pests and their effects on biotransformation or antioxidant enzymes (Zhang and Feng 2018).

Among the EO-producing species, those of the genus *Drimys* (Winteraceae) stand out, such as *Drymis angustifolia* Miers and *Drimys brasiliensis* Miers; these arboreal plants are endemic to the Atlantic Forest and popularly known as cataia or casca de anta, and its barks are widely used in folk medicine to treat different diseases and health problems (Amaral et al., 2017; Graf Júnior et al., 2021). Several studies have demonstrated that EOs from *D. brasiliensis* possess various biological properties (Ribeiro et al., 2008; Gomes et al., 2013; Graf Júnior et al., 2021), including insecticidal activity (Ribeiro et al., 2008; Anese et al., 2018). However, research on the insecticidal action of *D. brasiliensis* EO against lepidopteran pests and its effect on biochemical markers is lacking. Consequently, this study evaluated the contact toxicity of *D. brasiliensis* EO and its constituents against *S. frugiperda*, as well as its effects on lipid peroxidation (LPO) and on important biotransformation (esterase-α, EST-α; esterase-β, Est-β; glutathione S-transferase, GST), antioxidant (superoxide dismutase, SOD), and neurotransmission (acetylcholinesterase, AChE) enzymes.

## 2. Material and Methods

### 2.1 Plant material collection and essential oil extraction

To obtain *D. brasiliensis* EO, plant material was collected from Bio Estação Gaia in the municipality of Piraquara, Paraná, Brazil (-25.501217 S; -49.001598 W) in April 2022. After herborization and identification, the species was deposited at the Herbarium of the Municipal Botanical Museum in the Botanical Garden of Curitiba, Paraná, under MBM No. 052485. This research was also registered in SISGEN under the number AE4C4BF. Terminal branches with leaves were harvested, and the EO was extracted using the steam drag method in a vat for three hours.

**2.2 Identification of the chemical composition of the essential oil**

Analysis by gas chromatography was performed on a Shimadzu TQ8040 chromatograph coupled with mass spectrometry (GC-MS), utilizing an Rtx-5MS fused silica capillary column (30m x 0.25mm x 0.25μm) with helium as the carrier gas at a flow rate of 1.02 mL/min. The injector temperature remained constant at 250 ºC and the ionization system operated at 70 eV. The sample was injected with a split ratio of 1:90. The temperature of the capillary column was programmed to increase from 60 ºC to 250 ºC at a rate of 3 ºC/min.

The injected sample volume consisted of 1.0 μL of a solution comprising 1.0 μL of EO dissolved in 1 mL of hexane. The EO was identified by retention index calculated and mass spectra comparison with literature (Adams, 2007) and NIST 02 mass library (NIST, Gaithersburg, MD, USA). The retention index was calculated using a homologous series of alkanes (C8 to C19) (Van den Dool and Kratz, 1963).

**2.3 *Spodoptera frugiperda* breeding**

The breeding of *S. frugiperda* was performed in the laboratory, and the insects used in this research were obtained from stock breeding. During the larval phase, the larvae were reared using the methodology proposed by Parra (2001) and fed with an artificial diet according to Marchioro & Foerster (2012). Each larva was housed in a 100 mL plastic container containing approximately 40 mL of diet until it reached the pupal stage. Subsequently, they were transferred to transparent acrylic boxes (Gerbox®) measuring 11 cm in width, 11 cm in length, and 3.5 cm in height. After emergence, adults were housed in polyvinyl chloride (PVC) cages measuring 35 cm in height and 20 cm in diameter, which were closed with voile fabric at the top and lined with bond paper to serve as an oviposition surface for the females.

The adults were fed a 10% honey solution diluted in distilled water, provided in plastic containers with cotton wool soaked in the solution. Sheets of bond paper bearing the egg masses were replaced three times a week, and the egg masses were affixed with adhesive tape to the lids of plastic containers (300 mL) containing approximately 100 mL of artificial diet, ensuring that the newborn caterpillars had access to food. The breeding of *S. frugiperda* was conducted in a climate-controlled chamber, maintained at a temperature of 25 ± 1 ºC, 70 ± 10% RH, and a photophase of 14:10 hours, consistent across all developmental stages of the insect.

## 2.4 Insecticide potential of *D. brasiliensis* essential oil on *S. frugiperda*

Preliminary tests were conducted with *D. brasiliensis* EO at a concentration of 2.5% (v/v), diluted in acetone. Acetone (ALPHA024, 99.5% PA) served as the negative control, whereas the synthetic insecticide chlorfenapyr (Pirate®) at 0.75 L/ha was used as the positive control. The experimental design was completely randomized, with five replicates per treatment, and the experiment was repeated five times.

The methodology was adapted from Eccel et al. (2024) for this bioassay. Ten 3rd-instar larvae were placed in 145 mL plastic containers containing 25 g of artificial diet. Subsequently, 150 µL of the treatments were pipetted onto the diet and the larvae, using a Kasvi basic pipette (20–200 µL). After treatment application, the containers were sealed with voile fabric and placed in an incubator chamber maintained at 25 ± 1 ºC, 70 ± 10% RH, and a photophase of 14:10 hours. Mortality was assessed after 48 hours of exposure; larvae were gently prodded with a brush, and those that did not respond were considered dead.

## 2.5 Toxicity of *D. brasiliensis* essential oil on *S. frugiperda*

To determine the lethal concentrations ($LC_{50}$ and $LC_{90}$), a bioassay was conducted using eight concentrations ranging from 0.65% to 1.7%, diluted in acetone (used as the negative control). The experimental design and methodology were identical to those described in section 2.4.

**2.6 Effect of *D. brasiliensis* essential oil on biochemical markers of *S. frugiperda***

For enzymatic and LPO analysis, the insects were exposed to the $LC_{50}$ and $LC_{90}$ of *D. brasiliensis* EO, and the survivors were frozen at -80°C. Preliminary tests were conducted to ascertain the minimum larval count required to quantify enzymatic activity within the detection limits of the spectrophotometer (Multiskan Sky Thermo Scientific™). Ten pools of four larvae each were evaluated for both treatment and control groups, amounting to 40 caterpillars. Subsequently, the larvae were thawed and homogenized in 620 µL of Milli-Q water.

**2.6.1 Esterases**

The enzymatic activity of EST-α and EST-β was analyzed following the protocol outlined by Valle and Montella (2006). For both, 10 µL of the sample was added (replaced with 10 µL of Milli-Q water for the blank). Subsequently, for EST-α, 200 µL of alpha-naphthyl acetate/naphosphate (0.3 mM) was added, using alpha-naphthol (0.3 $mg.L^{-1}$) as a positive control. Meanwhile, for EST-β, 200 µL of beta-naphthyl acetate/naphosphate (0.3 mM) was added, with beta-naphthol (0.3 $mg.L^{-1}$) used as a positive control. The plates were not incubated; instead, 50 µL of Fast Blue dye (0.3%) was added, followed by a second incubation lasting 5 minutes. Subsequently, an endpoint reading was conducted at a wavelength of 570 nm. The results were expressed as nmol α-naphthol/mg ptn/min for EST-α and nmol beta-naphthol/mg ptn/min for EST-β. A standard curve was generated to convert absorbance values into alpha/beta naphthol content.

For the curve, masses of 0 µg, 1 µg, 2 µg, 3 µg, 4 µg, and 5 µg of alpha/beta naphthol were used, along with volumes of 0 µL, 2 µL, 4 µL, 6 µL, 8 µL, and 10 µL. Milli-Q water was added proportionally to complete the total volume of 10 µL. The curve was conducted in duplicate, and subsequently, the microplates were prepared and read following the same procedure.

**2.6.2 Glutathione S-transferase**

GST activity was analyzed following the protocol of Keen et al. (1976). For this, 15 µL of samples were added (replaced with 15 µL of Milli-Q water for the blank), along with 195 µL of a solution containing reduced glutathione (10 mM GSH) and chlorodinitrobenzene (21mM CDNB). Readings were performed at a wavelength of 340 nm, every minute, for 20 minutes. The results were expressed in µmoles/mg ptn/min.

**2.6.3 Superoxide dismutase**

SOD activity was assessed following the protocol outlined by Gao et al. (1998). First, 40 µL of the sample (with 40 µL of Milli-Q water for the blank) were aliquoted in duplicate into 1.5 mL microcentrifuge tubes. Subsequently, 885 µL of ethylenediamine tetraacetic acid tris buffer (EDTA; pH 8.0; 5 mM) and 50 µL of pyrogallic acid were added. The microtubes were then incubated for 30 minutes, following which 25 µL of HCl (1 N) was added to partially halt the reaction. Microplates for the control treatment underwent the same procedures except for the incubation step, which was absent. Next, 300 µL of the solution was added to the plate in triplicate, and readings were taken at a wavelength of 440 nm. The results were expressed in units (U) of SOD/mg of protein.

**2.6.4 Lipid peroxidation**

LPO was determined following the protocol described by Jiang et al. (1992). Initially, 70 µL of sample and 70 µL of methanol (PA) were combined in 1.5 mL microcentrifuge tubes. Subsequently, the samples were centrifuged at 5000xg for 5 minutes at 4°C. Following centrifugation, 100 µL of the supernatant (with 100 µL of methanol replaced by Milli-Q water for the blank) was transferred to a new microtube. To this, 900 µL of FOX 2 reagent (consisting of a methanolic solution of xylenol orange 0.1 mM and crystalline butylated hydroxytoluene (BHT) 4 mM in methanol PA) and 2500 µL of ferrous ammonium sulfate solution (containing H2SO4 and Milli-Q water) were added. Subsequently, the solution was dispensed into 96 microplate wells in triplicate, with a volume of 300 µL each. Readings were taken at 560 nm, and the results were expressed in nmol of hydroperoxides/mg of protein.

**2.6.5 Acetylcholinesterase**

First, 95 µL aliquots of each sample were separated. AChE enzymatic activity was then analyzed following the protocol outlined by Ellman et al. (1961), with modifications for microplate use by Silva de Assis (1998). Specifically, 25 µL of the samples were added (for the blank, 25 µL of Milli-Q water was substituted), along with 200 µL of 5,5-dithio-bis-2nitro-benzoate (DTNB; 0.75 mM) and 50 µL of iodetoacetylcholine (ATC; 10mM). Immediately after pipetting, the plate was incubated at room temperature and exposed to light for 30 minutes. Readings were taken every 30 seconds for five minutes, with a wavelength of 405 nm. The results were expressed in µmoles/mg ptn/min.

**2.6.6 Protein assay**

The total protein content was determined according to the protocol described by Bradford (1976). To achieve this, 10 µL of the samples, 10 µL of bovine serum albumin (BSA) for the positive control, and 250 µL of Bradford dye (prepared as 1 part of Bradford solution to 5 parts of Milli-Q water) were added. Readings were taken at a wavelength of 620 nm. For constructing the BSA standard curve, a serial dilution was conducted with quantities of 0 µg, 2.5 µg, 5 µg, 7.5 µg, 10 µg, and 15 µg of BSA dissolved in Milli-Q water. The highest concentration consisted of 150 µL of the stock solution (2 mg/ml BSA) mixed with 50 µL of Milli-Q water, while the blank consisted of 200 µL of Milli-Q water. Subsequently, 10 µL of the sample was pipetted in quadruplicate per concentration into a microplate. The absorbance readings followed the same protocol as for total protein measurement.

### 2.5 Statistical analysis

Insect mortality data were modeled using generalized linear models (GLM) with Poisson distribution. The data concerning insecticidal activity and its impact on biochemical markers were analyzed using Gaussian distribution. In both instances, analysis of variance (ANOVA) was conducted, and when statistically significant, Tukey's mean test was applied with a 5% probability of error. Lethal concentration data underwent Probit analysis using the "ecotox" package within the R software (R Core Team, 2021). All statistical analyses were performed in R.

## 3. Results

### 3.1 Chemical composition of *D. brasiliensis* essential oil

Twenty-nine compounds were identified in the *D. brasiliensis* EO sample by GC-MS, totaling 81.31% of its total chemical composition. Our sample has a high concentration of sesquiterpene (60.72%) and monoterpene (17.51%) compounds. The major compounds were α-pinene, germacrene D and bicyclogermacrene, which account for 49.3% of the total chemical composition (Table 1).

**Table 1**: Chemical composition of essential oil from leaves and terminal branches of *Drimys brasiliensis* collected in Piraquara (Paraná, Brazil), analyzed using gas chromatography and mass spectrometry.

| Compounds | RIlit[b] | RIcal[a] | %[c] SD[d] | Classes | Method of Identification |
|---|---|---|---|---|---|
| *α*-pinene | 932 | 934 | 11.38 ±0.04 | Monoterpene | RI, MS[e] |
| sabinene | 969 | 973 | 0.75 ±0.06 | Monoterpene | RI, MS |
| *β*-pinene | 974 | 979 | 3.32 ±0.08 | Monoterpene | RI, MS |
| Myrcene | 988 | 989 | 0.56 ±0.02 | Monoterpene | RI, MS |
| *δ*-3-carene | 1008 | 1010 | 0.31 ±0.04 | Monoterpene | RI, MS |
| *α*-terpineol | 1014 | 1018 | 0.25 ±0.01 | Oxygenated monoterpene | RI, MS |
| *β*-phellandrene | 1025 | 1031 | 0.18 ±0.03 | Monoterpene | RI, MS |

| | | | | | |
|---|---|---|---|---|---|
| γ-terpineol | 1054 | 1058 | 0.31 ±0.02 | Oxygenated monoterpene | RI, MS |
| Terpinolene | 1086 | 1087 | 1.01 ±0.02 | Monoterpene | RI, MS |
| Safrole | 1285 | 1291 | 0.45 ±0.03 | Oxygenated monoterpene | RI, MS |
| *α*-cubebene | 1348 | 1349 | 1.81 ±0.01 | Sesquiterpene | RI, MS |
| *α*-copaene | 1374 | 1378 | 0.59 ±0.02 | Sesquiterpene | RI, MS |
| *β*-bourbonene | 1387 | 1387 | 3.70 ±0.03 | Sesquiterpene | RI, MS |
| *β*-elemene | 1389 | 1391 | 1.53 ±0.02 | Sesquiterpene | RI, MS |
| (E)-caryophyllene | 1417 | 1423 | 2.41 ±0.10 | Sesquiterpene | RI, MS |
| *β*-copaene | 1430 | 1433 | 1.39 ±0.03 | Sesquiterpene | RI, MS |
| Aromadendrene | 1439 | 1442 | 0.42 ±0.01 | Sesquiterpene | RI, MS |
| *α*-humulene | 1452 | 1459 | 0.91 ±0.03 | Sesquiterpene | RI, MS |
| Dauc-5,8-diene | 1471 | 1475 | 0.60 ±0.02 | Sesquiterpene | RI, MS |
| *γ*-muurolene | 1478 | 1478 | 1.93 ±0.07 | Sesquiterpene | RI, MS |
| Germacrene D | 1480 | 1484 | 29.90 ±0.10 | Sesquiterpene | RI, MS |
| *γ*-amorphene | 1495 | 1495 | 1.63 ±0.03 | Sesquiterpene | RI, MS |
| Bicyclogermacrene | 1500 | 1499 | 8.02 ±0.08 | Sesquiterpene | RI, MS |
| *γ*-cadinene | 1513 | 1516 | 1.34 ±0.02 | Sesquiterpene | RI, MS |
| *δ*-cadinene | 1522 | 1521 | 4.29 ±0.10 | Sesquiterpene | RI, MS |
| Zonarene | 1528 | 1526 | 0.25 ±0.04 | Sesquiterpene | RI, MS |
| Spathulenol | 1577 | 1580 | 1.09 ±0.02 | Oxygenated sesquiterpene | RI, MS |
| *Epi*-*α*-muurolol | 1640 | 1647 | 0.53 ±0.07 | Oxygenated sesquiterpene | RI, MS |
| Drimenol | 1766 | 1775 | 0.45 ±0.08 | Oxygenated sesquiterpene | RI, MS |
| Classes of compounds | | | | | |
| Monoterpene | | | | | 17.51 |
| Oxygenated monoterpene | | | | | 1.01 |
| Sesquiterpene | | | | | 60.72 |
| Oxygenated sesquiterpene | | | | | 2.07 |
| Total | | | | | 81.31 |

[a]RIcal Experimental Retention Index. [b]RIlit Literature Retention Index. [c]Concentrations are means of three determinations. [d]Standard deviation. [e]RI: according to values reported in the ADAMS library, and MS: mass spectra aligned to those stored in the ADAMS, NIST 02 libraries.

### 3.2 Insecticide potential of *D. brasiliensis* essential oil on *S. frugiperda*

The mortality of 3rd instar *S. frugiperda* larvae exposed to *D. brasiliensis* EO was 98.6%, exhibiting a statistically significant difference ($\chi 2 = 57.7$; df = 2; $p < 0.05$) compared to the synthetic insecticide, which resulted in 100% mortality, and the control groups, where no mortality was observed.

### 3.3 Assessment of toxicity and estimation of the lethal concentration of *D. brasiliensis* essential oil on *S. frugiperda*

Following 48 hours of exposure, *D. brasiliensis* EO exhibited significant toxicity towards 3rd instar larvae of *S. frugiperda*, with $LC_{50}$ and $LC_{90}$ values of 0.90% and 1.40%, respectively, ($p$ =0.00000740). The mortality rate was 46% for $LC_{50}$ and 92% for $LC_{90}$, and no mortality was observed in the negative control group treated with acetone.

**Table 2:** Toxicity of *Drimys brasiliensis* EO essential oil to *Spodoptera frugiperda* by contact after 48 h of exposure.

| N | $LC_{50}$ (CI 95%) % (v/v) | $LC_{90}$ (CI* 95%) % (v/v) | $\chi^2$ | Slope |
|---|---|---|---|---|
| 2250 | 0.90 (0.79 – 1.71) | 1.40 (1.29 – 1.63) | 33.8 | 6.57 |

*95% CI: Confidence interval (95%).

### 3.4 Effect of *D. brasiliensis* essential oil on biochemical markers

Larvae exposed to the $LC_{90}$ concentration of *D. brasiliensis* EO showed significant alterations in various enzymatic activities following acute exposure compared to the controls groups. There was a significant increase in EST-α and EST-β enzymes compared to the control groups. However, regarding SOD activity, the treatment did not exhibit statistically significant differences from the acetone group (negative control). Both $LC_{50}$ and $LC_{90}$ treatments led to heightened AChE and LPO activities (Figure 1).

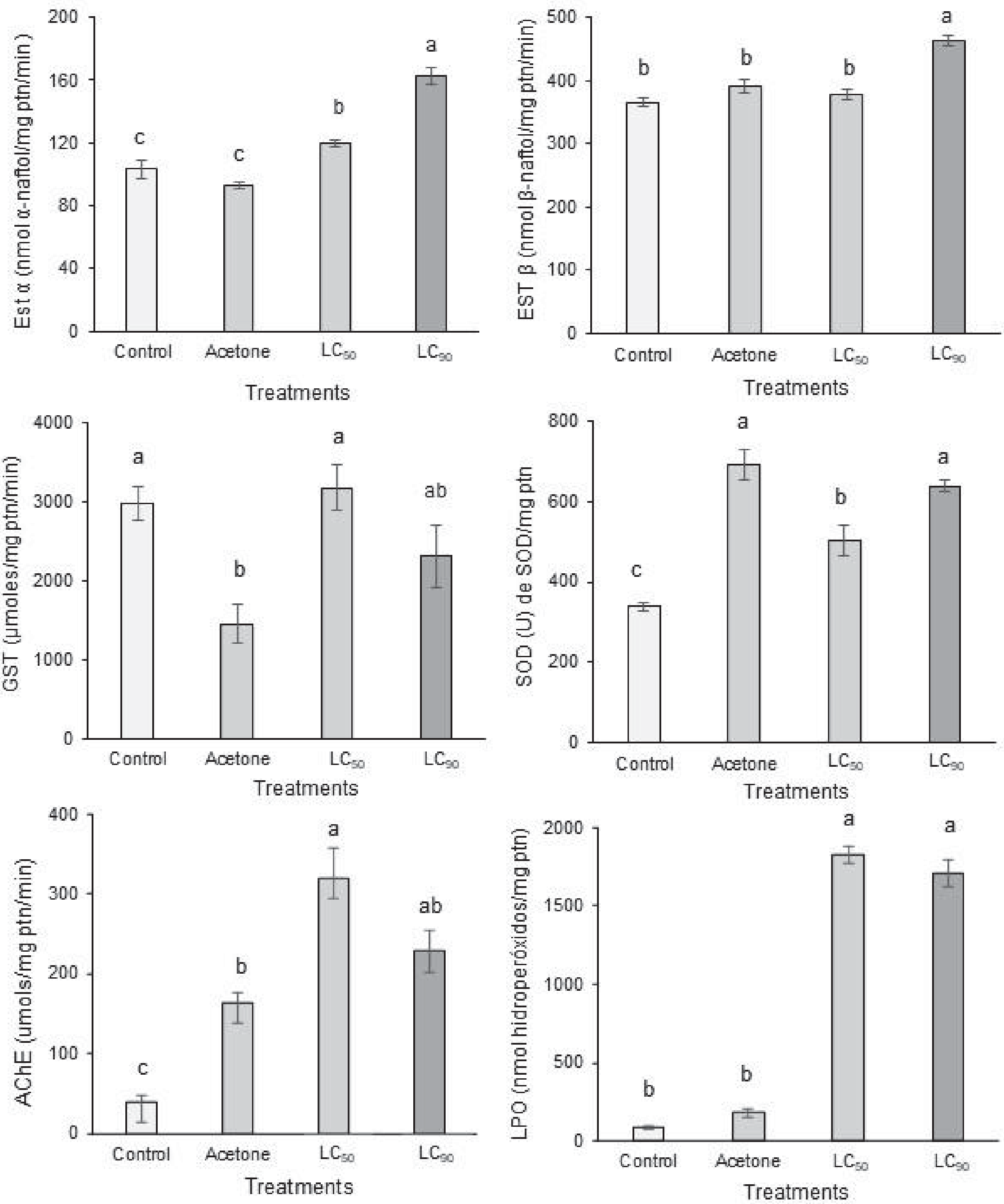


Fig. 2 Effect of control, acetone (negative control), and *Drimys brasiliensis* essential oil on EST-α, EST-β, GST, SOD, LPO, and AChE activities against *Spodoptera frugiperda*. Means sharing the same letter in the bar diagram indicate no significant difference according to One-way ANOVA and Tukey's multiple comparison tests at 5% of probability.

## 4. Discussion

EOs represent one of the most promising natural alternatives as biopesticides for integrated pest management of agricultural pests (Benelli et al., 2020). In this context, our study marks the inaugural investigation into the bioactivity of *D. brasiliensis* EO against *S. frugiperda*.

Our results reveal that the analyzed *D. brasiliensis* EO sample mainly consisted of sesquiterpenes followed by mono and, to a lesser extent, sesquiterpenes and mono oxygenated, respectively, with germacrene D, α-pinene, bicyclogermacrene, δ-cardiene, β-bourbonene, and β-pinene identified as the predominant compounds. However, previous studies have reported quantitative and qualitative variations in the chemical composition of this species by hydrodistillation method, and with distinct major compounds identified in our results. Although, bicyclogermacrene compound was identified in all samples reported in the literature as the majority compound, with proportions similar to those in our study, indicating that this compound could determine a chemotype for this species (Ribeiro et al., 2008; Lago et al., 2010; Gomes et al., 2013; Cruz et al., 2014; Zem et al., 2016; Graf Júnior et al., 2021). The variability observed in the chemical composition of EOs can be attributed to intrinsic and extrinsic factors of the plant. These factors include the plant part used for extraction, seasons of the year in which the plant was collected, extraction methods employed, ecological and geographical conditions of the region, population genetics, and even the plant's sex (Besten et al., 2014; Manfron et al., 2021).

EOs are defined as complex mixtures of highly variable chemical compounds that determine the biological activities of these products (Giunti et al., 2023). The specific array and proportions of these compounds directly influence the bioactivity of EOs, including their insecticidal effects on agricultural pests (Ainane et al., 2020; Abdoul-latif et al., 2020).

We found that *D. brasiliensis* EO induced mortality rates exceeding 80% in *S. frugiperda* 3rd instar larvae, within the standard threshold set by the Brazilian Ministry of Agriculture for registering insecticidal products (Filomeno et al., 2017; Zimmermann et al., 2021). This threshold also serves as a criterion for toxicity assessments. Additionally, other studies have reported similar tick and insecticidal activities for *D. brasiliensis* EO against *Rhipicephalus* (*Boophilus*) *microplus* Canestrini, *Rhipicephalus sanguineus* Latreille (Ribeiro et al., 2008), and *Cryptotermes brevis* Walker (Isoptera: Kalotermitidae) (Gomes et al., 2014). However, the major compounds in those studies differed qualitatively and quantitatively from those identified in our research. The insecticidal activity of other EOs against *S. frugiperda* has already been reported in the literature, demonstrating that these substances are effective in controlling the pest. The mainly botanical families studied that produce EO with insecticidal activity for this insect were Piperaceae, Lamiaceae and Verbenaceae. While the genera *Piper*, *Ocimum*, *Lippia* and *Eucalyptus* showed several species with potential use as contact and ingestion biopesticides to control *S. frugiperda* (Usseglio et al., 2023).

The toxicity of EOs is influenced by several factors, including the chemical composition, concentration, exposure method and duration, the developmental stage of the insect, temperature and the target species (Liao et al., 2017; Pavela and Sedlák, 2018; Benelli et al., 2019; Isman, 2019; Zimmermann et al., 2021; Renoz et al., 2022; Cortez-Vega et al., 2023). The major compounds identified in our EO sample germacrene D, α-pinene, bicyclogermacrene, δ-cardiene, β-bourbonene, and β-pinene have shown insecticidal activity against various pests. These include stored grain pests (Bai et al., 2019; Wang et al., 2019; Tampe et al., 2020; Liu et al., 2021; Zimmermann et al., 2022), different lepidopteran species (Alam et al., 2017; Liao et al., 2017; Vicenço et al., 2021; Santos et al., 2021; Silvestre et al., 2022; Al-Ghanim et al., 2023; Mayanglambam and Rajashekar, 2023), and dipterans of agricultural importance (Kumar et al., 2012; Souza et al., 2021; Al-Ghanim et al., 2023;

Zapata et al., 2010). Therefore, it is necessary to know the chemical composition of essential oils, which is extremely important in order to identify chemotype profiles for a given plant species or assist in the genetic selection of populations to standardize compounds that exhibit bioactivity (Isman, 2019).

Throughout the co-evolutionary process between plants and insects, various botanical species have evolved to synthesize several chemical compounds to counteract insect herbivory (Piri et al., 2020). Conversely, insects have developed enzymes capable of detoxifying these substances (Kiran et al., 2017; Ercan et al., 2022). However, there is a lack of research evaluating the mechanism of action in enzymatic responses of EOs against *S. frugiperda*, which implies the difficulty of formulating these products as biopesticides and including them within pest management (Usseglio et al., 2023). In this study, we observed that *D. brasiliensis* EO influenced biochemical markers, marking the first report of the use of this product on the enzymatic activity of *S. frugiperda*.

Detoxification enzymes play a crucial role in supporting and maintaining the primary physiological processes of insects when confronted with environmental challenges, such as exposure to toxic molecules (Shahriari et al., 2020; Ercan et al., 2022). In this context, ESTs are enzymes linked to the detoxification metabolism, working to hydrolyze ester chains found in synthetic insecticides (Marschall and Jiang, 2011). Our findings indicate that the $LC_{90}$ concentration of *D. brasiliensis* EO increased the activity of EST-α and EST-β, confirming the high toxicity of this EO against *S. frugiperda*.

GSTs are a group of enzymes found in various living organisms that serve dual functions: they aid in detoxification and defend against oxidative stress. These enzymes are part of phase II of biotransformation, and convert potentially toxic substances into smaller, more water-soluble molecules, facilitating their excretion (Marschall and Jiang, 2011; Mojarab-Mahboubkar et al., 2015; Shahriari et al., 2018). Another key enzyme in the defense against oxidative stress is SOD, which neutralizes free radicals and prevents the formation of reactive oxygen species (ROS) (Kiran et al., 2017; Shahriari et al., 2018; Shahriari et al., 2020).

We found no significant difference between treatments concerning the activity of GST and SOD, suggesting that *D. brasil*iensis EO may have led to an increase and accumulation of ROS within the cells, subsequently resulting in heightened LPO activity. ROS accumulation alters cell membrane permeability, potentially leading to their rupture. A consequence of the presence of these ROS and oxidative stress is measured through lipid peroxidation, which alters the permeability of cell membranes and consequently their integrity (Shahriari et al., 2020; Ercan et al., 2022). In the present research, there was a significant difference in the lipoperoxidation of organisms exposed to EO in relation to those exposed to controls.

In addition to causing biochemical damage, EOs can target various sites within the nervous system. We observed that both concentrations of *D. brasiliensis* EO increased AChE activity, indicating its neurotoxic effects on *S. frugiperda*. Research indicates that monoterpenes, a class of compounds commonly found in EOs, primarily affect nerve synapses (Kiran et al., 2017; Shahriari et al., 2020; Abdelgaleil et al., 2021; Gad et al., 2022). These compounds modulate AChE activity, either increasing or inhibiting it, which can lead to symptoms of neurotoxicity such as hyperexcitability, tremors, convulsions, paralysis, and ultimately, death of the insect.

## 5. Conclusion

Since EOs are composed of various chemical compounds, they possess insecticidal activity and hold the potential to replace synthetic insecticides within integrated pest management strategies. We found that *D. brasiliensis* EO exhibits significant potential in controlling *S. frugiperda* due to its toxicity and its effects on different mechanisms related to biotransformation enzymes, nervous system enzymes and in addition to causing damage to biomolecules. Due to its higher toxicity, combined with its diverse chemical composition, *D. brasiliensis* EO can be used as an alternative substance to synthetic insecticides in *S. frugiperda* management programs. However, further research is necessary to develop effective formulations, application methods for field use, and its toxicity on non-target organisms in addition to its effect on human health, with the aim of being used in large-scale systems for more sustainable agricultural models.

**References**

Abdelgaleil SAM, Gad HA, Ramadan GRM, El-Bakry AM, El-Sabrout AM (2021) Monoterpenes: chemistry, insecticidal activity against stored product insects and modes of action—a review. Int. J. Pest Manag. 1–23. https://doi.org/10.1080/09670874.2021.1982067

Abdoul-lafit FM, Ainane A, Abdoul-lafit TM, Ainane T (2020) Chemical study and evaluation of insectical properties of African *Lippia citriodora* essential oil. Journal of Biopesticides 13: 119 – 126.

Adams RP (2007) Identification of Essential Oil Components by Gas Chromatography/ Mass Spectroscopy. 4th ed., Carol Stream: Allured Publishing, 804 p.

Ainane A, Abdoul-lafit FM, Abdoul-lafit TM, Ainane T (2020) Evaluation of biological activities of two essential oils as a safe environmental bioinsecticides: case of *Eucalyptus globulus* and *Rosmarinus officinalis*. Scientific Review – Engineering and Environmental Sciences 29: 544 – 556. https://doi.org/10.22630/PNIKS.2020.29.4.47

Alam SB, Dib MEA, Djabou N, Tabti B, Benyelles NG, Costa J, Muselli A (2017) Essential Oils as Biocides for the Control of Fungal Infections and Devastating Pest (*Tuta absolute*) of Tomato (*Lycopersicon esculentum* Mill.). Chem. Biodiversity 4: e1700065.https://doi.org/10.1002/cbdv.201700065

Al-Ghanim KA, Krishnappa K, Pandiyan J, Nicoletti M, Gurunathan B, Govindarajan M (2023) Insecticidal Potential of *Matricaria* chamomilla's Essential Oil and Its Components (E)-β-Farnesene, Germacrene D, and α-Bisabolol Oxide A against Agricultural Pests, Malaria, and Zika Virus Vectors. Agriculture 13: 779. https://doi.org/10.3390/agriculture13040779

Amaral W, Deschamps C, Bizzo HR, Pinto MAS. Biasi LA, Silva LE (2017) Essential Oil Yield and Composition of Native Tree Species from Atlantic Forest, South of Brazil. J. Essent. Oil-Bear. 20, 1525 – 1535. https://doi.org/10.1080/0972060X.2017.1346484

Anese S, Gambarra WPT, Grisi PU, Gualtieri SCJ (2018) Insecticidal action of *Drimys brasiliensis* Miers on black citrus aphid. Rev. Ciênc. Agron. 49: 484 – 490. https://doi.org/10.5935/1806-6690.20180055

Bai L, Jiao ML, Zang HY, Guo SS, Wang Y, Sang YL, Du SS (2019) Chemical composition of essential oils from four *Rhododendron* species and their repellent activity against three stored-product insects. Environ Sci Pollut Res 26: 23198–23205.https://doi.org/10.1007/s11356-019-05577-1

Barros EM, Torres JB, Bueno AF (2010) Oviposition, development and reproduction of *Spodoptera frugiperda* (JE Smith) (Lepidoptera: Noctuidae) fed on different hosts of economic importance. Neotrop. Entomol. 39:996-1001.

Benelli G, Pavela R, Maggi F, Wandjou JGN, Fofie NGBY, Koné-Bamba D, Sagratini G, Vittori S, Caprioli G (2019) Insecticidal activity of the essential oil and polar extracts from *Ocimum gratissimum* grown in Ivory Coast: Efficacy on insect pests and vectors and impact on non-target species. Ind. Crops Prod. 132: 377-385. https://doi.org/10.1016/j.indcrop.2019.02.047

Benelli G, Pavoni L, Zeni V, Ricciardi R, Cosci F, Cacopardo G, Gendusa S (2020) Developing a Highly Stable *Carlina acaulis* Essential Oil Nanoemulsion for Managing *Lobesia botrana*. Nanomaterials 10: 1867. https://doi.org/10.3390/nano10091867

Besten AM, Nunes DS, Granato D, Sens SL, Wisniewski A, Simionatto EL, Scharf DR (2014) Chemical Composition of Essential Oils from Cladodes and Inflorescences from

Male and Female Specimens of *Baccharis milleflora*. J. Essent. Oil-Bear.17:899–905.https://doi.org/10.1080/0972060X.2014.890078

Bolzan A. Padovez FOE, Nascimento ARB, Kaiser IS et al. (2019) Selection and characterization of the inheritance of resistance of *Spodoptera frugiperda* (Lepidoptera: Noctuidae) to chlorantraniliprole and cross-resistance to other diamide insecticides. Pest Manag. Sci. 75.https://doi.org/10.1002/ps.5376

Borges, LP and Amorim, VA (2020) Secondary Plant Metabolites. Rev. Agrotec. 11: 54 – 67.

Bradford MM (1976) A Rapid and Sensitive Method for the Quantitation of Microgram Quantities of Protein Utilizing the Principle of Protein-Dye Binding. Anal. Biochem. 72: 248-254.

Carvalho RA, Omoto C, Field LM, Williamson MS, Bass C (2013) Investigating the molecular mechanisms of organophosphate and pyrethroid resistance in the fall armyworm, *Spodoptera frugiperda*. PloS One, 8: e62268. https://doi.org/10.1371/journal.pone.0062268

Cortez-Vega A, Jofré-Barud F, Andino N, Gómez MP, López ML (2023) Toxicological interactions between spinosad and essential oils in the Mediterranean fruit fly, *Ceratitis capitata*. J App Entomol 147: 834–842. https://doi.org/10.1111/jen.13175

Cruz I, Figueiredo M, Silva RB, Silva IF, Paula CS, Foster JE (2012) Using sex pheromone traps in the decision-making process for pesticide application against fall armyworm (*Spodoptera frugiperda*) (Smith) (Lepidoptera: Noctuidae) larvae in maize. Int. J. Pest Manag. 58: 83-90. https://doi.org/10.1080/09670874.2012.655702

Cruz BP, Castro EM, Cardoso MG, Souza KF, Machado SMF, Pompeu PV, Fontes MAL (2014) Comparison of leaf anatomy and essential oils from *Drimys brasiliensis* Miers in a montane cloud forest in Itamonte, MG, Brazil. Botanical Studies 55: 41.

Eccel C, Zimmermann RC, Giraldi GT, et al (2024) *Baccharis* essential oils from the Atlantic Forest as sources of natural pesticides. Ind Crops Prod 215:118589. https://doi.org/10.1016/j.indcrop.2024.118589

Ellman GL, Courtney KD, Andres Jr. V, Featherstone RM (1961) A new and rapid colorimetric determination of acetylcholinesterase activity. Biochem. Pharmacol. 7:88–95. https://doi.org/10.1016/0006-2952(61)90145-9

Erb M, Kliebenstein DJ (2020) Plant Secondary Metabolites as Defenses, Regulators, and Primary Metabolites: The Blurreb Functional Trichotomy. Plant Physiol. 184: 39-52. https://doi.org/10.1104/pp.20.00433

Ercan FS, Bas H, Azarkan SY (2022) In silico detection of Cucurbitacin-E on antioxidant enzymes of model organism *Galleria mellonella* L. (Lepidoptera: Pyralidae) and variation of antioxidant enzyme activities and lipid peroxidation in treated larvae. Beni-Suef University Journal of Basic and Applied Sciences, 11, 130. https://doi.org/10.1186/s43088-022-00310-3

Filomeno CA, Barbosa LCA, Teixeira RR, Pinheiro AL, Farias ES, Silva EMP, Picanço MC (2017) *Corymbia* spp. and *Eucalyptus* spp. essential oils have insecticidal activity against *Plutella xylostella*. Ind. Crops Prod. 109:374–383. https://doi.org/10.1016/j.indcrop.2017.08.033

Gad HA, Ramadan GRM, El-Bakry AM, El-Sabrout AM, Abdelgaleil SAM (2022) Monoterpenes: Promising natural products for public health insect control – A review. Int. J. Trop. Insect Sci. 42: 1059 – 1075. https://doi.org/10.1007/s42690-021-00692-4

Gao R, Yuan Z, Zhao Z, Gao X (1998) Mechanism of pyrogallol autoxidation and determination of superoxide dismutase enzyme activity. Bio Electrochem Bioenergy 45: 41–45. https://doi.org/10.1016/S0302-4598(98) 00072-5.

Giunti G, Campolo O, Laudani F, Palmeri V, Spinozzi E, Bonacucina G, Maggi F, et al. (2023) Essential oil-based nanoinsecticides: ecological costs and commercial potential, p. 375 - 441. In: Development and Commercialization of Biopesticides. Elsevier Inc. https://doi.org/10.1016/B978-0-323-95290-3.00002-9

Gomes MRF, Schuh RS, Bemvenuti ALJ, Dorneles GG, Montanha J, Roehe PM, Bordignon S et al. (2013) Biological assessment (antiviral and antioxidant) and acute toxicity of essential oils from *Drimys angustifolia* and *D. brasiliensis*. Brazilian Journal of Pharmacognosy, 23: 284 – 290.

Gomes MRF, Dorneles GG, Schuh RS, Jacques ALB, Bertholdo-Vargas LR, Bordignon SAL, Limberger RP (2014) Chemical composition of essential oils of *Drimys angustifolia* Miers and *Drimys brasiliensis* Miers and their repellency to drywood termite *Cryptotermes brevis* (Isoptera: Kalotermitidae). Journal of Basic and Applied Pharmaceutical Sciences 35: 41 -46.

Graf Júnior AL, Fontoura SB, Andrade GC, Costa JS, Itako AT, Soldi C (2021) Essential oil from cataia leaves (*Drimys brasiliensis*) on the mycelial growth of Alternaria porri. Green Magazine of Agroecology and Sustainable Development 16: 245 – 252.

Heinzmann BM, Spitzer V, Simões CMO (2017). Volatile oils. In: Simões, CMO, Schenkel, EP, Mello, JCP, Mentz, LA & Petrovick, PR Pharmacognosy: from plant to medicine (pp. 167-184). Artmed.

Hummelbrunner LA, Isman MB (2001) Acute, sublethal, antifeedant, and synergistic effects of monoterpenoid essential oil compounds on the tobacco cutworm, *Spodoptera litura* (Lep., Noctuidae). J. Agr. FoodChem. 49: 715 – 720. https://doi.org/10.1021/jf000749t

Isman MB (2019) Commercial development of plant essential oils and their constituents as active ingredients in bioinsecticides. Phytochem Rev. https://doi.org/10.1007/s11101-019-09653-9

Isman MB (2020) Bioinsecticides based on plant essential oils: a short overview. Z. Naturforsch. 72: 179-182. https://doi.org/10.1515/znc-2020-0038

Jiang Z, Hunt JV, Wolff SP (1992) Ferrous ion oxidation in the presence of xylenol orange for detection of lipid hydroperoxide in low density lipoprotein. Anal. Biochem. 202:384–389. https://doi.org/10.1016/0003-2697(92)90122-N

Keen JH, Habig WH, Jakoby WB (1976) Mechanism for the several activities of glutathione. J. Biol. Chem. 251: 6183–6188.

Kenis M, Benelli G, Biondi A, Calatayud PA, Day R, Desneux N, et al. (2023) Invasiveness, biology, ecology, and management of the fall armyworm, *Spodoptera frugiperda*. Entomol. Gen. 43: 187-241. https://doi.org/10.1127/entomologia/2022/1659

Kim J, Kim H, Beuchat LR, Ryu JH (2021) Synergistic antimicrobial activities of plant essential oils against *Listeria monocytogenes* in organic tomato juice. Food Control 125: 108000. https://doi.org/10.1016/j.foodcont.2021.108000

Kiran S, Kujur A, Patel L, Ramalakshmi K, Prakash B (2017) Assessment of toxicity and biochemical mechanisms underlying the insecticidal activity of chemically characterized *Boswellia carterii* essential oil against insect pest of legume seeds. Pestic. Biochem. Physiol. 139: 17 – 23. https://doi.org/10.1016/j.pestbp.2017.04.004

Kumar P, Mishra S, Malik A, Satya S (2012) Compositional analysis and insecticidal activity of *Eucalyptus globulus* (family:Myrtaceae) essential oil against housefly (*Musca domestica*). Acta Trop. 122: 212-218. https://doi.org/10.1016/j.actatropica.2012.01.015

Lago JHG, Carvalho LAC, Silva FS, Toyama DO, Fávero AO, Romoff P (2010) Chemical Composition and Anti- Inflammatory Evaluation of Essential Oils from Leaves and Stem Barks from *Drimys brasiliensis* Miers (Winteraceae). J. Brazil. Chem. Soc. 21: 1760 – 1765. https://doi.org/10.1590/S0103-50532010000900024

Liao M, Xiao JJ, Zhou LJ, Yao X, Tang F, Hua RM, Wu XW, Cao HQ (2017) Chemical composition, insecticidal and biochemical effects of *Melaleuca alternifolia* essential oil on the *Helicoverpa armigera*. J App Entomol 00: 1 - 8. https://doi.org/10.1111/jen.12397

Lira EC, Bolzan A, Nascimento ARB, Amaral FSA, Kanno RH, Kaiser IS, Omoto C (2020) Resistance of *Spodoptera frugiperda* (Lepidoptera:Noctuidae) to spinetoram: inheritance and cross-resistance to spinosad. Pest Manag. Sci. 76: 2674-2680. https://doi.org/10.1002/ps.5812

Liu H, Guo SS, Lu L, Li D, Liang J, Huang ZH, Zhou YM, Zhang WJ, Du S (2021) Essential oil from *Artemisia annua* aerial parts: composition and repellent activity against two storage pests. Nat. Prod. Res. 35: 822-825. https://doi.org/10.1080/14786419.2019.1599887

Manfron J, Raman V, Khan IA, Farago PV (2021) Essential Oils of *Baccharis*: Chemical Composition and Biological Activities. In: Fernandes, GW, Oki, Y., Barbosa, M. (eds) Baccharis. Springer, Cham.https://doi.org/10.1007/978-3-030-83511-8_10

Marchioro CA, Foerster LA (2012) Performance of the Wheat Armyworm, *Pseudaletia sequax* Franclemont, on Natural and Artificial Diets. Neotrop. Entomol. 41: 288-295. https://doi.org/10.1007/s13744-012-0046-8

Marschall HR, Jiang SY (2011) Tourmaline Isotopes: No Element Left Behind. Elements 7, 313 – 319. https://doi.org/10.2113/gselements.7.5.313

Mayanglambam S, Rajashekar Y (2023) Antifeedant effects of crofton weed, *Ageratina adenophora* extracts and their phytochemical compounds against three cabbage insect pest species. Entomologia Experimentalis et Applicata 71: 603 – 610 DOI: 10 .1111/eea.13309

Moscardini VF, Marques LH, Santos AC, Rossetto J, Silva OABN, Rampazzo PE, Castro BA (2020) Efficacy of *Bacillus thuringiensis* (Bt) maize expressing Cry1F, Cry1A.105, Cry2Ab2 and Vip3Aa20 proteins to manage the fall armyworm (Lepidoptera: Noctuidae) in Brazil. Crop Prot. 137: 105269. https://doi.org/10.1016/j.cropro.2020.105269

Mojarab-Mahboubkar M, Sendi JJ, Aliakbar A (2015) Effect of *Artemisia annua* L. essential oil on toxicity, enzyme activities, and energy reserves of cotton bollworm *Helicoverpa armigera* (Hübner) (Lepidoptera: Noctuidae). J. Plant Prot. Res. 55: 371 - 377. https://doi.org/10.1515/jppr-2015-0049

Ninkuu V. Zhang L, Yan J, Fu Z, Yang T, Zeng H (2021) Biochemistry of Terpenes and Recent Advances in Plant Protection. Int. J. Mol. Sci. 22: 5710. https://doi.org/10.3390/ijms22115710

NIST Mass Spectral Library, v11, National Institute of Standards and Technology, Gaithersburg, 2011.

Parra JRP Insect breeding techniques for biological control programs. Piracicaba, ESALQ/FEALQ, 137p. 2001.

Pavela R, Sedlák P (2018) Post-application temperature as a factor influencing the insecticidal activity of essential oil from *Thymus vulgaris*. Ind Crops Prod 113:46–49. https://doi.org/10.1016/j.indcrop.2018.01.021

Piri A, Sahebzadeh N, Zibaee A, Sendi JJ, Shamakhi L, Shahriari M (2020) Toxicity and physiological effects of ajwain (*Carum copticum*, Apiaceae) essential oil and its major constituents against *Tuta absolute* (Meyrick) (Lepidoptera: Gelechiidae). Chemosphere, vol. 256. https://doi.org/10.1016/j.chemosphere.2020.127103

Pogue GM (2002) A world revision of the genus *Spodoptera* Guenée (Lepidoptera: Noctuidae). Memoirs of the American Entomological Society 43:1-202.

Renoz F, Demeter S, Degand H, Nicolis SC, Lebbe O, Martin H, Deneubourg, JL, et al. (2022) The modes of action of *Mentha arvensis* essential oil on the granary weevil *Sitophilus granarius* revealed by a label-free quantitative proteomic analysis. J Pest Sci 95:381–395 https://doi.org/10.1007/s10340-021-01381-4

Ribeiro VLS, Rolim V, Borgignon S, Henriques AT, Dorneles GG, Liemberger RP, Poser G von (2008) Chemical composition and larvicidal properties of the essential oils from *Drimys brasiliensis* Miers (Winteraceae) on the cattle tick *Rhipicephalus (Boophilus) microplus* and the brow dog tick *Rhipicephalus sanguineus*. Parasitol. Res. 102: 531 – 535. https://doi.org/10.1007/s00436-007-0799-x

Santos AA, Dutra KA, Oliveira JV, Wanderley-Teixeira V, Santos G, Navarro DMAF, Lapa-Neto, CJC, et al. (2021). Essential oil toxicity on biological and reproductive parameters of *Alabama argillacea* (Hübner) (Lepidoptera: Erebidae). Acta Histochem. 123: 151714. https://doi.org/10.1016/j.actis.2021.151714

Shahriari M, Zibaee A, Sahebzadeh N, Shamakhi L (2018) Effects of α-pinene, trans-anethole, and thymol as the essential oil constituents on antioxidant system and acetylcholine esterase of *Ephestia kuehniella* Zeller (Lepidoptera: Pyralidae). Pestic. Biochem. Phys. 150: 40 - 47. https://doi.org/10.1016/j.pestbp.2018.06.015

Shahriari M, Zibaee A, Shamakhi L, Sahebzadeh N, Naseri D, Hoda H (2020) Bio-efficacy and physiological effects of *Eucalyptus globulus* and *Allium sativum* essential oils against *Ephestia kuehniella* Zeller (Lepidoptera: Pyralidae). Toxin Rev. 39: 422 – 433. https://doi.org/10.1080/15569543.2018.1554588

Silvestre WP, Vicenço CB, Thomazoni RA, Pauletti GF (2022) Insecticidal activity of *Callistemon speciosus* essential oil on *Anticarsia gemmatalis* and *Spodoptera frugiperda*. Int. J. Trop. Insect Sci 42: 1307–1314. https://doi-org.ez22.periodicos.capes.gov.br/10.1007/s42690-021-00648-8

Souza MT, Souza MT, Bernardi D, Melo DJ, Zarbin PHG, Zawadneak MAC (2021) Insecticidal and oviposition deterrent effects of essential oils of *Baccharis* spp. and histological assessment against *Drosophila suzukii* (Diptera: Drosophilidae). Sci. Rep. 11: 3944. https://doi.org/10.1038/s41598-021-83557-7

Taiz L, Zeiger E (2013) Plant Physiology, trans. Armando Molina Divan Junior, et al. 5 ed. Porto Alegre: Artmed.

Tak JH, Jovel E, Isman MB (2016) Comparative and synergistic activity of *Rosmarinus officinalis* L. essential oil constituents against the larvae and ovarian cell line of the cabbage looper, *Trichoplusia ni* (Lepidoptera: Noctuidae). Pest Manag. Sci. 72: 474 – 480. https://doi.org/10.1002/ps.4010

Tampe J, Espinoza J, Chacón-Fuentes M, Quiroz A, Rubilar M (2020) Evaluation of *Drimys winteri* (Canelo) Essential Oil as Insecticide against *Acanthoscelides obtectus* (Coleoptera: Bruchidae) and *Aegorhinus superciliosus* (Coleoptera: Curculionidae). Insects 11: 335. https://doi.org/10.3390/insects11060335

Usseglio, V.L., Dambolena, J.S., Zunino, M.P., 2023. Can Essential Oils Be a Natural Alternative for the Control of *Spodoptera frugiperda*? A Review of Toxicity Methods and Their Modes of Action. Plants 12. https://doi.org/10.3390/plants12010003

Valle D, Montella IR (2006) Quantification methodology for enzyme activity related to insecticide resistance in *Aedes aegypti*. Brazil. Ministry of Health. Oswaldo Cruz Foundation, 1, 128.

Van den Dool H, Kratz PD (1963) A generalization of the retention index system including linear temperature programmed gas liquid partition chromatography. J. of Chromatogr. 11: 463-471.

Vicenço CB, Silvestre WP, Menegol IR, Carraro MC, Pauletti GF (2021) Insecticidal Activity of *Lavandula dentata* L. Essential Oil on *Anticarsia gemmatalis* (Hübner, 1818). Braz. Arch. Biol. Technol. 64: e21210327.https://doi.org/10.1590/1678-4324-2021210327

Wang Y, Zhang LT, Feng YX, Zhang D, Guo SS, Pang X, Geng ZF, Xi C, Du SS (2019) Comparative evaluation of the chemical composition and bioactivities of essential oils from four spice plants (Lauraceae) against stored- product insects. Ind. Crops Prod. 140: 111640 https://doi.org/10.1016/j.indcrop.2019.111640

Zapata N, Budia F, Vinuela E, Medina P (2010) Bioactivity of essential oils from leaves and bark of *Laurelia sempervirens* and *Drimys winteri* against *Acyrthosiphon pisum*. Pest Manag Sci 66: 1324–1331. https://doi.org/10.1002/ps.2018

Zhang LB, Feng MG (2018) Antioxidant enzymes and their contributions to biological control potential of fungal insect pathogens. Appl. Microbiol. Biotechnol. 102: 4995 – 5004. https://doi.org/10.1007/s00253-018-9033-2

Zem LM, Zuffelato-Ribas KC, Radomski MI, Koehler HS, Deschamps C (2016) *Drimys brasiliensis* essential oil as a source of drimenol. Holos 32: 68 – 76. https://doi.org/10.15628/holos.2016.3192

Zimmermann RC, Aragão CEC, Araújo PJP, Benatto A, Chaaban A, Martins CEN et al. (2021) Insecticide activity and toxicity of essential oils Against two store-products insects. Crop Prot. 144: 105575. https://doi.org/10.1016/j.cropro.2021.105575

# CHAPTER 2: INSECTICIDAL AND TOXICITY ACTIVITIES OF *Elionurus muticus* ESSENTIAL OIL AGAINST *Spodoptera frugiperda*

* These results were submitted in Journal of Applied Entomology

**Abstract**

Several botanical groups produce essential oils (EOs) with different biological activities for agricultural purposes. However, there is a lack of studies on the potential use of *Elionurus* species to control agricultural pests. This study aimed to analyze the insecticidal action and toxicity of *E. muticus* EO against *Spodoptera frugiperda* larvae, as well as its effect on biomarkers and biological processes. The EO was extracted using the steam distillation method in a vat, and its chemical composition was determined using gas chromatography coupled with mass spectrometry (GC-MS). The insecticidal activity of this oil was assessed by the contact method to estimate the lethal concentration (LC) and evaluate the effects on glutathione S-transferase (GST), esterase-α (EST-α), esterase-β (EST-β), superoxide dismutase (SOD), acetylcholinesterase (AChE), and lipid peroxidation (LPO) in third-instar larvae. We found 14 compounds in the EO sample, accounting for 95.93% of its composition; neral and geranial were the major compounds. *E. muticus* EO resulted in 99.3% mortality of *S. frugiperda* larvae at 2.5%, with $LC_{50}$ and $LC_{90}$ values of 1.26% and 2.25%, respectively. Both lethal concentrations caused an increase in LPO, differing from both negative controls. $LC_{90}$ reduced the activity of EST-β and SOD enzyme, while $LC_{50}$ and $LC_{90}$ increased GST, compared to negative control. We conclude that *E. muticus* EO exhibits bioinsecticide activity against *S. frugiperda* with neurotoxic effects and cellular damage, underscoring its potential as a control method in managing this pest.

**Keywords:** Natural Compounds, Chemical Composition, Biopesticide, Biomarkers, Detoxification enzyme

## 1. Introduction

Essential oils (EOs) are characterized as complex mixtures of volatile, lipophilic, generally odorous, and liquid molecules derived from the secondary metabolism of plants. These compounds are produced by different botanical families and display various types of biological properties (Amoabeng et al., 2019; Garay et al., 2020; Kumar et al., 2022). Regarding the purpose of agricultural use, EOs can present insecticidal activity against different pests, with advantages such as low toxicity to non-target organisms, low persistence in field conditions, and minimal risk to the environment, human health, and the selection of resistant individuals (Giunti et al., 2022; Isman, 2020a). In recent years, there has been an increase in the number of research on bioprospecting EO-producing species as potential bioinsecticides for agricultural pest control (Eccel et al., 2024; Isman, 2020b, 2019; Murcia-Meseguer et al., 2018; Stevenson et al., 2020; Yang et al., 2020).

*Elionurus* (Poaceae) plants are distributed on the American and African continents and in Australia. This genus comprises approximately 15 species that produce natural compounds with medicinal properties. However, there are few studies on the potential of *Elionurus* EOs for agronomic purposes (Yedomon et al., 2017).

*Elionurus muticus* (Poaceae) is popularly known as lemongrass; it occurs in high altitude, floodplain, and rocky fields (Chagonda et al., 2000; Füller et al., 2014). This plant is native to Argentina (Celaya et al., 2023) and has a geographic distribution in the southern region of Brazil (Füller et al., 2014). Research points to the diverse biological properties displayed by lemongrass EO, such as antioxidant, antimicrobial, and antifungal activities (Cacciabue et al., 2005; Sabini et al., 2006; Hess et al., 2007), and that is why this species has aroused significant economic interest, especially for the pharmaceutical industry (Füller et al., 2010). However, there is a lack of studies on the potential insecticidal effect of *E. muticus* EO on lepidopterans, which is considered an agricultural pest.

The fall armyworm *Spodoptera frugiperda* (Lepidoptera: Noctuidae) is a pest of great economic importance for several crops, especially maize (*Zea mays*) (Guerrero et al., 2014; Usseglio et al., 2023). The primary tool for its control is the use of synthetic insecticides and genetically modified plants with Bt technology (Bolzan et al. 2019, Lira et al. 2019). However, due to the intensive and inadequate use of these techniques, this insect has become resistant to them (Carvalho et al. 2013, Kenis et al. 2023). Studies demonstrate that EOs have insecticidal activity against *S. frugiperda*, indicating the potential of these substances as promising alternatives to control the pest (de Oliveira et al., 2018; Dutra et al., 2019; Ferreira de Carvalho et al., 2019; Sombra et al., 2020; Usseglio et al., 2023). In this context, the present study evaluated the contact toxicity of *E. muticus* EO against *S. frugiperda*, as well as its impact on biochemical processes, including lipid peroxidation (LPO), key detoxification enzymes (Est-α, Est-β, GST), antioxidant defense systems (SOD), and neurotransmission-related enzyme activity (AChE).

## 2. Material and Methods

### 2.1 Rearing of *Spodoptera frugiperda*

During the larval phase, the larvae were raised according to the methodology proposed by Parra (2001) and fed with an artificial diet by Marchioro and Foerster (2012), supplied in 100 mL plastic containers containing approximately 40 mL of diet. One larva was kept in each container until the pupal stage. They were later transferred to transparent acrylic boxes (Gerbox® 11 cm wide x 11 cm long x 3.5 cm high). After emergence, adults were kept in polyvinyl chloride (PVC) cages (35 cm high x 20 cm diameter), closed with voile fabric at the upper end, and covered with bond paper as an oviposition surface for the females.

The adults were fed with a 10% honey solution diluted in distilled water and supplied in plastic containers containing cotton wool soaked in the solution. The sulfite sheets containing the egg masses were changed three times a week, and the egg masses were fixed with adhesive tape to the lids of plastic containers (300 ml) containing approximately 100 ml of artificial diet so that the newborn larvae had access to food.

**2.2 Collection of plant material and extraction of *E. muticus* essential oil**

In April 2022, plant material was collected at Bio Estação Gaia, in the municipality of Piraquara, Paraná, Brazil (-25.501217 S; - 49.001598 W). EO was extracted from the leaves using the steam drag method in a vat for three hours. After herborization and identification, the species was listed in the Herbarium of the Municipal Botanical Museum, located in the Botanical Garden of Curitiba, Paraná, under the number MBM052485. This research was registered in SISGEN under number AE4C4BF.

**2.3 Identification of the chemical composition of the essential oil**

The phytochemical analysis was performed using a gas chromatograph coupled with mass spectrometry (GC-MS-Shimadzu-2010 Plus, Shimadzu Corporation, Kyoto, Japan). The equipment was operated under Rtx-5MS fused silica capillary column conditions (30m x 0.25mm x 0.25µm) and helium as carrier gas (1.02 $mL.min^{-1}$), an injector temperature of 250º C with flow division of 1:90; the column was programmed at an initial temperature of 60º C, with an increase of 3º $C.min^{-1}$ until reaching 250 ºC. The mass detector was operated in scanning mode and electron impact ionization at 70 eV.

The sample volume injected was 1.0 µL of a solution of 10 µL of EO in 1 mL of hexane. Under the same sample conditions, a series of linear hydrocarbon standards (C8 – C19) were injected. The EO components were identified by comparing the retention indices obtained from the Van den Dool and Krats (1963) equation with the retention indices recorded in the literature (Adams, 2007) and the NIST 02 mass library (NIST, Gaithersburg, MD, USA).

**2.4 Larvicidal activity of *E. muticus* essential oil on *S. frugiperda***

Preliminary tests were conducted with *E. muticus* EO at 2.5% (v:v), diluted in acetone. This solvent (ALPHA024, 99.5% PA) and the synthetic insecticide chlorfenapyr (Pirate®) at 0.75 L/ha were used as negative and positive controls, respectively. The experimental design was completely randomized, with five replicates per treatment, and the experiment was repeated five times.

For this bioassay, the methodology used was adapted from Eccel et al. (2024). Ten third-instar larvae were placed in 145 mL plastic containers containing 25 g of artificial diet. Then, 150 μL of treatments were applied to the larvae. After applying the treatments, the containers were closed with voile fabric and placed in an incubator chamber at 25 ± 1º C, 70 ± 10% relative humidity (RH), and a photophase of 14:10 hours. Mortality was assessed after 48 hours of exposure, and individuals were lightly touched with a brush, and those that did not respond to touch were considered dead.

**2.5 Assessment of the toxicity of *E. muticus* essential oil on *S. frugiperda* larvae**

To determine the lethal concentrations ($LC_{50}$ and $LC_{90}$), a bioassay was carried out covering eight concentrations, with values between 0.65 and 1.7%, diluted in acetone (negative control). The experimental design and methodology adopted were described in topic 2.4.

**2.6 Effect of essential oil on biochemical markers of *S. frugiperda***

For enzymatic and LPO analysis, the insects were exposed to the $LC_{50}$ and $LC_{90}$ of *E. muticus* EO, and the survivors were frozen in a freezer at -80° C. For each treatment and control group, 10 pools of four larvae were evaluated, totaling 40 larvae. The larvae were thawed and homogenized in 620 μL of Milli-Q water.

**2.6.1 Esterases**

The enzymatic activity of EST-α and EST-β was analyzed according to the protocol of Valle and Montella (2006). For both assays, 10 μL of the sample was added (10 μL of

Milli-Q water was used for the blank). For EST-α, 200 μL of α-naphthyl acetate/naphosphate (0.3 mM) was added, with α-naphthol (0.3 $mg.L^{-1}$) serving as the positive control. For EST-β, 200 μL of β-naphthyl acetate/naphosphate (0.3 mM) was added, using β-naphthol (0.3 $mg.L^{-1}$) as the positive control. The plates were not incubated; 50 μL of Fast Blue dye (0.3%) was added, and incubation was carried out for 5 minutes. A reading was then carried out at a wavelength of 570 nm. The results were expressed as nmol α-naphthol/ mg pt/ min for EST-α and nmol β -β-naphthol/ mg pt/ min for EST-β. A standard curve was used to convert absorbance values into α/β naphthol content.

For the standard curve, masses of 0 μg, 1 μg, 2 μg, 3 μg, 4 μg, and 5 μg of α/β naphthol were used. Corresponding volumes of 0 μL, 2 μL, 4 μL, 6 μL, 8 μL, and 10 μL of α/β naphthol were prepared, with Milli-Q water added proportionally to complete a total volume of 10 μL. The curve was prepared in duplicate, following the same procedure for preparing and reading the microplates as described earlier.

### 2.6.2 Glutathione S-transferase

The enzymatic activity of GST was assessed following the protocol by Keen et al. (1976). For each sample,15 μL was added (replaced with 15 μL of Milli-Q water for the blank), along with 195 μL of a solution containing 10 mM of reduced glutathione (GSH) and 21mM of chlorodinitrobenzene (CDNB). The absorbance was measured at 340 nm every minute for 20 minutes.The results were expressed in μmoles/min/mg protein.

### 2.6.3 Superoxide dismutase

SOD activity was measured following the protocol proposed by Gao et al. (1998). For this assay, 40 μL of the sample (blank: 40 μL of Milli-Q water) was aliquoted in duplicate into 1.5 mL microcentrifuge tubes. Next, 885 μL of ethylenediamine tetraacetic acid (EDTA)-tris buffer (5 mM; pH 8.0) and 50 μL of pyrogallic acid were added. The microtubes were incubated for 30 minutes, after which 25 μL of HCl (1 N) was added to partially stop the reaction. Microplates for handling the control were prepared using the same procedure but without the incubation step. Afterward, 300 µL of the solution was added to the microplates in triplicate, and absorbance was measured at 440 nm. The results were expressed in units (U) of SOD/ mg of protein.

**2.6.4 Lipid peroxidation**

LPO was determined using the protocol of Jiang et al. (1992). Initially, 70 µL of sample and 70 µL of methanol (PA) were combined in 1.5 mL microcentrifuge tubes. Subsequently, the samples were centrifuged at 5000xg for 5 minutes at 4°C. Following centrifugation, 100 µL of the supernatant (with 100 µL of methanol replaced by Milli-Q water for the blank) was transferred to a new microtube. To this, 900 µL of FOX 2 reagent (consisting of a methanolic solution of xylenol orange 0.1 mM and crystalline butylated hydroxytoluene (BHT) 4 mM in methanol PA) and 2500 µL of ferrous ammonium sulfate solution (containing H2SO4 and Milli-Q water) were added The solution was then transferred to 96-well microplates in triplicate, with 300 µL per well. Absorbance was measured at 560 nm, and the results were expressed in nmol of hydroperoxides/mg of protein.

**2.6.5 Acetylcholinesterase**

To measure AChE activity, 95 µL aliquots of each sample were previously separated, and AChE enzymatic activity was assessed following the protocol of Ellman et al. (1961), as modified for microplates by Silva de Assis (1998). For each sample, 25 µL was added (with 25 µL of Milli-Q water for the blank), along with 200 µL of 5,5-dithio-bis-2nitro-benzoate (DTNB; 0.75 mM) and 50 µL of iodetoacetylcholine (ATC; 10mM). Immediately after pipetting, the plate was incubated at room temperature under light for 30 minutes. Absorbance was measured every 30 seconds for 5 minutes at a wavelength of 405 nm. The results were expressed in µmoles/min/mg protein.

**2.6.6 Protein assay**

Total protein content was determined following the Bradford method (Bradford, 1976). For each sample, 10 µL was added, along with 10 µL of bovine serum albumin (BSA) as the positive control and 250 µL of Bradford reagent (diluted 1:5 with Milli-Q water). Absorbance was measured at 620 nm. A BSA standard curve was created using serial dilutions of 0 µg, 2.5 µg, 5 µg, 7.5 µg, 10 µg, and 15 µg of BSA in Milli-Q water. The highest concentration was prepared by mixing 150 µL of the stock solution (2 mg/ml BSA) with 50 µL of Milli-Q water, and the blank consisted of 200 µL of Milli-Q water. For each concentration, 10 µL of the sample was pipetted in quadruplicate into a microplate. Absorbance readings were performed using the same protocol as for total protein.

### 2.7 Statistical analysis

Insect mortality data were analyzed using generalized linear models (GLM) with a Poisson distribution. For the data on insecticidal activity and biochemical markers, a Gaussian distribution was applied. An analysis of variance (ANOVA) was conducted for these datasets. Tukey's mean test was used for post-hoc comparisons where significant differences were found, with a significance level set at 5% probability. Lethal concentration data were subjected to the Probit analysis using the "ecotox" package in the R software (R Core Team, 2021).

## 3. Results

### 3.1 Chemical composition of *E. muticus* essential oil

Fourteen compounds were identified in the *E. muticus* EO sample, accounting for 95.93% of its total chemical composition. The EO exhibited a predominance of monoterpenes, constituting 89.36% of the composition. Among these, neral and geranial were the major compounds, comprising 79.95% of the total composition (Table 1).

Table 1. Chemical composition of the essential oil from *Elionurus muticus* leaves collected in Piraquara (Paraná, Brazil) using gas chromatography coupled with mass spectrometry.

| Compounds | R lita | R calb | ±SD | % | Classes |
|---|---|---|---|---|---|
| Myrcene | 988 | 989 | 0.05 | 0.65 | |
| p-Cymene | 1020 | 1025 | 0.02 | 0.23 | |
| (Z)-β-Ocimene | 1032 | 1035 | 0.01 | 2.27 | Monoterpenes |
| (E)-β-Ocimene | 1044 | 1046 | 0.03 | 1.72 | |
| γ-Terpinene | 1054 | 1058 | 0.01 | 0.10 | |
| Linalool | 1095 | 1100 | 0.01 | 1.58 | |
| Exo-Isocitral | 1144 | 1143 | 0.02 | 0.29 | |
| (Z)-Isocitral | 1160 | 1161 | 0.03 | 0.87 | |
| (E)-Isocitral | 1177 | 1180 | 0.04 | 1.61 | Oxygenated monoterpenes |
| Neral | 1235 | 1238 | 0.08 | 24.92 | |
| Geraniol | 1249 | 1251 | 0.04 | 0.19 | |
| Geranial | 1264 | 1269 | 0.02 | 54.93 | |
| Isoledene | 1374 | 1372 | 0.02 | 4.13 | Sesquiterpene |
| Geranyl acetate | 1379 | 1377 | 0.09 | 2.44 | Oxygenated sesquiterpenes |
| Monoterpenes | | | | 4.97 | |
| Oxygenated monoterpenes | | | | 84.39 | |
| Sesquiterpenes | | | | 4.13 | |
| Oxygenated sesquiterpenes | | | | 2.44 | |
| Total | | | | 95.93 | |

[a]RI lit: Literature Retention Index. [b]RI cal: Experimental Retention Index. [c]Standard deviation.

[d]Concentrations are means of three determinations.

## 3.2 Insecticidal activity

The mortality rate of *S. frugiperda* third-instar larvae exposed to *E. muticus* EO was 99.3%. This result showed a statistically significant difference compared to the synthetic insecticide ($\chi 2 = 24.7$; df = 3; $p < 0.01$). No mortality was observed in the control groups.

## 3.3 Assessment of toxicity and estimation of the lethal concentration of the essential oil on *S. frugiperda*

After 48 hours of exposure, *E. muticus* EO showed high toxicity to third-instar larvae of *S. frugiperda*, with values $LC_{50}$ and $LC_{90}$ of 1.26% and 2.25%, respectively, and a slope of 5.11 ($\chi2 = 31.5$; $p = 0.0000203$). No mortality was observed in the negative control (acetone).

**3.4 Effect of essential oil on biochemical markers**

There was variation in the effect of *E. muticus* EO concentrations and controls on biochemical markers of *S. frugiperda* larvae, except for EST-α. Both lethal concentrations increased LPO compared to the negative controls. $LC_{90}$ reduced the activity of ES-β and SOD enzymes relative to the negative control, while GST activity increased for both $LC_{50}$ and $LC_{90}$ compared to the negative control.

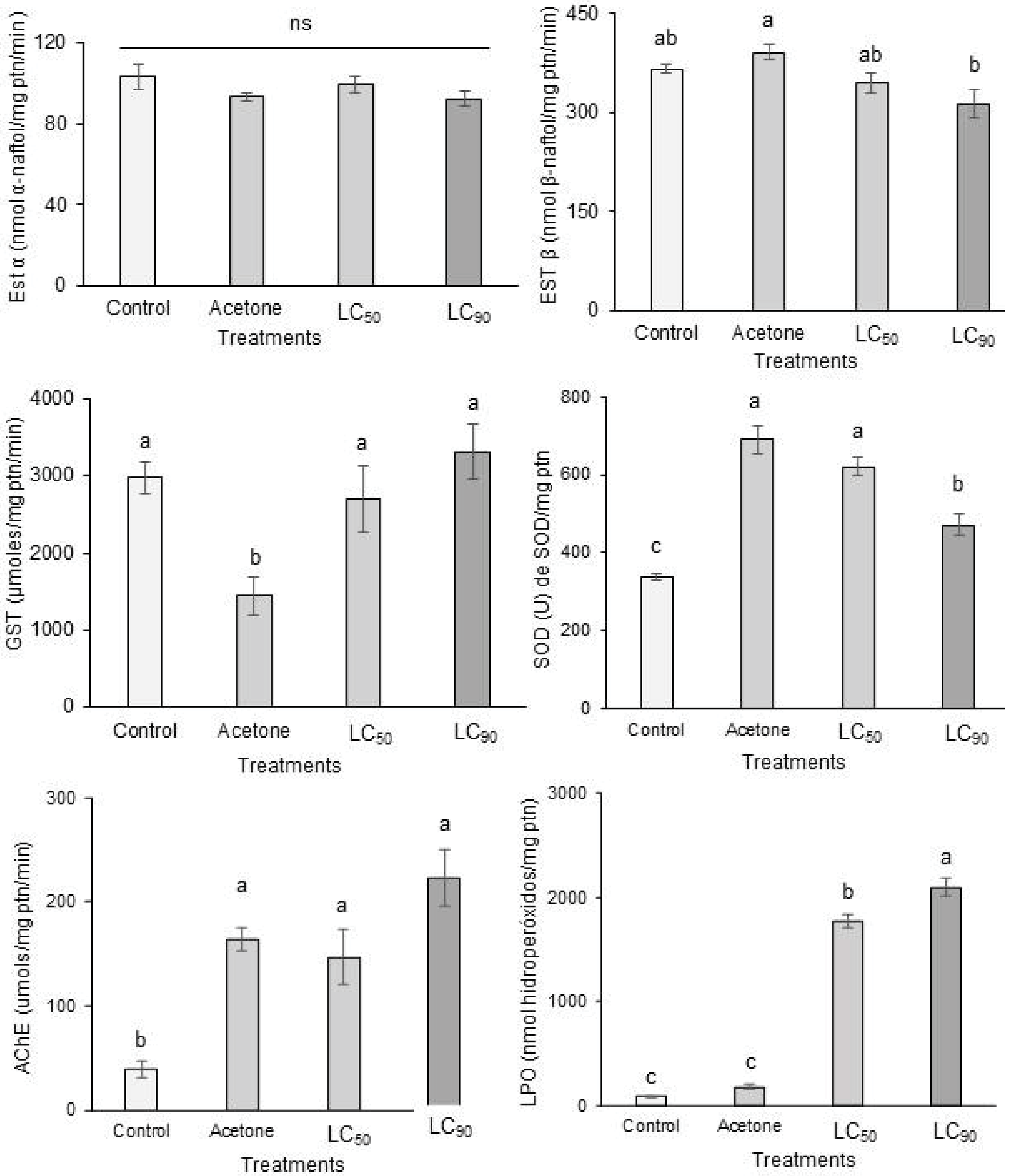


Figure 1: Effect of control (acetone as negative control) and *Elionurus muticus* essential oil on EST-α, EST-β, GST, SOD, LPO, and AChE against *Spodoptera frugiperda*. Means followed by the same letter in the bar diagram are not significantly different according to ANOVA and Tukey’s multiple comparison tests.

## 4. Discussion

Throughout their evolutionary history, plants have developed the ability to synthesize EOs as a defense mechanism against various abiotic and biotic stresses. EOs are typically composed of diverse chemical compounds, predominantly monoterpenes and sesquiterpenes (Crescente et al., 2023).

We found that the EO sample of *E. muticus* primarily consisted of geranial and neral, which together accounted for almost the entire chemical composition. Similar results were observed with samples collected in other countries (Chagonda et al., 2000; Stefanazzi et al., 2011) and in Rio Grande do Sul, Brazil (Füller et al., 2014). Notably, Chagonda et al. (2000) reported that neral and geranial were the predominant compounds in both wild and cultivated populations of *E. muticus*. However, other research has shown that EO compositions can vary significantly in quantity and quality depending on the region and plant parts used (Celaya et al., 2023; Füller et al., 2017).

The variations in chemical composition observed in the EO of the same species can be attributed to several factors related to the interaction of the specific population with intrinsic and extrinsic elements. Key factors influencing these differences include the extraction method and time, the plant part used, the stage of phenological development, population genetics (which helps identify chemotypes), geographic location, and the relationship with edaphoclimatic conditions. Additionally, interactions with abiotic and biotics can influence the secondary metabolic pathways involved in the synthesis of these compounds (Celaya et al., 2023; Crescente et al., 2023; Faria et al., 2023; Füller et al., 2014).

Among the various chemical groups that combat herbivory caused by insects, EOs are known for their insecticidal activity. They can act as fumigants, contact insecticides, or repellents against pests of agricultural interest, including *Spodoptera* species. In this regard, this is the first report of the insecticidal activity of *E. muticus* against *S. frugiperda*.

We observed that *E. muticus* EO caused a high mortality rate in third-instar larvae of *S. frugiperda* by the contact method. To date, there is only one report on the insecticidal activity of *E. muticus* EO, which evaluated its toxicity via fumigation, contact, and repellency methods against *Tribolium castaneum* (Coleoptera: Tenebrionidae) and *Sitophilus oryzae* (Coleoptera: Curculionidae) (Stefanazzi et al., 2011). The authors identified geranial and neral as the major compounds in the EO.

The insecticidal activity of *E. muticus* EO may be attributed to the presence and proportion of geranial and neral in its chemical composition. Monoterpenes have demonstrated insecticidal effects against various agricultural pests, primarily exerting neurotoxic action by inhibiting enzymes responsible for synapses. Notably, the insecticidal properties of these isolated compounds have also been reported for other insects (Aungtikun et al., 2021; Jang et al., 2017; Kim et al., 2013; Moungthipmalai and Soonwera, 2023; Reis et al., 2016; Yeom et al., 2015).

The toxicity of *E. muticus* EO against *S. frugiperda* observed in the present study may be associated with the type of interaction between the major and minor compounds in its chemical composition. Generally, EO compounds have synergistic effects, where minor compounds enhance or potentiate the toxic effects of the major compounds, leading to increased mortality rates (Aungtikun et al., 2021; Moungthipmalai and Soonwera, 2023).

EOs, composed of diverse compounds and chemical groups, exert insecticidal activity on various systems. They can impact the nervous or muscular system and also influence the endocrine system (Abdelgaleil et al., 2021; Aungtikun et al., 2021; Liu et al., 2022; Renoz et al., 2022). In this context, our study marks a significant milestone as the first to explore the effect and toxicity of *E. muticus* EO on the biochemical parameters of insects.

Due to co-evolutionary processes with plants, insects have developed various enzymes with detoxifying activities to counteract allelochemical substances produced by them (Julio et al., 2017; Shahriari et al., 2020). Esterases and GST are keys in the metabolic biotransformation process of organic substances: esterases are involved in Phase I reactions, while GST is responsible for Phase II reactions. Chemical compounds such as drugs and toxins are transformed by hydrolysis and conjugation into molecules different from those originally present in the body, making them less toxic and soluble in water for excretion. These enzymes are among those responsible for detoxifying insecticides and are associated with insect resistance to synthetic insecticides, in addition to mitigating oxidative stress in cells (Hu et al., 2019; Mojarab-Mahboubkar et al., 2015; Piri et al., 2020; Shahriari et al., 2020).

Our results showed that *E. muticus* EO inhibited EST- β activity at $LC_{90}$ and increased GST activity at both $LC_{90}$ and $LC_{50}$ compared to the negative control. Similar findings have been observed with various EOs in other Lepidoptera species, such as *Tuta absoluta* (Gelechiidae) (Piri et al., 2020), *Helicoverpa armigera* (Noctuidae) (Mojarab-Mahboubkar et al., 2015), and *Ephestia kuehniella* (Pyralidae) (Shahriari et al., 2020). The bioactivity of *E. muticus* EO on esterases and GST may linked to its monoterpene content, which has an inhibitory effect on the synthesis of detoxifying enzymes (Liu et al., 2022). For instance, Jang et al. (2017) demonstrated that neral and geranial affected the synthesis or activity of this enzyme in *Drosophila suzukii* (Diptera: Drosophilidae), impairing their function during acute intoxication.

In addition to affecting detoxification enzymes, our findings indicated that *E. muticus* EO caused changes in LPO in *S. frugiperda* larvae. Increased LPO activity suggests an increase and accumulation of reactive oxygen species (ROS), which can damage fatty acid chains in cell membranes, resulting in the degradation of the plasma membrane and, consequently, in the rupture of the cell, leading to the leakage of cellular contents (Ercan et al., 2022; Olmedo et al., 2015; Shahriari et al., 2020). Similar results have been observed in *E.*

*kuehniella* (Shahriari et al., 2020) and *T. castaneum* (Olmedo et al., 2015) after exposure to different EOs and monoterpenes.

SOD is a key antioxidant enzyme that combats oxidative stress in insect tissues, maintaining cellular homeostasis by preventing the accumulation of free radicals and ROS (Chaudhari et al., 2021; Pan et al., 2022; Shahriari et al., 2020, 2018; Upadhyay et al., 2019). We found that both concentrations of *E. muticus* EO led to increased SOD activity in *S. frugiperda* larvae, suggesting oxidative stress and ROS accumulation. Similar effects of different EOs on SOD activity have been reported for *D. suzukii* (Pan et al., 2022), *E. kuehniella* (Shahriari et al., 2020, 2018), *T. castaneum* (Upadhyay et al., 2019), *S. oryzaeI,* and *Oryzaephilus surinamensis* (Coleoptera: Silvanidae) (Kiran and Prakash, 2015), with different results in enzymatic activity.

AChE is one of the main enzymes acting in the synaptic cleft and is a primary target for insecticides, as it causes high mortality rates in a short period (Giunti et al., 2023; Piri et al., 2020; Usseglio et al., 2023). We found that *E. muticus* EO caused increased (although not significant) AChE activity in *S. frugiperda* compared to the negative control. AChE acts in the transmission of insect nerve impulses by causing the hydrolysis of acetylcholine, which is one of the main neurotransmitters. This leads to the interruption of the transmission process and ensures the intermittency of nerve impulses. Disruption of AChE activity can cause neurotoxicity, leading to hyperexcitability, tremors, convulsions, and death of the insect (Hu et al., 2019; Piri et al., 2020; Shahriari et al., 2018; Sombra et al., 2020). The observed effects on AChE may be associated with the neral and geranial compounds in *E. muticus* EO, similar to findings in *D. suzukii* (Jang et al., 2017).

## 5. Conclusion

EOs offer a promising alternative to synthetic insecticides for controlling agricultural pests, aligning with the demand for organic production. The EO of *E. muticus* demonstrates a diverse chemical composition and presents high toxicity against *S. frugiperda*, with various mechanisms of action. However, further studies are needed to explore formulation technologies and field applications to optimize pest control using this EO.

**References**

Abdelgaleil, S.A.M., Gad, H.A., Ramadan, G.R.M., El-Bakry, A.M., El-Sabrout, A.M., 2021. Monoterpenes: chemistry, insecticidal activity against stored product insects and modes of action—a review. Int. J. Pest Manag. https://doi.org/10.1080/09670874.2021.1982067

Adams, R. P. 2007. Identification of essential oil components by gas chromatography/ mass spectrometry, 4th Edition.

Amoabeng, B.W., Johnson, A.C., Gurr, G.M., 2019. Natural enemy enhancement and botanical insecticide source: a review of dual use companion plants. Appl. Entomol. Zool. https://doi.org/10.1007/s13355-018-00602-0

Aungtikun, J., Soonwera, M., Sittichok, S., 2021. Insecticidal synergy of essential oils from *Cymbopogon citratus* (Stapf.), *Myristica fragrans* (Houtt.), and *Illicium verum* Hook. f. and their major active constituents. Ind. Crops Prod. 164, 113386. https://doi.org/10.1016/j.indcrop.2021.113386

Bolzan A., Padovez, F. O. E., Nascimento, A. R. B., Kaiser, I. S., Lira, E. C., Amaral, F. S. A., Kanno, R. H., Malaquias, J. B., Omoto, C., 2019. Selection and characterization of the inheritance of resistance of *Spodoptera frugiperda* (Lepidoptera: Noctuidae) to chlorantraniliprole and cross-resistance to Other diamide insecticides. Pest Manag. Sci. 75. https://doi.org/10.1002/ps.5376

Bradford, M. M., 1976. A Rapid and Sensitive Method for the Quantitation of Microgram Quantities of Protein Utilizing the Principle of Protein-Dye Binding. Anal. Biochem. 72: 248-254.

Cacciabue, M. et al., 2005. *Elionurus muticus* from north of Argentina: evaluation of the antibacterial activity of three essencial oil chemotypes. Biocell, v.29, n.2, p.223.

Carvalho, R. A., Omoto, C., Field, L. M., Williamson, M. S., Bass, C., 2013. Investigating the molecular mechanisms of organophosphate and pyrethroid resistance in the fall armyworm, *Spodoptera frugiperda*. PloS One, 8: e62268. https://doi.org/10.1371/journal.pone.0062268

Celaya, L.S., Le Vraux, M.A., Heit, C. I., Viturro, C.I., Martina, P. F., 2023. Phytochemical and Biological Profile of Essential Oils of *Elionurus muticus* (Spreng.) Growing in Northeastern Argentina. Chem. Biodiversity 20, e202201105. doi: https://doi.org/10.1002/cbdv.202201105

Chagonda, L.S., Makanda, C., Chalchat, J.C., 2000. The essential oils of wild and cultivated *Cymbopogon validus* (Stapf) Stapf ex Burtt Davy and *Elionurus muticus* (Spreng.) Kunth from Zimbabwe. Flavour Fragr. J. 15, 100–104. https://doi.org/10.1002/(SICI)1099-1026(200003/04)15:2<100::AID-FFJ874>3.0.CO;2-Y

Chaudhari, A.K., Singh, V.K., Kedia, A., Das, S., Dubey, N.K., 2021. Essential oils and their bioactive compounds as eco-friendly novel green pesticides for management of storage insect pests: prospects and retrospects. Environ. Sci. Pollut. Res. 28, 18918–18940. https://doi.org/10.1007/s11356-021-12841-w

Colpo, J. F., Jahnke, S.M., Füller, T., 2014. Potencial inseticida de óleos de origem vegetal sobre *Grapholita molesta* (Busck) (Lepidoptera: Tortricidae). Rev. Bras. Pl. Med., Campinas, 16(2), 182-188.

Crescente, G., Bouymajane, A., Cascone, G., Squillaci, G., Morana, A., Moccia, S., 2023. Essential Oils: An Overview of Extraction Methods and Food Applications. Curr. Nutraceuticals 4. https://doi.org/10.2174/2665978604666230601104713

de Oliveira, E.R., Alves, D.S., Carvalho, G.A., de Oliveira, B.M.R.G., Aazza, S., Bertolucci, S.K.V., 2018. Toxicity of *Cymbopogon flexuosus* essential oil and citral for *Spodoptera* *frugiperda*. Cienc. e Agrotecnologia 42, 408–419. https://doi.org/10.1590/1413-70542018424013918

Dutra, K.A., Wanderley Teixeira, V., Cruz, G.S., Silva, C.T.S., D´Assunção, C.G., Ferreira, C.G.M., Monteiro, A.L.B., Agra Neto, A.C., Lapa Neto, C.J.C., Teixeira, A.A.C., Navarro, D.M.A.F., 2019. Morphological and immunohistochemical study of the midgut and fat body of *Spodoptera frugiperda* (J.E. Smith) (Lepidoptera: noctuidae) treated with essential oils of the genus *Piper*. Biotech. Histochem. 94, 498–513. https://doi.org/10.1080/10520295.2019.1599144

Eccel, C., Zimmermann, R.C., Giraldi, G.T., Foerster, L.A., de Bitencourt Frasson, V., Chaaban, A., do Amaral, W., Sales Maia, B.H.L.N., Dos Santos, E.F., Poitevin, C.G., Martins, C.E.N., 2024. *Baccharis* essential oils from the Atlantic Forest as sources of natural pesticides. Ind. Crops Prod. 215, 118589. https://doi.org/10.1016/j.indcrop.2024.118589

Ercan, F.S., Baş, H., Azarkan, S.Y., 2022. In silico detection of Cucurbitacin-E on antioxidant enzymes of model organism *Galleria mellonella* L. (Lepidoptera: Pyralidae) and variation of antioxidant enzyme activities and lipid peroxidation in treated larvae. Beni-Suef Univ. J. Basic Appl. Sci. 11. https://doi.org/10.1186/s43088-022-00310-3

Ellman, G. L., Courtney, K. D., Andres Jr., V., Featherstone, R. M., 1961. A new and rapid colorimetric determination of acetylcholinesterase activity. Biochem. Pharmacol. 7: 88–95. https://doi.org/10.1016/0006-2952(61)90145-9

Faria, R.D., Cabral, I.R., dos Santos Oliveira, T.A., Thiesen, L.V., Rakes, M., Nesi, C.N., Raetano, C.G., da Glória, E.M., Crotti, A.E.M., do Prado Ribeiro, L., 2023. Essential oils from *Cordia verbenacea* and *Elionurus latiflorus* and their binary mixture: Bioactivity against the Mexican bean weevil and an aflatoxin-producing fungal species. Ind. Crops Prod. 206. https://doi.org/10.1016/j.indcrop.2023.117674

Ferreira de Carvalho, G.H., Lucília dos Santos, M., Monnerat, R., Aparecida Andrade, M., Gonçalves de Andrade, M., Barbosa dos Santos, A., Marques Dourado Bastos, I., de Santana, J.M., 2019. Ovicidal and Deleterious Effects of Cashew (*Anacardium occidentale*) Nut Shell Oil and Its Fractions on *Musca domestica*, *Chrysomya megacephala*, *Anticarsia gemmatalis* and *Spodoptera frugiperda*. Chem. Biodivers. 16. https://doi.org/10.1002/cbdv.201800468

Füller, T.N., Bertrand, C., Antonello, B., Wesp, C., de Barros, I.B.I., Barbosa Neto, J.F., 2017. Chemical diversity of wild populations of *Elionurus muticus* (Spreng.) and the allelopathic effect of its essential oil. J. Essent. Oil Res. 29, 499–506. https://doi.org/10.1080/10412905.2017.1313786

Füller, T.N., Bertrand, C., Simon, A., de Barros, I.B.I., Neto, J.F.B., 2014. *Elionurus muticus* as an alternative source of citral from pampa biome, Brazil. J. Oleo Sci. 63, 1109–1116. https://doi.org/10.5650/jos.ess13234

Füller, T.N., Tessele, C., Barros, I.B.I., Barbosa Neto, J.F., 2010. Phenotypical, phytochemical and molecular characterization of “capim-carona” [*Elionurus muticus* (Spreng.) Kuntze] populations. Rev. Bras. Plantas Med. 12, 261–268. https://doi.org/10.1590/S1516-05722010000300003

Gao, R., Yuan, Z., Zhao, Z., Gao, X., 1998. Mechanism of pyrogallol autoxidation and determination of superoxide dismutase enzyme activity. Bio Electrochem Bioenergy 45: 41– 45. https://doi.org/10.1016/S0302-4598(98) 00072-5.

Garay, J., Brennan, T., Bon, D., 2020. Review: Essential Oils A Viable Pest Control Alternative. Int. J. Ecotoxicol. Ecobiol. 5, 13. https://doi.org/10.11648/j.ijee.20200502.11

Giunti, G., Campolo, O., Laudani, F., Palmeri, V., Spinozzi, E., Bonacucina, G., Maggi, F., Pavela, R., Canale, A., Lucchi, A., Benelli, G., 2023. Essential oil-based nanoinsecticides, in: Development and Commercialization of Biopesticides. Elsevier, pp. 375–402. https://doi.org/10.1016/B978-0-323-95290-3.00002-9

Guerrero, A., Malo, E.A., Coll, J., Quero, C., 2014. Semiochemical and natural product-based approaches to control Spodoptera spp. (Lepidoptera: Noctuidae). J. Pest Sci. (2004). 87, 231–247. https://doi.org/10.1007/s10340-013-0533-7

Hess, S.C. et al. Evaluation of seasonal changes in chemical composition and antibacterial activity of *Elyonurus muticus* (Sprengel) O. Kuntze (Gramineae). Química Nova, v.30, n.2, p.370-3, 2007.

Hu, J., Wang, W., Dai, J., Zhu, L., 2019. Chemical composition and biological activity against *Tribolium castaneum* (Coleoptera: Tenebrionidae) of *Artemisia brachyloba* essential oil. Ind. Crops Prod. 128, 29–37. https://doi.org/10.1016/j.indcrop.2018.10.076

Isman, M.B., 2020a. Botanical insecticides in the twenty-first century-fulfilling their promise? Annu. Rev. Entomol. 65, 233–249. https://doi.org/10.1146/annurev-ento-011019-025010

Isman, M.B., 2020b. Bioinsecticides based on plant essential oils: A short overview. Zeitschrift fur Naturforsch. - Sect. C J. Biosci. 75, 179–182. https://doi.org/10.1515/znc-2020-0038

Isman, M.B., 2019. Commercial development of plant essential oils and their constituents as active ingredients in bioinsecticides. Phytochem. Rev. 9. https://doi.org/10.1007/s11101-019-09653-9

Jang, M., Kim, J., Yoon, K.A., Lee, S.H., Park, C.G., 2017. Biological activity of Myrtaceae plant essential oils and their major components against Drosophila suzukii (Diptera: Drosophilidae). Pest Manag. Sci. 73, 404–409. https://doi.org/10.1002/ps.4430

Jiang, Z., Hunt, J. V., Wolff, S. P., 1992. Ferrous ion oxidation in the presence of xylenol orange for detection of lipid hydroperoxide in low density lipoprotein. Anal. Biochem. 202: 384–389. https://doi.org/10.1016/0003-2697(92)90122-N

Julio, A.H.F., Gigliolli, A.A.S., Cardoso, K.A.K., Drosdoski, S.D., Kulza, R.A., Seixas, F.A.V., Ruvolo-Takasusuki, M.C.C., de Souza, C.G.M., Lapenta, A.S., 2017. Multiple resistance to pirimiphos-methyl and bifenthrin in Tribolium castaneum involves the activity of lipases, esterases, and laccase2. Comp. Biochem. Physiol. Part C Toxicol. Pharmacol. 195, 27–43. https://doi.org/10.1016/j.cbpc.2017.01.011

Keen, J. H., Habig, W. H., Jakoby, W. B., 1976. Mechanism for the several activities of the glutathione. J. Biol. Chem. 251: 6183–6188

Kenis, M., Benelli, G., Biondi, A., Calatayud, P. A., Day, R., Desneux, N., et al. 2023. Invasiveness, biology, ecology, and management of the fall armyworm, *Spodoptera frugiperda*. Entomol. Gen. 43: 187-241. https://doi.org/10.1127/entomologia/2022/1659

Kim, S.W., Kang, J., Park, I.K., 2013. Fumigant toxicity of Apiaceae essential oils and their constituents against Sitophilus oryzae and their acetylcholinesterase inhibitory activity. J. Asia. Pac. Entomol. 16, 443–448. https://doi.org/10.1016/j.aspen.2013.07.002

Kiran, S., Prakash, B., 2015. Toxicity and biochemical efficacy of chemically characterized Rosmarinus officinalis essential oil against Sitophilus oryzae and Oryzaephilus surinamensis. Ind. Crops Prod. 74, 817–823. https://doi.org/10.1016/j.indcrop.2015.05.073

Kumar, S., Mahapatro, G.K., Yadav, D.K., Tripathi, K., Koli, P., Kaushik, P., Sharma, K., Nebapure, S., 2022. Essential oils as green pesticides: An overview. Indian J. Agric. Sci. 92, 1298–1305. https://doi.org/10.56093/ijas.v92i11.122746

Lira, E. C., Bolzan, A., Nascimento, A. R. B., Amaral, F. S. A., Kanno, R. H., Kaiser, I. S., Omoto, C., 2020. Resistance of *Spodoptera frugiperda* (Lepidoptera:Noctuidae) to spinetoram: inheritance and cross-resistance to spinosad. Pest Manag. Sci. 76: 2674-2680. https://doi.org/10.1002/ps.5812

Liu, Z., Li, Q.X., Song, B., 2022. Pesticidal Activity and Mode of Action of Monoterpenes. J. Agric. Food Chem. 70, 4556–4571. https://doi.org/10.1021/acs.jafc.2c00635

Marchioro, C. A., Foerster, L. A., 2012. Performance of the Wheat Armyworm, *Pseudaletia sequax* Franclemont, on Natural and Artificial Diets. Neotrop. Entomol. 41: 288-295. https://doi.org/10.1007/s13744-012-0046-8

Mojarab-Mahboubkar, M., Sendi, J.J., Aliakbar, A., 2015. Effect of *Artemisia annua* L. essential oil on toxicity, enzyme activities, and energy reserves of cotton bollworm *Helicoverpa armigera* (Hübner) (Lepidoptera: Noctuidae). J. Plant Prot. Res. 55, 371–377. https://doi.org/10.1515/jppr-2015-0049

Moungthipmalai, T., Soonwera, M., 2023. Adulticidal activity against houseflies (*Musca domestica* L.; Muscidae: Diptera) of combinations of *Cymbopogon citratus* and *Eucalyptus globulus* essential oils and their major constituents. Int. J. Agric. Technol. 19, 1127–1134.

Murcia-Meseguer, A., Alves, T.J.S., Budia, F., Ortiz, A., Medina, P., 2018. Insecticidal toxicity of thirteen commercial plant essential oils against *Spodoptera exigua* (Lepidoptera: Noctuidae). Phytoparasitica 46, 233–245. https://doi.org/10.1007/s12600-018-0655-9

NIST Mass Spectral Library, v 11, 2011. National Institute of Standards and Technology, Gaithersburg.

Olmedo, R., Herrera, J.M., Lucini, E.I., Zunino, M.P., Pizzolitto, R.P., Dambolena, J.S., Zygadlo, J.A., 2015. Essential oil of *Tagetes filifolia* against the flour beetle *Tribolium* *castaneum* and its relation to acetylcholinesterase activity and lipid peroxidation. AgriScientia 32, 113–121.

Pan, Z., Liu, S., Chen, Y.C., Wang, Y.D., Gu, Q., Song, D., 2022. As natural phytocide: Biomarker assessment of *Litsea cubeba* (Lour.) Persoon essential oil against *Drosophila suzukii* Matsumura (Diptera: Drosophilidae.). Ind. Crops Prod. 187, 115421. https://doi.org/10.1016/j.indcrop.2022.115421

Parra, J. R. P., 2001. Técnicas de criação de insetos para programas de controle biológico. Piracicaba, ESALQ/FEALQ, 137p.

Piri, A., Sahebzadeh, N., Zibaee, A., Sendi, J.J., Shamakhi, L., Shahriari, M., 2020. Toxicity and physiological effects of ajwain (*Carum copticum*, Apiaceae) essential oil and its major constituents against *Tuta absoluta* (Meyrick) (Lepidoptera: Gelechiidae). Chemosphere 256, 127103. https://doi.org/10.1016/j.chemosphere.2020.127103

Reis, S.L., Mantello, A.G., Macedo, J.M., Gelfuso, E.A., Da Silva, C.P., Fachin, A.L., Cardoso, A.M., Beleboni, R.O., 2016. Typical monoterpenes as insecticides and repellents against stored grain pests. Molecules 21, 1–10. https://doi.org/10.3390/molecules21030258

Renoz, F., Demeter, S., Degand, H., Nicolis, S.C., Lebbe, O., Martin, H., Deneubourg, J., Fauconnier, M.-L., Morsomme, P., Hance, T., 2022. The modes of action of *Mentha arvensis* essential oil on the granary weevil Sitophilus granarius revealed by a label-free quantitative proteomic analysis. J. Pest Sci. (2004). 95, 381–395. https://doi.org/10.1007/s10340-021-01381-4

Sabini, L.I. et al. Study of the citotoxic and antifungal activity of the essencial oil of *Elyonurus muticus* against *Candida* spp. Molecular Medicinal Chemistry, v.11, p.31-3, 2006.

Shahriari, M., Zibaee, A., Sahebzadeh, N., Shamakhi, L., 2018. Effects of α-pinene, trans-anethole, and thymol as the essential oil constituents on antioxidant system and acetylcholine esterase of *Ephestia kuehniella* Zeller (Lepidoptera: Pyralidae). Pestic. Biochem. Physiol. 150, 40–47. https://doi.org/10.1016/j.pestbp.2018.06.015

Shahriari, M., Zibaee, A., Shamakhi, L., Sahebzadeh, N., Naseri, D., Hoda, H., 2020. Bio-efficacy and physiological effects of *Eucalyptus globulus* and *Allium sativum* essential oils against *Ephestia kuehniella* Zeller (Lepidoptera: Pyralidae). Toxin Rev. 39, 422–433. https://doi.org/10.1080/15569543.2018.1554588

Sombra, K.E.S., de Aguiar, C.V.S., de Oliveira, S.J., Barbosa, M.G., Zocolo, G.J., Pastori, P.L., 2020. Potential pesticide of three essential oils against *Spodoptera frugiperda* (J.e. smith) (lepidoptera: Noctuidae). Chil. J. Agric. Res. 80, 617–628. https://doi.org/10.4067/S0718-58392020000400617

Stefanazzi, N., Stadler, T., Ferrero, A., 2011. Composition and toxic, repellent and feeding deterrent activity of essential oils against the stored-grain pests *Tribolium castaneum* (Coleoptera: Tenebrionidae) and *Sitophilus oryzae* (Coleoptera: Curculionidae). Pest Manag. Sci. 67, 639–646. https://doi.org/10.1002/ps.2102

Stevenson, P.C., Belmain, S.R., Isman, M.B., 2020. Pesticidal plants: From smallholder use to commercialisation, Plants.

Upadhyay, N., Singh, V.K., Dwivedy, A.K., Das, S., Chaudhari, A.K., Dubey, N.K., 2019. Assessment of *Melissa officinalis* L. essential oil as an eco-friendly approach against biodeterioration of wheat flour caused by *Tribolium castaneum* Herbst. Environ. Sci. Pollut. Res. 1996. https://doi.org/10.1007/s11356-019-04688-z

Usseglio, V.L., Dambolena, J.S., Zunino, M.P., 2023. Can Essential Oils Be a Natural Alternative for the Control of Spodoptera frugiperda? A Review of Toxicity Methods and Their Modes of Action. Plants 12. https://doi.org/10.3390/plants12010003

Valle, D., Montella, I. R., 2006. Quantification methodology for enzyme activity related to insecticide resistance in Aedes aegypti. Brasil. Ministério da Saúde. Fundação Oswaldo Cruz, 1, 128.

Yang, Y., Isman, M.B., Tak, J.H., 2020. Insecticidal activity of 28 essential oils and a commercial product containing *Cinnamomum cassia* bark essential oil against *Sitophilus zeamais* Motschulsky. Insects 11, 1–15. https://doi.org/10.3390/insects11080474

Yedomon, B.H., Saves, I., Mtimet, N., Raoelison, E.G., Constant, P., Daffé, M., Bouajila, J., 2017. *Elionurus tristis* Essential Oil: GC-MS Analysis and Antioxidant and Antituberculosis Activities. Nat. Prod. Commun. 12, 615–618. https://doi.org/10.1177/1934578x1701200436

Yeom, H.J., Jung, C.S., Kang, J., Kim, J., Lee, J.H., Kim, D.S., Kim, H.S., Park, P.S., Kang, K.S., Park, I.K., 2015. Insecticidal and acetylcholine esterase inhibition activity of *Asteraceae* plant essential oils and their constituents against adults of the German cockroach (*Blattella germanica*). J. Agric. Food Chem. 63, 2241–2248. https://doi.org/10.1021/jf505927n

# CHAPTER 3: ESSENTIAL OIL OF THE GENUS *Baccharis* AND ITS TOXICITY ON *Spodoptera frugiperda* (LEPIDOPTERA: NOCTUIDAE) AND ITS EFFECT ON *Telenomus remus* (HYMENOPTERA: SCELIONIDAE)

* These results will be submitted in Chemosphere


## Abstract

The species *Spodoptera frugiperda* is considered a key pest of corn crops and has shown resistance to several active ingredients. In this sense, botanical insecticides such as essential oils (EOs) may be a promising alternative and can be used with other control strategies, such as biological control. In this context, the objective of this study was to evaluate the bioactivity of EOs of *Baccharis articulata*, *Baccharis calvescens*, *Baccharis dracunculifolia*, *Baccharis milleflora* and *Baccharis uncinella* in the control of *S. frugiperda*, and their effect on the parasitoid *Telenomus remus*. The identification of the chemical composition of the EOs was performed by gas chromatography coupled to mass spectrometry (GC-MS). The insecticidal activity of the EOs was evaluated by contact and ingestion, and the toxicity of the EOs through biochemical markers. Subsequently, the effect of the EOs on different developmental stages of *T. remus* was evaluated. The number of compounds identified in the evaluated EO ranged from 7 for *B. articulata* to 27 for *B. milleflora*. There was variation in the toxicity of *Baccharis* EOs in *S. frugiperda*, with neurotoxic effect and damage by lipid peroxidation. The species *B. calvescens* and *B. milleflora* did not cause mortality in *T. remus* eggs and pupae, but demonstrated repellency ranging from 40 to 55%. The genus *Baccharis* demonstrates insecticidal activity for *S. frugiperda*, with evidence of neurotoxicity, and are selective for *T. remus*, proving to be promising botanical insecticides as an alternative to synthetic insecticides aiming at sustainable agricultural production models.


**Keywords: Natural products, Biopesticides, Biomarkers, Parasitoids**

## 1. Introduction

Maize (*Zea mays*) is a plant of the Poaceae family and is among the three most cultivated cereals in the world, being used mainly for human and animal consumption due to its high energy value (Pinheiro et al., 2021). Despite its significant production, corn cultivation has several phytosanitary obstacles that can cause significant damage and even compromise production (Montezano et al., 2018; Harrison et al., 2019), among which we can highlight the occurrence of pests, such as species of the genus *Spodoptera*, considered one of the main pests of the crop (Bernal et al., 2015; Arias et al., 2019, Oliveira et al., 2023).

The fall armyworm, *Spodoptera frugiperda* (Lepidoptera: Noctuidae), is considered a key pest of corn crops. The species is polyphagous and the damage it causes is significant, as it can feed on all plant structures, mainly leaves and ears (Nurnina; Muis, 2022). This pest causes significant yield losses, which can vary from 17 to 72%, depending on the location and the insect's development conditions (Murúa et al., 2019; Maruthadurai; Ramesh, 2020).

Chemical control is the most widely used method to reduce *S. frugiperda* populations in corn crops. However, the strong selection pressure caused by intensive and sometimes inadequate use has contributed to the evolution of the species resistance to several active ingredients and modes of action (Okuma et al., 2017; Bolzan et al., 2019; Guan et al., 2020; Garlet et al., 2021; Muraro et al., 2021), making research necessary to evaluate new methods and molecules for pest management in the crop.

In recent years, biological control (BC) with macroorganisms has been a strategy used to reduce the population of this insect, with emphasis on egg parasitoids that are more effective (Mahjan and Bhamare, 2023, Navik et al., 2023, Lacerda et al., 2023), among which the species *Telenomus remus* (Hymenoptera: Scelionidae) is the main bioagent in the management of *S. frugiperda* (Colmenarez et al., 2022; Chen et al., 2021).

EOs are products of the secondary metabolism of plants and present in their chemical composition a broad complex mixture of chemical compounds (Hikal et al., 2017, Velasques et al., 2017). In recent years, research has shown that these products have insecticidal action and that they can be promising substances as an alternative to synthetic insecticides (Isman, 2019). Studies with the genus *Baccharis* (Asteraceae) present reports of repellent, deterrent and insecticidal activity for different insects (Souza et al., 2021; Zimmermann et al., 2021; Eccel et al., 2024), including *S. frugiperda* (Usseglio et al., 2023; Giraldi et al., 2024). One of the main advantages of botanical insecticides is that they are selective, that is, they do not cause harm to beneficial organisms and can be used within integrated pest management (IPM) programs. However, for these products to be used in IPM programs, it is necessary to evaluate their effect on beneficial organisms, especially BC agents.

In view of this scenario, the present study evaluated the insecticidal action by contact and ingestion of EOs from the species *B. articulata*, *B. calvescens*, *B. dracunculifolia*, *B. milleflora* and *B. uncinella* in the control of *S. frugiperda*, and their toxicity in biochemical markers, and the selectivity of EO from *B. calvescens* and *B. milleflora* in the development of *T. remus*.

## 2. Material and Methods

### 2.1. Rearing of *S. frugiperda*

During the larval stage, the larvae were reared according to the methodology proposed by Parra (2001) and fed with an artificial diet of Marchioro; Foerster (2012), provided in 100 mL plastic containers containing approximately 40 mL of diet. One caterpillar was kept in each container until it reached the pupal stage, when they were transferred to transparent Gerbox® boxes (11 cm wide x 11 cm long x 3.5 cm high). After emergence, the adults were kept in polyvinyl chloride (PVC) cages (35 cm high x 20 cm diameter), closed with voile fabric at the upper end, and lined with sulfite paper as an oviposition surface for the females.

Adults were fed with a 10% honey solution diluted in distilled water and provided in plastic containers containing cotton soaked in the solution. The paper sheets containing the egg masses were changed three times a week, and the egg masses were fixed with adhesive tape to the lids of plastic containers (300 ml) containing approximately 100 ml of artificial diet, so that the neonate larvaes had access to food. S. frugiperda was reared in a climate-controlled chamber with a temperature of 25 ± 1 ºC, 70 ± 10% RH and a photophase of 14:10 hours, during all stages of insect development.

**2.2. Rearing of *T. remus***

The eggs parasitoid was reared in test tubes, closed with cotton. Cards with S. frugiperda eggs up to 24 hours old were provided daily in glass tubes measuring 7.5 cm in height and 1.0 cm in diameter, so that the females could oviposit. After 24 hours, the card was removed and placed in another tube so that the parasitoids could develop until emergence. The adult insects were fed with pure honey, 3 times a week and all the rearing was kept in a climate chamber with a temperature of 25 ± 1 ºC, 70 ± 10% RH and a photophase of 14:10 hours, in all stages of insect development.

**2.3. Collection of plant material and extraction of essential oils from the genus *Baccharis***

To obtain the EOs, the plant materials were collected at Bio Estação Gaia, in the municipality of Piraquara, Paraná, Brazil (-25.501217 S and - 49.001598 W). The samples of *B. dracunculifolia* and *B. uncinella* were collected in May/2019, and the samples of *B. articulata*, *B. calvescens* and *B. milleflora* were collected in April/2022.

The EO of all species was extracted from terminal branches with leaves and flowers, and terminal branches with cladodes by the steam distillation method, in a vat, for a period of 3 h. After herborization and identification, the species *B. articulata*, B. calvescens and *B.*

*milleflora* were deposited in the Herbarium of the Botanical Museum, located in the Botanical Garden of Curitiba, PR, under the numbers MBM nº 256683, MBM nº MBM nº 3222203 and MBM nº 078951, respectively. Meanwhile, the species *B. dracunculifolia* and *B. uncinella* were deposited in the Herbarium of Faculdades Integradas Espírita, Curitiba, Paraná, Brazil, under the numbers HFIE nº 8372 and HFIE nº 9004, respectively. This research was also registered in SISGEN under number AE4C4BF.

**2.4. Identification of the chemical composition of essential oils of the genus *Baccharis***

The analysis was performed by gas chromatography, in a Shimadzu TQ8040 gas chromatograph coupled to mass spectrometry (GC-MS). A Rtx-5MS fused silica capillary column (30m x 0.25mm x 0.25μm) and helium as carrier gas (1.02 mL min -1) were used. The injector was operated at a temperature of 250 ºC and the ionization system was operated at 70 eV, in a 1:90 split injection mode. The temperature of the capillary column varied from 60 ºC to 250 ºC, at a rate of 3 ºC min -1.

The injected sample volume was 1.0 µL of a 10 µL EO solution in 1 mL of hexane. For identification of EO components, the experimental mass spectra were compared with literature data (Adams 2007) and the NIST 02 mass library (NIST, Gaithersburg, MD, USA).

**2.5. Insecticidal activity of *Baccharis* EOs against *S. frugiperda***

Preliminary tests were conducted with the EOs of the five *Baccharis* species at a concentration of 2.5% (v:v), diluted in acetone. The solvent acetone (ALPHA024, 99.5% PA) and the synthetic insecticide Chlorfenapyr (Pirate®) at a concentration of 0.75 L/ha were used as negative and positive controls, respectively. The experimental design was completely randomized, with 5 replicates per treatment, and the experiment was repeated five times in time.

**2.5.1. Contact mode of action**

For this bioassay, the methodology used was adapted from Eccel et al. (2024). Ten third-instar larvae were placed in 145 ml plastic containers containing 25 grams of artificial diet. Subsequently, 150 µL of the treatments were pipetted in to the larvae, using a Kasvi basic pipette (20 – 200 µL). After applying the treatments, the containers were sealed with voile fabric and placed in an incubator chamber at 25 ± 1 ºC, 70 ± 10% RH and a photophase of 14:10 hours. Mortality was assessed after 48 hours of exposure. At this stage, the individuals were lightly touched with a brush, and those that did not respond to touch were considered dead.

### 2.5.2 Mode of action by ingestion

For this bioassay, the methodology used was adapted from De Menezes et al. (2020). Ten third-instar larvae were placed in 145 ml plastic containers. A 25 grams portion of corn leaves (cultivate: SCS 155 CATARINA) was treated by immersion in 150 µL of the treatments. After applying the treatments to the leaves, they were left for 10 minutes on sulfite paper for the acetone to evaporate. The leaves were then placed in the containers and made available to the larvae. The containers were then sealed with voile fabric and placed in an incubator chamber at 25 ± 1 ºC, 70 ± 10% RH, and a photophase of 14:10 hours. Mortality was assessed after 48 hours after ingestion of corn leaves. The individuals were lightly touched with a brush, and those that did not respond to touch were considered dead.

### 2.6 Evaluation of the toxicity of *Baccharis* EOs against *S. frugiperda*

The EOs that obtained a mortality result higher than 80%, which is the standard limit used by the Brazilian Ministry of Agriculture to register products as insecticides (Filomeno et al., 2017, Zimmermann et al., 2021), were selected for toxicity evaluation. To determine the lethal concentrations ($LC_{50}$ and $LC_{90}$), a bioassay was performed including 7 to 9 concentrations, with values between 0.25 and 2.3%, diluted in acetone (negative control). The experimental design and methodology used were described in topic 2.5.1.

**2.7 Effect of EOs on biochemical markers of *S. frugiperda***

For enzymatic analyses and lipid peroxidation, the insects were exposed to $LC_{50}$ and $LC_{90}$ of *Baccharis* EOs and the survivors were frozen in a freezer at -80 °C. For each treatment and control group, 10 pools of 4 larvae were evaluated, totaling 40 larvae stored individually in 1.5 mL centrifuge microtubes. Each pool was homogenized in 620 µL of milli-Q water, and subsequently centrifuged (except the samples for measuring acetylcholinesterase activity) at 12000×g at 4 °C for one minute and then stored at −80 °C. Assays were carried out on a 96-well microplate and absorbances measured using spectrophotometry.

The methodology used was that described by Giraldi et al. (2024). AChE activity was evaluated using 25 µL of homogenate, 200 µL of 5,5-dithio-bis-2-nitro-benzoate (DTNB; 0.75 mM), and 50 µL acetylthiocholine iodine (10 mM), as described by Ellman et al. (1961), adapted for microplate by Dizer et al. (2001). To measure GST activity, 15 µL of soluble phase of homogenate, 195 µL of solution (reduced glutathione 10 mM), and 2,4-dinitrochlorobenzene were added, following Keen et al. (1976). Using the protocol established by Jiang et al. (1992), lipid peroxidation was determined by adding 70 µL of soluble phase of homogenate, 70 µL methanol (100%) and 900 µL of a solution of xylenol Orange (butylated hydroxytoluene (4 mM), ammonium ferrous sulfate (2500 µM), and methanol (100%). The Bradford assay (Bradford, 1976) was applied to determine total protein contents by adding 10 µL of soluble phase of homogenate, 10 µL of bovine serum albumin as the standard, and 250 µL of Bradford reagent (Sigma ®). Using the protocol established by Valle and Montella (2006) EST-α and EST-β activity was evaluated using for each enzyme 10 µl of homogenate, 200 µl of alpha-naphthyl acetate/Naphosphate (0.3 mM) or beta-naphthyl acetate/Naphosphate (0.3 mM) and 50 µl of Fast Blue dye (0.3%). Alpha-naphthol (0.3 $mg.L^{-1}$) and beta-naphthol (0.3 $mg.L^{-1}$) were using as a positive control. A standard curve was performed to convert absorbance values into alpha/beta-naphthol content.

### 2.8 Repellency and toxicity tests of EOs on *T. remus*

To evaluate the repellency and toxicity in *T. remus*, the methodology proposed by Bibiano et al. (2022), with adaptations, was used. The test was conducted in the laboratory using cards with 100 ± 20 *S. frugiperda* eggs. The eggs were treated with *B. calvescens* and *B. milleflora* EOs, at LC 90 concentrations (2.05% (v:v) and 2.2% (v:v)), respectively, for 5 seconds. Subsequently, they were stored at room temperature for 30 minutes for solvent evaporation, and then the cards were placed in glass tubes measuring 7.5 cm in height and 1.0 cm in diameter.

For the repellency test, 3 females were added to the glass tube containing the cards and parasitism was allowed for 24 h. After 12 days, the number of parasitized eggs was evaluated. To evaluate the toxicity of *Baccharis* EOs on *T. remus* eggs, the egg packs were placed in test tubes containing 3 females per tube. After 24 hours in contact with the eggs, the females were removed from the tube and the treatments were applied to the egg packs. To evaluate the toxicity to pupae, after 11 days, the treatments were applied to the egg packs parasitized by *T. remus* and the evaluation occurred on the 12th day.

The experimental design was completely randomized, with 20 replicates per treatment for each experiment. The solvent acetone (ALPHA024, 99.5% P.A.) and the synthetic insecticide chlorfenapyr (Pirate®) at a concentration of 0.75 L/ha were used as negative and positive controls, respectively. A control without application of any treatment was also performed as a parameter of biological activities.

### 2.9 Statistical Analysis of Data

Insect mortality data were adjusted by generalized linear models (GLM) using the Poisson distribution. For insecticide activity data and the effect on biochemical markers, the Gaussian distribution was used. Analysis of variance (ANOVA) was performed in both cases and, when significant, Tukey's mean test was applied with a 5% probability of error. Biomarker results were integrated using the Integrated Biomarker Response Index (IBR) described by Beliaeff and Burgeot (2002). Lethal concentration data were subjected to the Probit analysis method, using the “ecotox” package of the R software. All results were analyzed in the R software (R Core Team, 2021).

## 3. Results

### 3.1. Chemical composition of Baccharis essential oils

There was a variation in the amount of compounds present among the *Baccharis* species, with variability of 7 compounds for *B. articulata* EO to 27 for *B. milleflora* EO. A variability was identified in the total value of identified compounds, *B. uncinella* EO presented 80.04% and *B. articulata* EO 93.16%, being the lowest and highest values, respectively. The *B. articulata* EO presented a higher proportion of monoterpenes (73.11%), while for sesquiterpenes *B. milleflora* EO (50.9%) presented the highest value (Table 1).

For *B. articulata* EO, 3 major compounds were identified, namely β-pinene, limonene and germacrene D, totaling 78.59% of the compounds present. For EOs from *B. calvescens*, *B. dracunculifolia* and *B. uncinella*, 4 major compounds were identified, totaling 69.88%, 58.07% and 55.52%, respectively. And for *B. milleflora*, 8 major compounds were identified, totaling 64.57% of the compounds present in the EO. Among the compounds identified in all species, the molecule β-pinene was identified as the major compound in all oils, with the exception of *B. milleflora* EO (Table 1).

Table 1. Chemical composition of essential oils from species of the genus *Baccharis* collected in Piraquara (Paraná, Brazil), by gas chromatography and mass spectrometry method.

| Nº | Compounds (%) | RIlit | RIcalc | *B. articulata* | *B. calvescens* | *B. dracunculifolia* | *B. milleflora* | *B. uncinella* |
|---|---|---|---|---|---|---|---|---|
| 1 | α-tujeno | 924 | 924 | - | - | - | - | 3,80 |
| 2 | *α*-pineno | 932 | 930 | 3,48 | 15,55 | 4,49 | 6,82 | 17,27 |
| 3 | sabineno | 969 | 969 | - | - | - | 0,34 | 1,67 |
| 4 | *β*-pineno | 974 | 975 | 52,24 | 25,12 | 21,58 | 0,90 | 11,96 |
| 5 | mirceno | 988 | 990 | - | 2,03 | 1,77 | 5,26 | 1,77 |
| 6 | *α*-felandreno | 1002 | 1005 | - | - | - | 0,55 | - |
| 7 | limoneno | 1024 | 1027 | 17,39 | 22,75 | 13,45 | 2,13 | 0,29 |
| 8 | *β*-felandreno | 1025 | 1028 | - | - | - | 5,89 | - |
| 9 | (Z)-β-ocimeno | 1032 | 1026 | - | - | - | - | 16,98 |
| 10 | *(E)-β*-ocimeno | 1044 | 1044 | - | - | 1,27 | 2,35 | - |
| 11 | γ-terpineno | 1054 | 1055 | - | - | - | - | 1,01 |
| 12 | terpinen-4-ol | 1174 | 1173 | - | - | - | - | 1,99 |
| 13 | α-terpineol | 1186 | 1187 | - | - | - | - | 0,42 |
| 14 | *α*-ylangeno | 1373 | 1371 | - | 0,68 | - | 0,48 | - |
| 15 | β- elemeno | 1389 | 1385 | - | 1,76 | - | 0,51 | - |
| 16 | *α*-gurjuneno | 1409 | 1401 | - | - | - | 0,77 | - |
| 17 | *(E)*-cariofileno | 1417 | 1413 | 3,93 | 3,3 | 1,34 | 11,87 | 1,96 |
| 18 | *β*-gurjuneno | 1431 | 1424 | - | - | - | 0,34 | - |
| 19 | aromadendreno | 1439 | 1432 | - | - | - | 1,49 | - |
| 20 | *α*-humuleno | 1452 | 1449 | - | 1,20 | - | 5,88 | 0,35 |
| 21 | *allo*-aromadendreno | 1458 | 1454 | - | - | - | 0,88 | - |
| 22 | *γ*-gurjuneno | 1475 | 1467 | - | - | - | 0,45 | - |
| 23 | trans-cadina-1(6),4-dieno | 1475 | 1474 | - | - | 2,18 | - | - |
| 24 | *γ*-muuroleno | 1478 | 1470 | - | - | - | 0,68 | - |
| 25 | amorfa-4,7(11)-dieno | 1479 | 1471 | - | - | - | 1,10 | - |
| 26 | germacreno D | 1480 | 1475 | 8,96 | 6,46 | - | 10,11 | 0,76 |
| 27 | *γ*-amorfeno | 1495 | 1485 | - | - | 0,1 | 2,13 | - |
| 28 | biciclogermacreno | 1500 | 1490 | 4,56 | 4,40 | 3,61 | 12,06 | - |
| 29 | α-muuroleno | 1500 | 1494 | - | - | - | - | 0,34 |
| 30 | *β*-bisaboleno | 1505 | 1505 | - | - | - | 0,23 | - |
| 31 | *δ*-amorfeno | 1511 | 1513 | 2,6 | - | 1,67 | 1,92 | - |
| 32 | *γ*-cadineno | 1513 | 1507 | - | 0,39 | - | - | - |
| 33 | iso-epoxido de italeceno | 1514 | 1502 | - | - | - | - | 3,46 |

| Nº | Compounds (%) | RIlit | RIcalc | *B. articulata* | *B. calvescens* | *B. dracunculifolia* | *B. milleflora* | *B. uncinella* |
|---|---|---|---|---|---|---|---|---|
| 34 | δ-cadineno | 1522 | 1513 | - | 2,01 | - | - | 1,52 |
| 35 | germacreno *B* | 1559 | 1552 | - | 1,44 | - | - | - |
| 36 | (E)-nerolidol | 1561 | 1563 | - | - | 17,01 | - | - |
| 37 | espatulenol | 1577 | 1570 | - | 1,95 | 6,03 | 0,44 | 9,31 |
| 38 | oxido de cariofileno | 1582 | 1575 | - | - | 2,59 | - | 3,22 |
| 39 | globulol | 1590 | 1587 | - | - | 3,03 | 6,68 | 1,25 |
| 40 | ledol | 1602 | 1594 | - | - | 1,69 | - | - |
| 41 | *cis*-cadin-4-en-7-ol | 1635 | 1629 | - | - | - | 0,83 | - |
| 42 | epi-α-cadinol | 1639 | 1636 | - | 0,25 | 1,89 | - | - |
| 43 | epi-α-muurolol | 1640 | 1639 | - | - | 0,50 | - | - |
| 44 | α-muurolol | 1644 | 1643 | - | - | 0,37 | - | - |
| 45 | α-cadinol | 1652 | 1647 | - | - | 2,03 | - | 0,71 |
| 46 | selin-11-en-4-α-ol | 1658 | 1658 | - | 1,75 | - | - | - |
| | Monoterpene | | | **73,11** | **65,45** | **42,56** | **24,24** | **54,75** |
| | Oxygenate monoterpenes | | | **-** | **-** | **-** | **-** | **2,41** |
| | Sesquiterpene | | | **20,05** | **8,90** | **8,9** | **50,9** | **8,39** |
| | Oxygenate sesquiterpenes | | | | **35,14** | **35,14** | **7,95** | **14,49** |
| | **Total** | **-** | **-** | **93,16** | **91,04** | **86,06** | **83,09** | **80,04** |

### 3.2. Insecticidal activity by contact mode of action of *Baccharis* EOs against *S. frugiperda*

All treatments showed insecticidal activity against *S. frugiperda*, resulting in a mortality rate of 100%. There was no mortality in the negative control.

### 3.3. Insecticidal activity by mode of action by ingestion of *Baccharis* EOs against *S. frugiperda*

Treatments with *Baccharis* EO did not show insecticidal activity against *S. frugiperda*, presenting a mortality rate of less than 5%, as well as the control. Only the synthetic insecticide Pirate® presented a mortality rate of 100%.

### 3.4. Toxicity of *Baccharis* EO against *S. frugiperda*

There was variation in the toxicity of EOs from *Baccharis* species against *S. frugiperda*. The EO from *B. milleflora* presented the lowest values for $LC_{50}$, while the EO from *B. calvescens* presented the lowest values for $LC_{90}$. Among the other treatments, the EO from *B. articulata* presented the highest values for $LC_{50}$ and $LC_{90}$ (Table 2).

Table 2. Toxicity of EOs from *Baccharis* species against 3rd instar caterpillars of *S. frugiperda*, after 48 h of exposure.

| Species | N | $LC_{50}$ (CI 95%) | Slope | $LC_{90}$ (CI 90%) | Slope | Chi-square | P value |
|---|---|---|---|---|---|---|---|
| *B. articulata* | 2250 | 1.55 (1.42–1.67) | 7.44 | 2.31 (2.08-2.78) | 7.44 | 40.8 | 0.0000000891 |
| *B. calvescens* | 1750 | 1.23 (1.05-1.34) | 5.78 | 2.05 (1.83-2.61) | 5.78 | 24.4 | 0.000178 |
| *B. dracunculifolia* | 2250 | 1.53 (1.44-1.61) | 8.76 | 2.14 (2.00-2.42) | 8.76 | 40.4 | 0.00000105 |
| *B. milleflora* | 2000 | 0.67 (0.43-0.88) | 2.50 | 2.20 (1.55-4.82) | 2.50 | 49.0 | 0.000000000734 |
| *B. uncinella* | 2000 | 1.28 (1.12-1.39) | 5.82 | 2.13 (1.91-2.59) | 5.82 | 33.6 | 0.00000808 |

### 3.5. Enzymatic activity of essential oils of the genus *Baccharis* in *Spodoptera frugiperda*

Our results showed enzymatic alterations in relation to EOs and negative controls, indicating that acetone (solvent) is a factor that causes enzymatic alterations. For our data, acetone caused a reduction in GST activity and an increase in SOD and AChE. This pattern occurred for EOs of all *Baccharis* species, so the interpretation was based on enzymatic alterations and LPO in relation to the water control.

For $LC_{50}$, exposure to *B. articulata* EO caused an increase in the enzymatic activity of EST-α, EST-β and SOD, and reduced GST activity (Fig. 1). *B. calvescens* EO increased EST-β, SOD, AChE activity, reduced EST-α activity and caused LPO (Fig. 2). *B. dracunculifolia* EO increased EST-α, EST-β, SOD activity and caused LPO (Fig. 3). Meanwhile, *B. milleflora* EO increased EST-β, SOD, AChE, reduced GST and caused LPO (Fig. 4). Finally, *B. uncinella* EO caused increased EST-β and SOD activity (Fig. 5).

For $LC_{90}$, exposure to *B. articulata* EO increased the activity of EST-α, GST, and AChE and caused LPO (Fig. 1). *B. calvescens* EO increased the activity of EST-α, GST, and AChE and caused LPO (Fig. 2). *B. dracunculifolia* EO reduced the activity of EST-α and EST-β, increased the activity of GST, SOD, and AChE and caused LPO (Fig. 3). *B. milleflora* EO increased the activity of EST-α, GST, SOD, and AChE and caused LPO (Fig. 4). Finally, *B. uncinella* EO increased the activity of EST-α, GST, and AChE and caused LPO (Fig. 5).

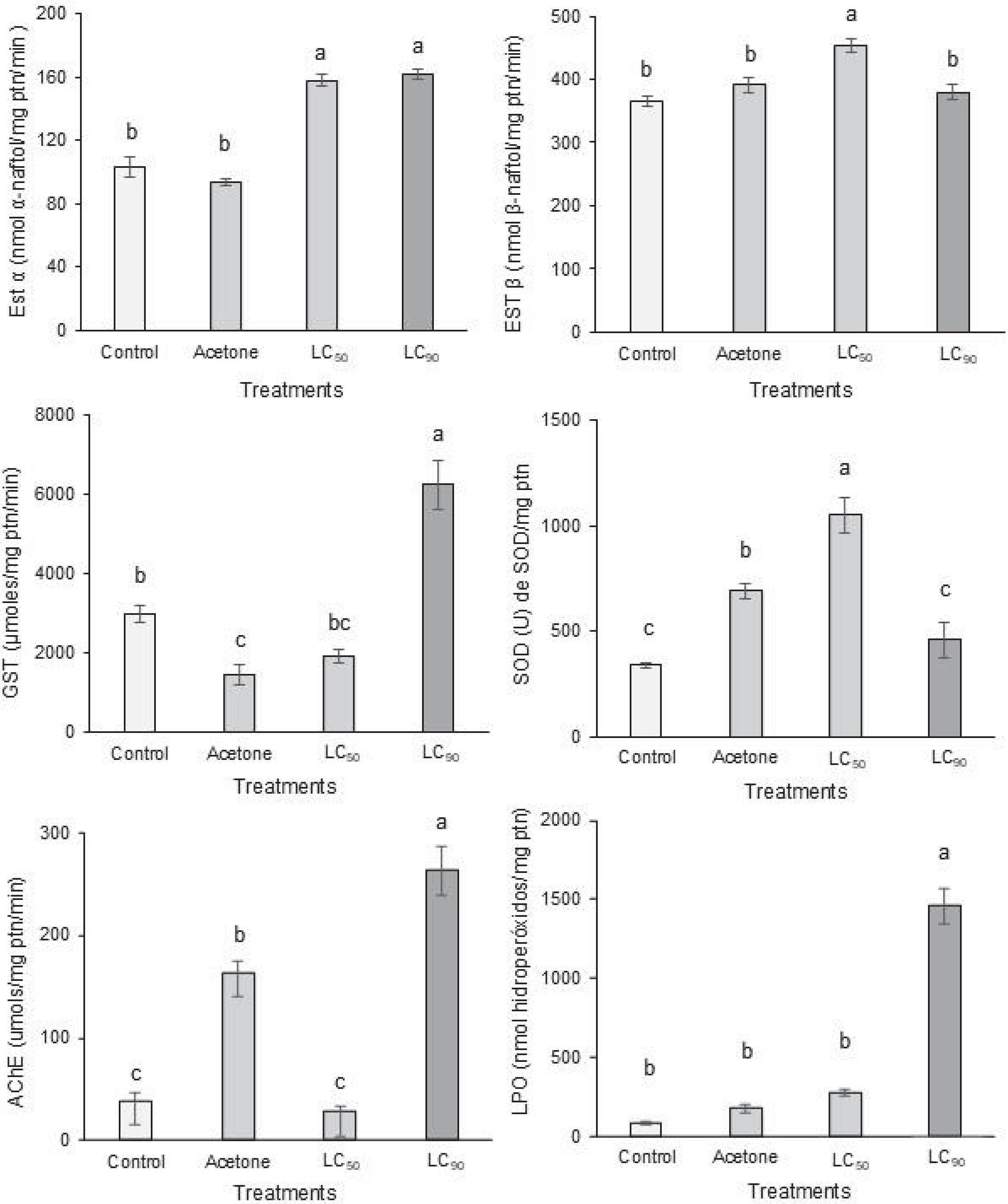


Figure 1: Effect of control, acetone (negative control) and *Baccharis articulata* essential oil on EST-α, EST-β, GST, SOD, LPO, and AChE against *Spodoptera frugiperda*. The means followed by the same letter in the bar diagram are not significantly different according to ANOVA and Tukey's multiple comparison tests.

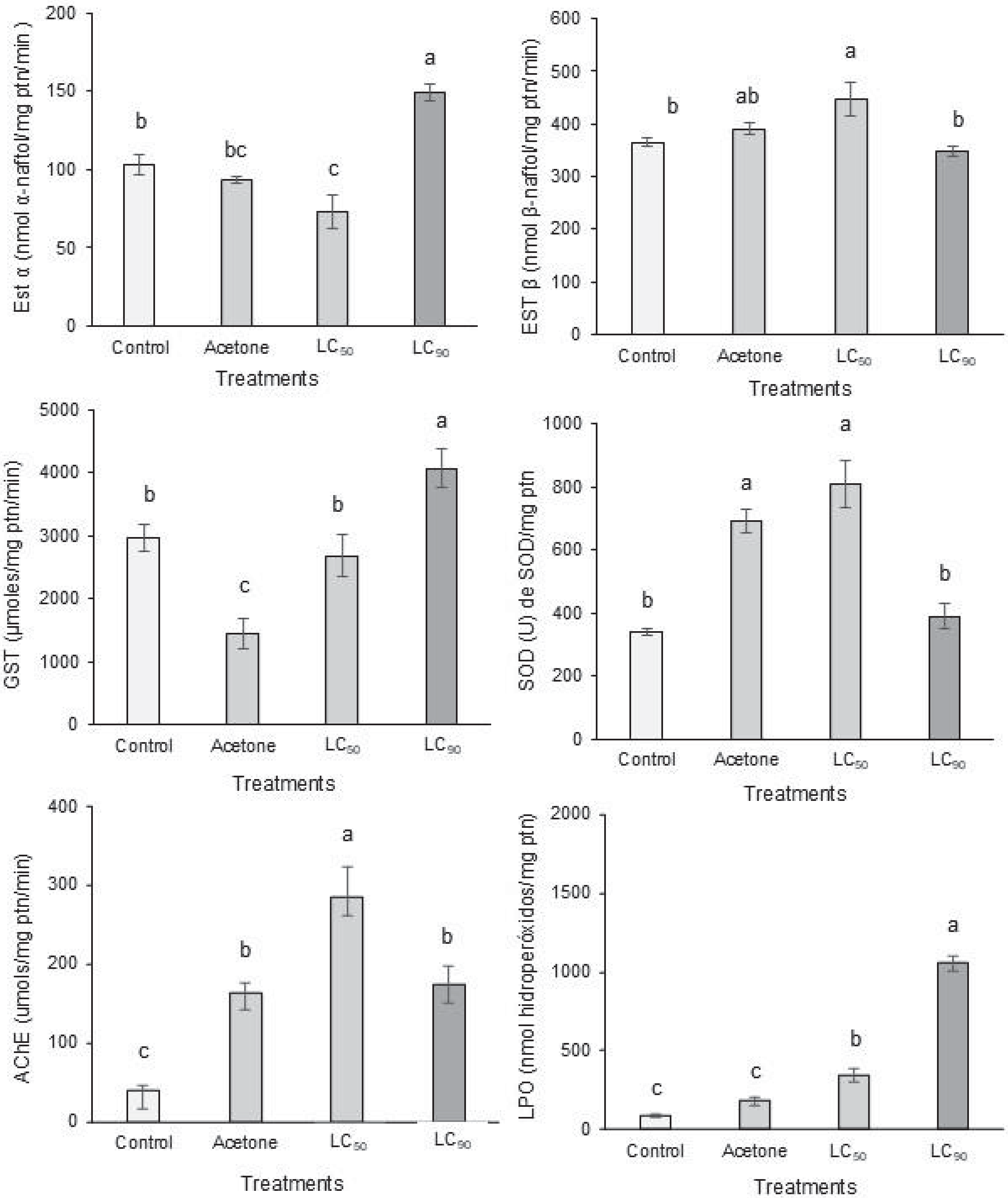


Figure 2: Effect of control, acetone (negative control) and *Baccharis calvescens* essential oil on EST-α, EST-β, GST, SOD, LPO, and AChE against *Spodoptera frugiperda*. The means followed by the same letter in the bar diagram are not significantly different according to ANOVA and Tukey's multiple comparison tests.

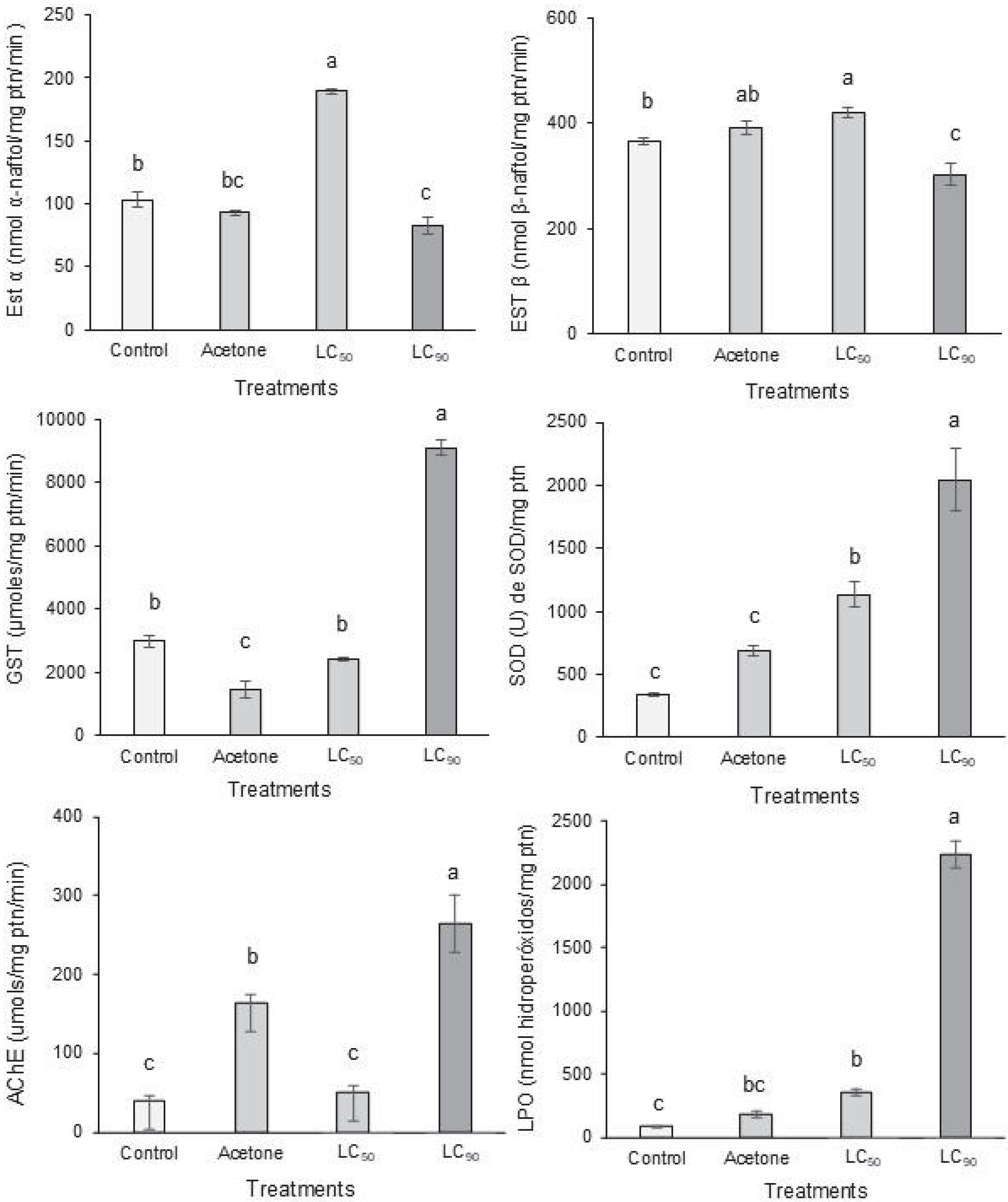


Figure 3: Effect of control, acetone (negative control) and *Baccharis dracunculifolia* essential oil on EST-α, EST-β, GST, SOD, LPO, and AChE against *Spodoptera frugiperda*. The means followed by the same letter in the bar diagram are not significantly different according to ANOVA and Tukey's multiple comparison tests.

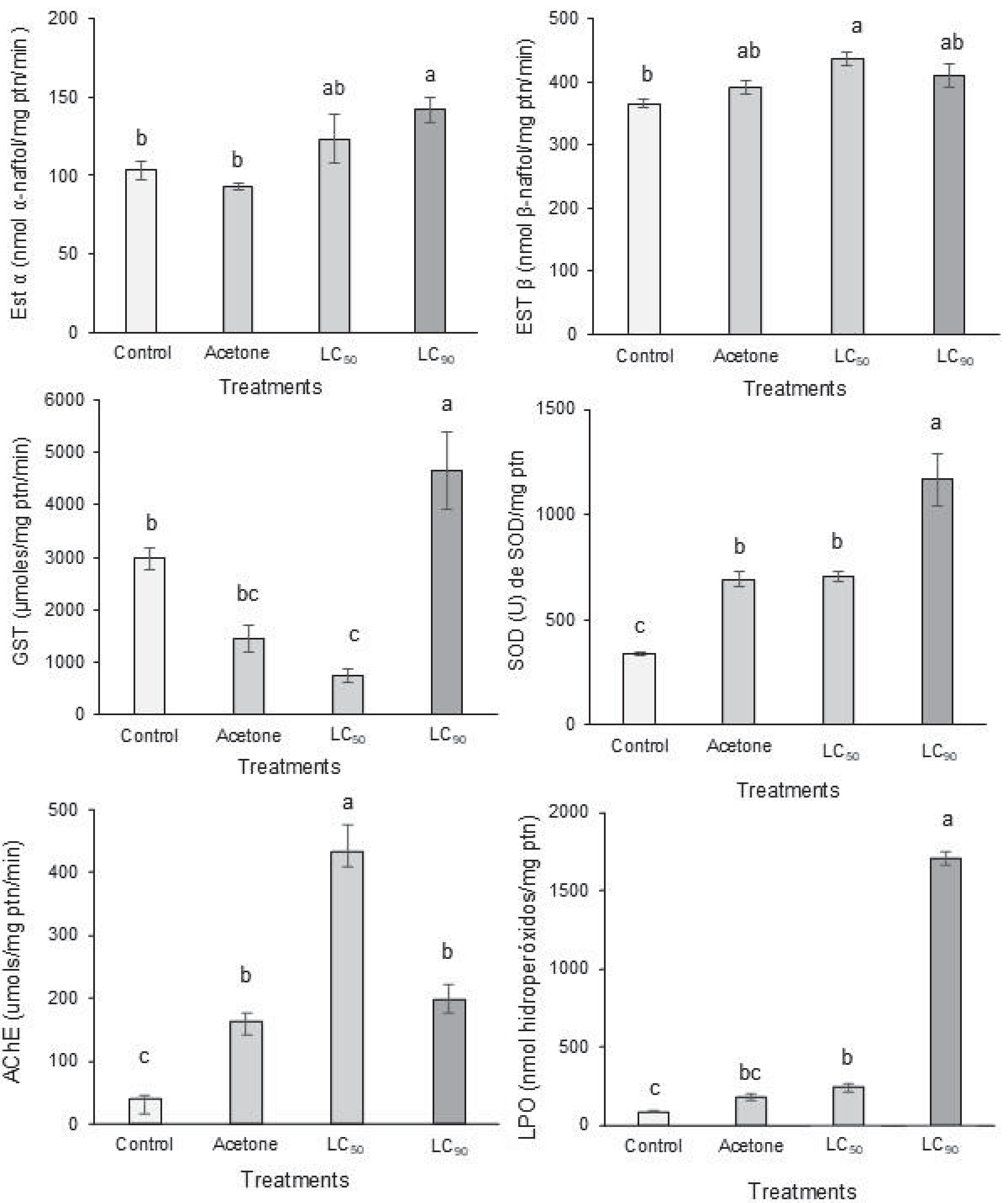


Figure 4: Effect of control, acetone (negative control) and *Baccharis milleflora* essential oil on EST-α, EST-β, GST, SOD, LPO, and AChE against *Spodoptera frugiperda*. The means followed by the same letter in the bar diagram are not significantly different according to ANOVA and Tukey's multiple comparison tests.

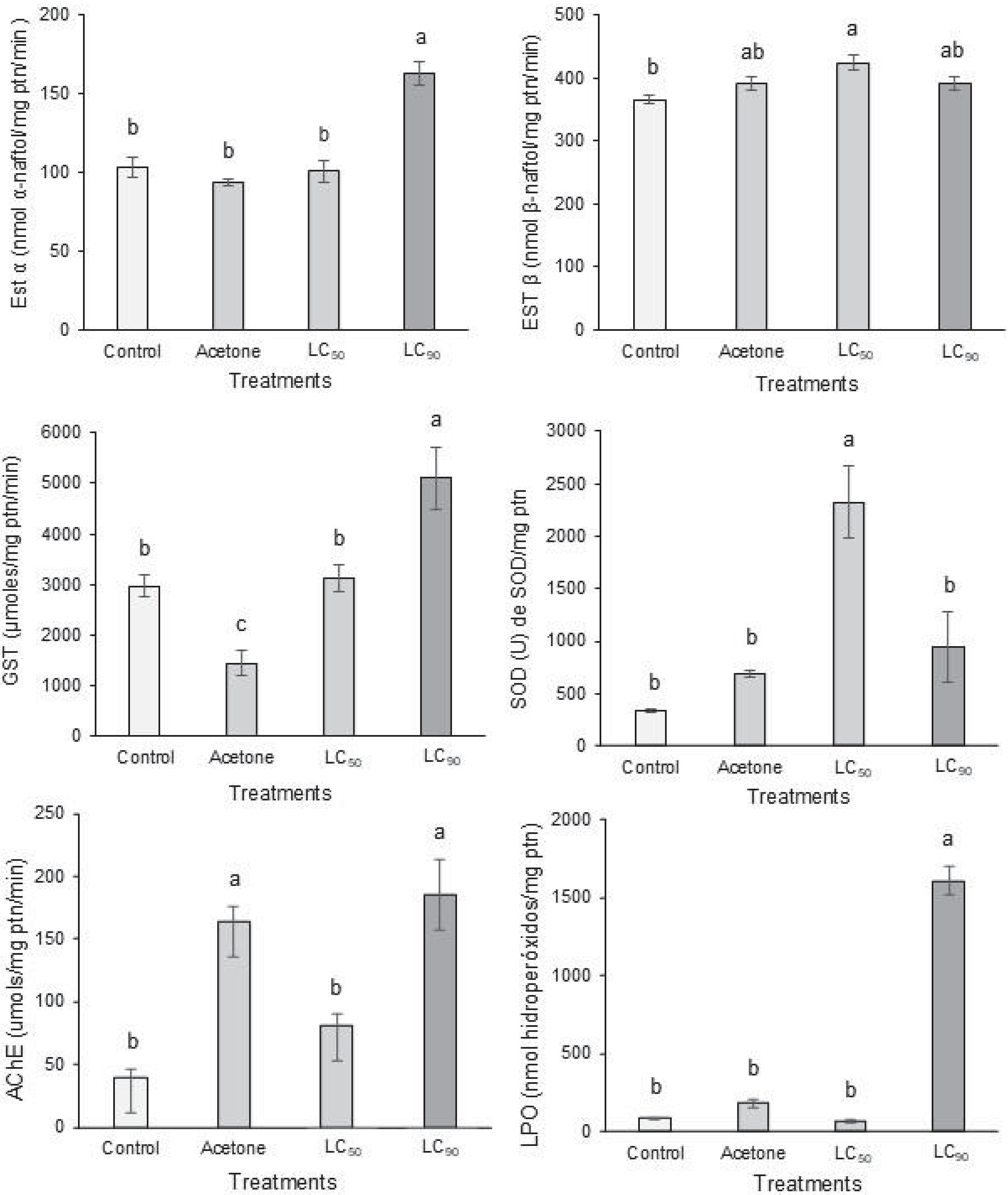


Figure 5: Effect of control, acetone (negative control) and *Baccharis uncinella* essential oil on EST-α, EST-β, GST, SOD, LPO, and AChE against *Spodoptera frugiperda*. The means followed by the same letter in the bar diagram are not significantly different according to ANOVA and Tukey's multiple comparison tests.

Based on the analysis of the integrated biomarker index (IBR), it was possible to verify that acetone, used as a solvent for EOs, increased AChE activity and inhibited GST activity.

For $LC_{50}$, the EOs of *B. articulata, B. dracunculifolia* and *B. uncinella* had the greatest influence on the antioxidant enzyme SOD, while *B. calvescens* and *B. milleflora* had the greatest effect on AChE activity (Fig. 6). For $LC_{90}$, *Baccharis* species showed higher scores of biomarker alterations in relation to the values of $LC_{50}$, with *B. milleflora* presenting the highest score, followed by *B.dracunculifolia* (Fig. 7). For all *Baccharis* at this concentration, there was an increase in AChE and LPO activity.

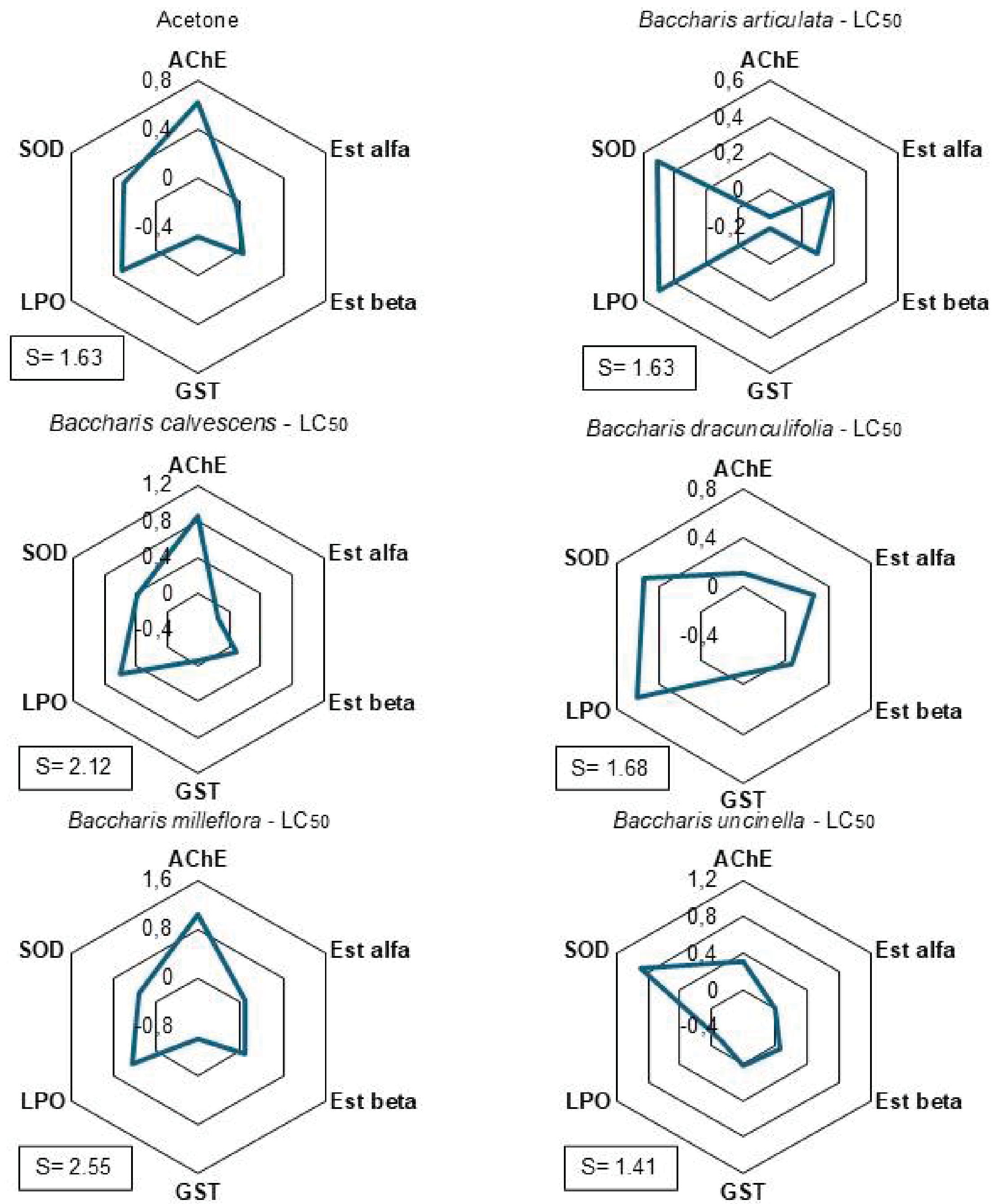


Figure 6: Integrated Biomarker Index (IBR) for each $LC_{50}$ of essential oil from the *Baccharis* genus tested. AChE = acetylcholinesterase. GST = glutathione S-transferase. EST alpha = α-Esterase. EST beta = β-esterase. SOD = Superoxide dismutase. The S value represents the result of the sum of the values attributed to each of the biomarkers in relation to the control. The results are presented as radar graphs indicating the deviation of all biomarkers in relation to the control. Values above the zero line represent the induction of biomarkers, while values below zero represent inhibition of biomarkers. The higher the S value, the greater the accumulation of biomarker changes in exposure to the essential oil.

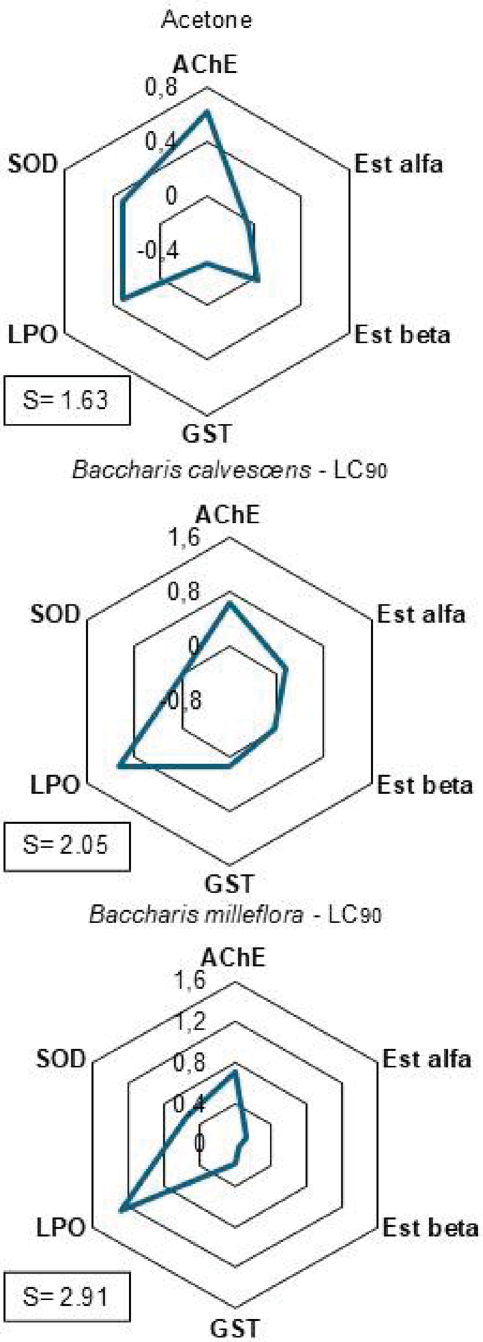


Figure 7: Integrated Biomarker Index (IBR) for each LC90 of essential oil from the genus Baccharis tested. AChE = acetylcholinesterase. GST = glutathione S-transferase. EST alpha = α-Esterase. EST beta = β-esterase. SOD = Superoxide dismutase. The S value represents the result of the sum of the values attributed to each of the biomarkers in relation to the control. The results are presented as radar graphs indicating the deviation of all biomarkers in relation to the control. Values above the zero line represent the induction of biomarkers, while values below zero represent inhibition of biomarkers. The higher the S value, the greater the accumulation of biomarker alteration in exposure to the essential oil.

### 3.6 Baccharis EOs repellency to *T. remus*

Treatments with *Baccharis* EOs showed a repellent effect for *T. remus*, with a significant difference when compared to the negative (acetone) and positive (Chlorfenapyr) controls. However, there was no statistical difference between the species *B. calvescens* and *B. milleflora*.

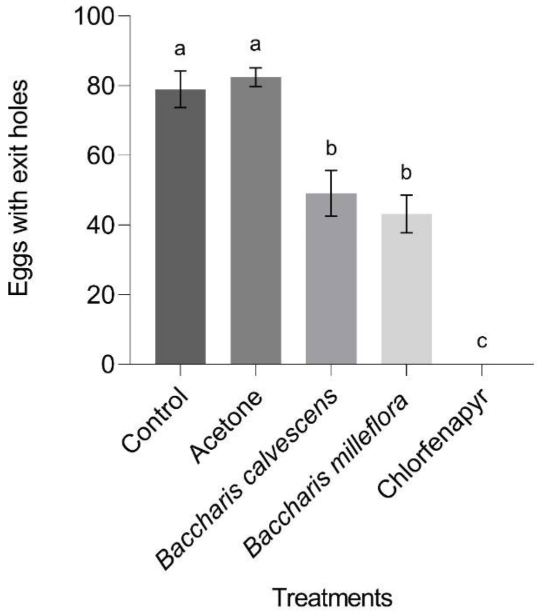


Figure 8: Repellent effect of *Baccharis calvescens* and *Baccharis milleflora* EOs on $LC_{90}$ concentration (2.05% e 2.20%) on adults of *Telenomus remus*. Acetone and the insecticide Chlorfenapyr were used as negative and positive controls, respectively. Treatments with the same letters did not differ from each other by Tukey's test (p <0.001)

### 3.7 Ovicidal activity of Baccharis EOs on *T. remus*

*Baccharis* EOs did not show significant ovicidal activity against *T. remus*, not differing from the control and negative control (acetone). However, the synthetic insecticide Chlorfenapyr caused 100% mortality.

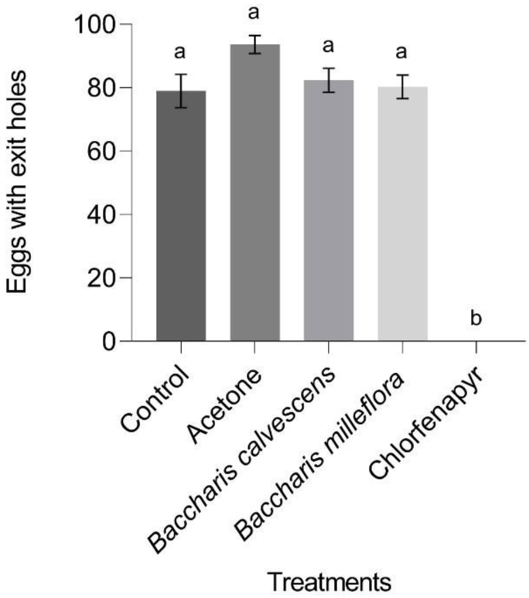


Figure 9: Ovicidal activity of *Baccharis calvescens* and *Baccharis milleflora* at $LC_{90}$ (2.05% e 2.20%) concentration on *Telenomus remus*. Treatments with the same letters did not differ from each other by Tukey's test (p <0.001).

### 3.8 Activity of Baccharis EOs in *T. remus* pupae

*Baccharis* EOs did not show significant insecticidal activity in the pupal stage of *T. remus*, not differing from the control and negative control. However, the synthetic insecticide Chlorfenapyr caused 100% mortality.

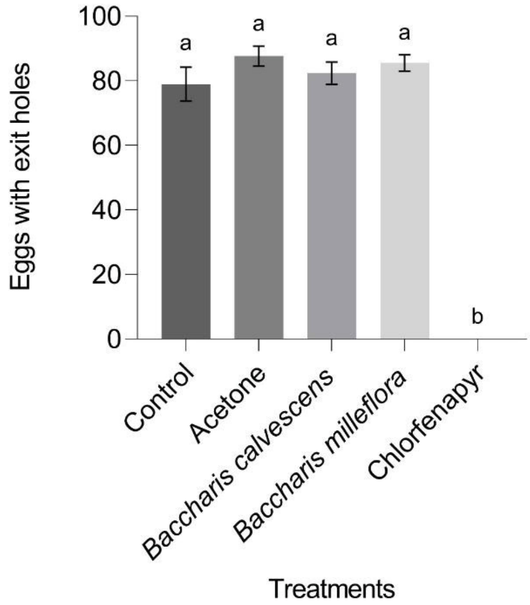


Figure 10: Insecticidal activity of *Baccharis calvescens* and *Baccharis milleflora* at $LC_{90}$ concentration (2.05% e 2.20%) on *Telenomus remus* pupae. Treatments with the same letters did not differ from each other by Tukey's test ($p < 0.001$).

## 4. Discussion

During their evolutionary process, some plant species began to synthesize a wide range of chemical compounds, from different secondary metabolism routes with effects aimed at avoiding or inhibiting herbivory caused by insects.(Piri et al., 2020).

Our results demonstrate that there was quantitative and qualitative variation in the chemical composition among the species of the genus *Baccharis*, and the insecticidal activity of all EOs against *S. frugiperda* was confirmed. This study describes the first report on the insecticidal activity and toxicity of *Baccharis* EOs on *S. frugiperda*.

For *B. articulate* EO, the compounds in the greatest proportion were β-pinene, limonene and germacrene D, and to date there are reports on the repellent effect of this species for *Tribolium castaneum* (Coleoptera: Tenebrionidae) and Acanthoscelides obtectus (Coleoptera: Chrysomelidae) (Campos et al., 2014; Saran et al., 2019), however, the authors did not report the chemical composition of the EOs. For *B. calvescens* EO, the major compounds were α-pinene, β-pinene, limonene and germacrene D; while the *B. dracunculifolia* EO presented as major compounds β-pinene, limonene, (E)-nerolidol and spathulenol, being one of the most studied species within the genus *Baccharis*, with insecticidal activity reported for different types of insects, and with wide variability in its chemical composition (Chaaban et al., 2018; Souza et al., 2021; Zimmermann et al., 2021). In our sample of *B. milleflora* EO, the compounds in greatest proportion were α-pinene, myrcene, β-phellandrene, (E)-caryophyllene, α-humulene, germacrene D, bicyclogermacrene and globulol, and for *B. uncinella* EO, the major compounds were α-pinene, β-pinene, (Z)-β-ocimene and spathulenol.

Corroborating our results, the insecticidal activity of EOs from *B. calvescens*, *B. milleflora* and *B. uncinella* was reported for *Drosophila suzukii* (Diptera: Drosophilidae) (Souza et al., 2021), with variations in the major compounds in quantitative and qualitative terms, and for *Anticarsia gemmatalis* (Lepidoptera: Noctuidae), *Sitophilus oryzae* (Coleoptera: Curculionidae), *Sitophilus zeamais* (Coleoptera: Curculionidae), and *Lucilia cuprina* (Diptera: Calliphoridae) with same chemical composition (Eccel et al., 2024). However, Zimmermann et al. (2021) found that for *S. oryzae* and *S. zeamais*, the insecticidal activity of *B. dracunculifolia* and *B. uncinella* EOs was not significant, with mortality below 40%, with major compounds similar to that of our study.

The diversity and complexity of the chemical compounds presented in our results and compared with the literature indicate that the variation in the chemical composition of EOs may be related to the influence of intrinsic and extrinsic factors. Aspects such as seasonality, geographic location, population genetics, extraction method, plant organ used, edaphoclimatic conditions, interaction with biotic factors, among others, may result in quantitative and qualitative changes in the substances present in EOs (Leal et al., 2022; Cipriano et al., 2023).

The compounds present in EOs are associated with the biological activities that these products may present (Basaid et al., 2020; Kumar et al., 2022). The insecticidal activity of EOs may be associated with mono and sesquiterpene compounds (Abdelgaleil et al., 2021; Jankowska et al., 2018), which in general are present in greater proportion, being called major compounds (Garay et al., 2020). However, in addition to the chemical composition, the insecticidal activity of EOs can be influenced by factors such as time and method of exposure, concentration, target organism and its stage of development (Koyama, Heinbockel, 2020; Fernandes et al., 2021; Silveira et al., 2022).

EOs are a complex of volatile lipophilic chemical substances that have several effects in the control of agricultural pests, and can perform insecticidal action (by contact, fumigation or ingestion) or repellency (Basaid et al., 2020; Dhifi et al., 2016; Usseglio et al., 2023). In this context, the present study evaluated the bioactivity of EOs from the genus *Baccharis* by contact and ingestion against *S. frugiperda*, observing that the toxicity was greater by contact and indicating that this physicochemical property of EOs favors the penetration of the compounds into the insect's body through the cuticle. Therefore, the exposure method is one of the main factors that can influence the toxicity of EOs against insects (Usseglio et al., 2023; Chaudhari et al., 2021; Wang et al., 2019; Hashem et al., 2018).

Our results demonstrate that the increase in EO concentration caused a higher mortality rate of *S. frugiperda*. In general, the insecticidal activity of EOs is attributed to monoterpenes, which demonstrate a toxic effect on *Spodoptera littoralis* (Lepidoptera: Noctuidae) and *S. frugiperda* (Abdelgaleil et al., 2022; Al-Nagar et al., 2020). However, *B. milleflora* EO showed greater diversity and proportion of chemical compounds in addition to greater toxicity, indicating that there is possibly a synergistic effect between all chemical compounds, contributing to a greater lethal effect (Hummelbrunner and Isman, 2001; Chen et al., 2021; Kim et al., 2021).

Because they are made up of different substances, EOs can act in different mechanisms of action, interfering mainly in the physiology of the nervous system of insects (Jankowska et al., 2018; Piri et al., 2020; Usseglio et al., 2023). However, there is few researches that aims to elucidate the effect of these substances on biochemical markers of agricultural pests.

This study is the first report of the effect of EOs from the genus *Baccharis* on biochemical markers of *S. frugiperda*. Our results indicate that EOs from this genus cause different changes in the enzymes and, in higher concentrations, cause high levels of lipid peroxidation. However, we found that acetone alone, the main solvent used, is also a factor that influenced the biochemistry of insects, causing a reduction in GST activity and an increase in SOD and AChE. A study conducted by Tunç et al. (1997) demonstrated that acetone is extremely toxic to storage insects, although we found no reports of toxicity to caterpillars and found that EO caused significant changes in the enzymes.

In exposure to $LC_{50}$, the GST enzyme showed inhibition in exposure to *B. milleflora* EO, indicating that this product can strongly inhibit its enzymatic action. At a higher concentration ($LC_{90}$), exposure to EOs from all *Baccharis* species increased bioactivity, possibly indicating an attempt to detoxify the insect organism due to the high toxicity of EOs. The GST enzyme is one of the main enzymes responsible for the detoxification process of chemical substances, especially insecticides, as it catalyzes these toxic products into water-soluble molecules through glutathione, making them less toxic to the organism and allowing them to be excreted by the organism (Mojarab-Mahboubkar et al., 2015; Liao et al., 2017; Moustafa et al., 2021). In addition to this function, the enzyme is also responsible for reducing possible negative effects of oxidative stress in cells (Liao et al., 2017; Awad et al., 2024). Similar results were reported for *S. frugiperda* (Giraldi et al., 2024), *Spodoptera littoralis* (Lepidoptera: Noctuidae) (Moustafa et al., 2023; Awad et al., 2024), *Spodoptera* *litura* (Lepidoptera: Noctuidae) (Ruttanaphan et al., 2019), and for other lepidopteran species such as *Tuta absoluta* (Meyrick) (Lepidoptera: Gelechiidae) (Piri et al., 2020), *Helicoverpa armigera* (Lepidoptera: Noctuidae) (Mojarab-Mahboubkar et al., 2015; Liao et al., 2017), and *Agrotis ipsilon* (Lepidoptera: Noctuidae) (Moustafa et al., 2021).

Although acetone causes an increase in AChE activity, when compared to exposure to the water control, and exposure to $LC_{50}$, *B. articulata*, *B. dracunculifolia* and B. uncinella returned to baseline AChE values, indicating possible inhibition of EO despite the solvent. In contrast, the combination of EO from *B. calvescens* and *B. milleflora* with the solvent appears to have potentiated the activity of AChE, which had greater activity than the solvent alone. For $LC_{90}$, exposure to the EO of *B. articulata, B. dracunculifolia* enhanced AChE activity compared to solvent alone. Similar results of these products in AChE were observed by Giraldi et al. (2024) when evaluating the toxicity and EO effect of *Drimys brasiliensis* (Winteraceae) on *S. frugiperda* biomarkers.

AChE is the main enzyme responsible for catalyzing acetylcholine in the synaptic cleft. The increase in activity may be linked to the insect's need for detoxification caused by the increase in synaptic activity upon exposure to EOs. To explain this, we suggest two hypotheses: the first is related to the possibility that EOs mimic acetylcholine, and the second is related to changes at the transcriptional level that caused an increase in AChE translation. In contrast, the present research and other studies conducted with different EOs demonstrate that these substances can act as AChE inhibitors in *S. frugiperda*.(de Oliveira et al., 2018; Usseglio et al., 2023; Giraldi et al., 2024), and this bioactivity has already been reported for the species *S. littoralis* and *Spodoptera exígua* (Lepidoptera: Noctuidae) (Chen et al., 2021; Fergani et al., 2020). Inhibition of AChE activity causes continuous transmission of the impulse in the synaptic cleft, leading to hyperexcitability of the nervous system, causing paralysis of the insect's muscular and respiratory system, resulting in its death.(Jankowska et al., 2018; Piri et al., 2020; Usseglio et al., 2023).

In addition to the effects on enzymatic activities, EOs can cause damage at the cellular level through oxidative stress resulting in lipid peroxidation. In our study, we found high levels of lipid peroxidation in *S. frugiperda* larvae exposed to the highest EO exposure concentration of all *Baccharis* species. High levels of plasma membrane damage can lead to cell death. The cascade effect of peroxidation and cell death may explain the mortality of insects at this concentration (Olmedo et al., 2015; Basile et al., 2022), similar lipid peroxidation results were observed by Giraldi et al (2024) in *S. frugirpeda*.

Synthetic insecticides can cause resistance because they have a single mode of action, and another aggravating factor is that they lack selectivity, causing negative consequences for biodiversity. Thus, one of the premises in the search for alternative substances is that these products present high selectivity, and therefore do not cause impacts on beneficial organisms, especially BC agents. Research with botanical extracts of species of the Asteraceae family demonstrated high toxicity against *S. frugiperda* but no negative effects on the development of *T. remus*, suggesting that chemical compounds present in species of this botanical family may present high selectivity with the possibility of being implemented in IPM programs (Tavares et al., 2009).

In this context, our results demonstrated that EOs of *B. calvescens* and *B. milleflora* did not cause mortality in eggs and pupae of *T. remus*, indicating the possibility of combined use of these two methods for the integrated management of this pest. While the synthetic insecticide (Chlorfenapyr) caused mortality of adults before they could parasitize. To date, there are no studies on the impact of EOs on *T. remus*, and this study is the first report. Similar results to those of our research with several EOs were observed for other egg parasitoids *Trichogramma pretiosum* (Hymenoptera: Trichogrammatidae) (Bibiano et al., 2022; Parreira et al., 2019), *Trichogramma galloi* (Hymenoptera: Trichogrammatidae) (La Cruz et al., 2021; Parreira et al., 2018), *Trichogramma embryophagum* (Poorjavad et al., 2014), *Trichogramma evanescens* (Hymenoptera: Trichogrammatidae) (Elbehery and Ibrahim, 2024), *Telenomus podisi* (Hymenoptera: Platygastridae) (Zachrisson et al., 2019) and *Trissolcus urichi* (Hymenoptera: Platygastridae) (Turchen et al., 2016), demonstrating that there is compatibility between these two control strategies for *S. frugiperda*.

Although they do not present insecticidal activity against different stages of *T. remus* development, *Baccharis* EOs have been shown to have a repellent effect on adults and consequently reduced the parasitism capacity of *S. frugiperda* eggs, unlike the synthetic insecticide, which caused the mortality of adult females before they oviposited. The repellent effect of EOs may be related to the presence of monoterpenes, which are aromatic chemical substances with low molecular weight and high volatility. Due to these characteristics, these compounds can be detected by several sensory organs of insects, such as antennae or tarsi (Parreira et al., 2019) and cause a repellent effect on the insect due to interactions in olfactory receptors due to the presence of carbon in hydroxyl groups that can cause electrolytic changes (Nerio et al., 2010).

## 5. Conclusion

EOs of the *Baccharis* genus have insecticidal activity against *S. frugiperda* by contact mode of action, with evidence of action at sites of the nervous system and cause damage by lipid peroxidation. The species *B. calvescens* and *B. milleflora* did not cause mortality in eggs and pupae of *T. remus*, showing selectivity for the natural enemy. However, due to the repellent effect, studies are needed to develop formulations that minimize possible adverse effects on natural enemies or pollinating agents, aiming at the development of commercial botanical insecticides.

## Referências

Abdelgaleil, S.A.M., Al-Nagar, N.M.A., Abou-Taleb, H.K., Shawir, M.S, 2022. Effect of monoterpenes, phenylpropenes and sesquiterpenes on development, fecundity and fertility of *Spodoptera littoralis* (Boisduval). **Int J Trop Insect Sci**, v. 42, p. 245–253. https://doi.org/10.1007/s42690-021-00539-y

Abdelgaleil, S.A.M., Gad, H.A., Ramadan, G.R.M., El-Bakry, A.M., El-Sabrout, A.M., 2021. Monoterpenes: chemistry, insecticidal activity against stored product insects and modes of action—a review. **Int. J. Pest Manag**. https://doi.org/10.1080/09670874.2021.1982067

Adams, R. P., 2007. Identification of Essential Oil Components by Gas Chromatography/ Mass Spectroscopy.

Al-Nagar, N.M.A., Abou-Taleb, H.K., Shawir, M.S., Abdelgaleil, S.A.M., 2020. Comparative toxicity, growth inhibitory and biochemical effects of terpenes and phenylpropenes on *Spodoptera littoralis* (Boisd.). **J. Asia Pac. Entomol.** v. 23, p. 67–75. https://doi.org/10.1016/j.aspen.2019.09.005

Arias, O., Cordeiro, E., Corrêa, A.S., Domingues, F. A., Guidolin, A.S., Omoto, C., 2019. Population genetic structure and demographic history of *Spodoptera frugiperda* (Lepidoptera: Noctuidae): implications for insect resistance management programs. **Pest Manag. Sci**. v. 75, n.11, p. 2948–2957. https://doi.org/10.1002/ps.5407

Awad, M., Hassan, N. N., Alfuhaid, N. A., Amer, A., et al., 2024. Insecticidal and biochemical impacts with molecular docking analysis of three essential oils against *Spodoptera littoralis* (Lepidoptera: Noctuidae). **Crop Protection**, 180. https://doi.org/10.1016/j.cropro.2024.106659

Basaid, K., Chebli, B., Mayad, E.H., Furze, J.N., Bouharroud, R., Krier, F., Barakate, M., Paulitz, T., 2021. Biological activities of essential oils and lipopeptides applied to control plant pests and diseases: a review, **Int. J. Pest Manag**. v. 67, n.2, p. 155-177. https://doi.org/10.1080/09670874.2019.1707327

Basile, S., Badalamenti, N., Riccobono, O., Guarino, S., et al., 2022. Chemical Composition and Evaluation of Insecticidal Activity of *Calendula incana* subsp. maritima and *Laserpitium* *siler* subsp. siculum Essential Oils against Stored Products Pests. **Molecules**, 27, 588. https://doi.org/10.3390/molecules27030588

Beliaeff, B.; Burgeout, T. 2002. Integrated biomarker response: a useful tool for ecological risk assessment. **Env. Toxic. and Chem**. 21:1316– 1322.

Bernal, J. S., Melancon, J. E., Zhu-Salzman, K., 2015. Clear advantages for fall armyworm larvae from feeding on maize relative to its ancestor Balsas teosinte may not be reflected in their mother's host choice. **Entomol Exp Appl**. 155, 206–217. https://doi.org/10.1111/eea.12299

Bibiano, C. S., Alves, D. S., Freire, B. C., Bertolucci, S. K. V., Carvalho, G. A., 2022 Toxicity of essential oils and pure compounds of Lamiaceae species against Spodoptera frugiperda (Lepidoptera: Noctuidae) and their safety for the nontarget organism Trichogramma pretiosum (Hymenoptera: Trichogrammatidae). **Crop Protection**, 158, https://doi.org/10.1016/j.cropro.2022.106011

Bolzan, A., Padovez, F.E.O., Nascimento, A.R.B., Kaiser, I.S., Lira, E.C., Amaral, F.S.A., Kanno, R.H., et al., 2019. Selection and characterization of the inheritance of resistance of *Spodoptera frugiperda* (Lepidoptera: Noctuidae) to chlorantraniliprole and cross-resistance to other diamide insecticides. **Pest Manag. Sci**. v. 75, p. 2682–2689. https://doi.org/10.1002/ps.5376

Campos, A.C.T., Radunz, L.L., Radünz, A.L., Mossi, A.J., Dionello, R.G., 2014. Atividade repelente e inseticida do óleo essencial de carqueja doce sobre o caruncho do feijão. **Rev. Bras. Eng. Agríc. Ambient**. v. 18, n. 8. https://doi.org/10.1590/1807-1929/agriambi.v18n08p861-865

Chaaban, A., Martins, C.E.N., Bretanha, L.C., Micke, G.A., Carrer, A.R., Rosa, N.F., Ferreira, L., Molento, M.B., 2018. Insecticide activity of *Baccharis dracunculifolia* essential oil against *Cochliomyia macellaria* (Diptera: Calliphoridae). **Nat. Prod. Res.** v. 32, n. 24. https://doi.org/10.1080/14786419.2017.1392947

Chaudhari, A.K., Singh, V.K., Kedia, A., Das, S., Dubey, N.K., 2021. Essential oils and their bioactive compounds as eco-friendly novel green pesticides for management of storage insect pests: prospects and retrospects. Environ. Sci. Pollut. Res. 28, 18918–18940.

https://doi.org/10.1007/s11356-021-12841-w

Chen, Y., Luo, J., Zhang, N., Yu, W., Jiang, J., Dai, G., 2021. Insecticidal activities of *Salvia hispanica* L. essential oil and combinations of their main compounds against the beet armyworm *Spodoptera exigua*. **Ind Crops Prod**, v. 162. https://doi.org/10.1016/j.indcrop.2021.113271

Cipriano, R.R., Duarte, M.C.T., Tomazzoli, M.M., Maia, B.H.N.S., Deschamps, C., 2023. Yield, composition and biological activities of *Eugenia uniflora* L. essential oil according to seasonality. **J. Essent. Oil Res**. p. 1–8. https://doi.org/10.1080/10412905.2023.2192210

Colmenarez, Y.C., Babendreier, D., Ferrer Wurst, F.R. et al. The use of T*elenomus remus* (Nixon, 1937) (Hymenoptera: Scelionidae) in the management of *Spodoptera* spp.: potential, challenges and major benefits. CABI Agric Biosci 3, 2022. DOI: https://doi.org/10.1186/s43170-021-00071-6

Cruz, R. A., Parreira, D. S., Dimaté, F. A. R., Batista, L. D. et al., 2021. Effects of essential oils on biological attributes of *Trichogramma galloi* adults. **Journal of Asia-Pacific Entomology**, 24. https://doi.org/10.1016/j.aspen.2021.04.002

de Menezes, C.W.G., Carvalho, G.A., Alves, D.S. et al. Biocontrol potential of methyl chavicol for managing Spodoptera frugiperda (Lepidoptera: Noctuidae), an important corn pest. Environ Sci Pollut Res 27, 5030–5041 (2020). https://doi.org/10.1007/s11356-019-07079-6

de Oliveira, E.R., Alves, D.S., Carvalho, G.A., de Oliveira, B.M.R.G., Aazza, S., Bertolucci, S.K.V., 2018. Toxicity of *Cymbopogon flexuosus* essential oil and citral for *Spodoptera frugiperda*. **Cienc. e Agrotecnologia**, v. 42, p. 408–419. https://doi.org/10.1590/1413-70542018424013918

Dhifi, W., Bellili, S., Jazi, S., Bahloul, N., Mnif, W., 2016. Essential Oils' Chemical Characterization and Investigation of Some Biological Activities: A Critical Review. **Medicines** v. 3, n. 25. https://doi.org/10.3390/medicines3040025

Eccel C, Zimmermann RC, Giraldi GT, et al. 2024. *Baccharis* essential oils from the Atlantic Forest as sources of natural pesticides. Ind Crops Prod 215:118589. https://doi.org/10.1016/j.indcrop.2024.118589

Elbehery, H.H., Ibrahim, S.S., 2024. Potential fumigant toxicity of essential oils against Sitotroga cerealella (Olivier) (Lepidoptera: Gelechiidae) and its egg parasitoid Trichogramma evanescens (Hymenoptera: Trichogrammatidae). **Sci Rep** 14, 6253. https://doi.org/10.1038/s41598-024-56611-3

Ellman, G.L., Courtney, K.D., Andres jr, V., Featherstone , R.M., 1961. A new and rapid colorimetric determination of acetylcholinesterase activity. **Biochem. Pharmacol**. 7, 88–95. https://doi.org/10.1016/0006-2952(61)90145-9

Fergani, Y., Elbanna, H., Hamama, H., 2020. Genotoxicity of Some Plant Essential Oils in Cotton Leafworm, *Spodoptera Littoralis* (Lepidoptera: Noctuidae): the Potential Role of Detoxification Enzymes. **Egypt. J. Zool**. v. 73, p. 53–66. https://doi.org/10.21608/ejz.2020.28358.1029

Fernandes, T.O.M., Queiroz, T.B., Rocha, S.M.G., da Fonseca, F.S.A., Azevedo, A.M., Teixeira, G.L., Martins, E.R., 2021. Seasonal variation in the essential oil from  Jacq. accessions. **Bol. latinoam. Caribe Plantas Med. Aromát**. v. 20, n. 6, p. 672-686. https://doi.org/10.37360/blacpma.21.20.6.48

Filomeno, C.A., Barbosa, L.C.A., Teixeira, R.R., Pinheiro, A.L., Farias, E.S., Silva, E.M.P., Picanço, M.C., 2017. *Corymbia* spp. and *Eucalyptus* spp. essential oils have insecticidal activity against *Plutella xylostella*. **Ind Crops Prod**. v. 109, p. 374–383. https://doi.org/10.1016/j.indcrop.2017.08.033

Garay, J., Brennan, T., Bon, D., 2020. Review: Essential Oils a Viable Pest Control Alternative. **International Journal of Ecotoxicology and Ecobiology**, v. 5, n. 13. https://doi.org/10.11648/j.ijee.20200502.11

Garlet, C.G., Gubiani, P.S., Palharini, R.B., Moreira, R.P., Godoy, D.N., Farias, J.R., Bernardi, O., 2021. Field-evolved resistance to chlorpyrifos by *Spodoptera frugiperda* (Lepidoptera: Noctuidae): Inheritance mode, cross-resistance patterns, and synergism. **Pest Manag. Sci.** v. 77, n. 12, p. 5367-5374. https://doi.org/10.1002/ps.6576

Giraldi, G. T., Amaral, W., Zimmermann, R. C., Mazarotto, E. J. et al. Insecticidal activity, toxicity and biochemical alterations of *Drimys brasiliensis* essential oil against *Spodoptera frugiperda*. **Journal of Pest Science**, 2024. https://doi.org/10.1007/s10340-024-01827-5

Guan, F., Zhang, J., Shen, H., Wang, X., Padovan, A., Walsh, T.K., Tay, W.T., et al., 2020. Whole-genome sequencing to detect mutations associated with resistance to insecticides and Bt proteins in *Spodoptera frugiperda*. **Insect Sci.** v. 28, p. 627–638. https://doi.org/10.1111/1744-7917.12838

Harrison, R.D., Thierfelder, C., Baudron, F., Chinwada, P., Midega, C., Schaffner, U., Van den Berg, J., 2019. Agro-ecological options for fall armyworm (*Spodoptera frugiperda* JE Smith) management: Providing low-cost, smallholder friendly solutions to an invasive pest. **J. Environ. Manage.** v. 243, p. 318-330. https://doi.org/10.1016/j.jenvman.2019.05.011

Hashem, A.S., Awadalla, S.S., Zayed, G.M. et al. Pimpinella anisum essential oil nanoemulsions against Tribolium castaneum—insecticidal activity and mode of action. **Environ Sci Pollut Res** 25, 18802–18812 (2018). https://doi.org/10.1007/s11356-018-2068-1

Hikal, W.M., Baeshen, R.S., Said-Al Ahl, H.A.H., 2017. Botanical insecticide as simple extractives for pest control. **Cogent Biol.** v. 3. https://doi.org/10.1080/23312025.2017.1404274

Hummelbrunner, L.A., Isman, M.B., 2001. Acute, sublethal, antifeedant, and synergistic effects of monoterpenoid essential oil compounds on the tobacco cutworm, *Spodoptera litura* (Lep., Noctuidae). **J. Agric. Food Chem.** v. 49, p. 715–720. https://doi.org/10.1021/jf000749t

Isman, M.B., 2019. Commercial development of plant essential oils and their constituents as active ingredients in bioinsecticides. **Phytochem Rev**. https://doi.org/10.1007/s11101-019-09653-9

Jankowska, M., Rogalska, J., Wyszkowska, J., Stankiewicz, M., 2018. Molecular targets for components of essential oils in the insect nervous system—a review. **Molecules** v. 23, p. 1–20. https://doi.org/10.3390/molecules23010034

Kim, S., Yoon, J., Tak, J.H., 2021. Synergistic mechanism of insecticidal activity in basil and mandarin essential oils against the tobacco cutworm. **J Pest Sci**, v. 94, p. 1119–1131. https://doi.org/10.1007/s10340-021-01345-8

Koyama, S.; Heinbockel, T., 2020. The Effects of Essential Oils and Terpenes in Relation to Their Routes of Intake and Application. **Int. J. Mol. Sci.** v. 21, n. 5. https://doi.org/10.3390/ijms21051558

Kumar, S., Mahapatro, G.K., Yadav, D.K., Tripathi, K., Koli, P., Kaushik, P., Sharma, K., et al., 2022. Essential oils as green pesticides: An overview. **Indian J. Agric. Sci.** v. 92, n. 11, p.1298–130. https://doi.org/10.56093/ijas.v92i11.122746

Lacerda, L. F. et al. Biological basis for adoption of an isoline of *Telenomus remus* (Hymenoptera: Scelionidae) for an augmentative biological-control program for Spodoptera frugiperda (Lepidoptera: Noctuidae). **Journal of Insect Science**, 23, 2023. DOI: https://doi.org/10.1093/jisesa/iead045

Leal, A.L.A.B., Bezerra, C.F., Ferreira e Silva, A.K., da Silva, L.E., Bezerra, L.L., Almeida-Neto, F.W., Marinho, E.M., Fernandes, C.F.C., et al., 2022. Seasonal variation of the composition of essential oils from *Piper cernuum* Vell and *Piper rivinoides* Kunth, ADMET study, DFT calculations, molecular docking and dynamics studies of major components as potent inhibitors of the heterodimer methyltransferase complex NSP16-NSP10 SARS COV-2 protein. **J. Biomol. Struct. Dyn.** https://doi.org/10.1080/07391102.2022.2107072

Liao, M., Xiao, J. J., Zhou, L. J., Yao, X., et al., 2017. Chemical composition, insecticidal and biochemical effects of *Melaleuca alternifolia* essential oil on the *Helicoverpa armigera*. **J App Entomol**, 1 - 8. https://doi.org/10.1111/jen.12397

Mahajan, R. S., Bhamare, V. K. Residual toxicity of insecticides to egg parasitoids of *Spodoptera frugiperda* (J E SMITH). Indian Journal of Entomology, 85, 2023. DOI: https://doi.org/10.55446/IJE.2023.1203

Marchioro, C.A., Foerster, L.A., 2012. Performance of the Wheat Armyworm, *Pseudaletia sequax* Franclemont, on Natural and Artificial Diets. **Neotrop. Entomol.** v. 41, n. 4, p. 288-295. https://doi.org/10.1007/s13744-012-0046-8

Maruthadurai, R., Ramesh, R., 2020. Occurrence, damage pattern and biology of fall armyworm, *Spodoptera frugiperda* (J.E. smith) (Lepidoptera: Noctuidae) on fodder crops and green amaranth in Goa, India. **Phytoparasitica**, v. 48, p. 15–23. https://doi.org/10.1007/s12600-019-00771-w

Mojarab-Mahboubkar, M., Sendi, J. J., Aliakbar, A., 2015. Effect of *Artemisia annua* L. essential oil on toxicity, enzyme activities, and energy reserves of cotton bollworm *Helicoverpa armigera* (Hübner) (Lepidoptera: Noctuidae). **Journal of Plant Protection Research**, 55. https://doi.org/10.1515/jppr-2015-0049

Montezano, D.G., Specht, A., Sosa-Gómez, D.R., Roque-Specht, V.F., Sousa-Silva, J.C., Paula-Moraes, S.V., Peterson, J.A., et al., 2018. Host plants of *Spodoptera frugiperda* (Lepidoptera: Noctuidae) in the Americas. **Afr Entomol**. v. 26, n. 2, p. 286 – 300. https://doi.org/10.4001/003.026.0286

Moustafa, M.A.M., Awad, M.; Amer, A., Hassan, N.N., Ibrahim, E.-D.S., Ali, H.M., Akrami, M., Salem, M.Z.M., 2021. Insecticidal Activity of Lemongrass Essential Oil as an Eco-Friendly Agent against the Black Cutworm Agrotis ipsilon (Lepidoptera: Noctuidae). **Insects**, 12, 737. https://doi.org/10.3390/insects12080737

Moustafa, M.A.M., Hassan, N.N., Alfuhaid, N. A., Amer, A. et al., 2023. Insights into the toxicity, biochemical activity, and molecular docking of *Cymbopogon citratus* essential oils and citral on *Spodoptera littoralis* (Lepidoptera: Noctuidae). **Journal of Economic Entomology**, 116. https://doi.org/10.1093/jee/toad093

Muraro, D.S., Abbade Neto, D.O., Kanno, R.H., Kaiser, I.S., Bernardi, O., Omoto, C., 2021. Inheritance patterns, cross-resistance and synergism in *Spodoptera frugiperda* (Lepidoptera: Noctuidae) resistant to emamectin benzoate. **Pest Manag. Sci.** v. 77, n. 11, p. 5049-5057. https://doi.org/10.1002/ps.6545

Murúa, M. G., Vera, M. A., Michel, A., Casmuz, A. S., Fatoretto, J., Gastaminza, G., 2019. Performance of field-collected *Spodoptera frugiperda* (Lepidoptera: Noctuidae) strains exposed to different transgenic and refuge maize hybrids in Argentina. **J. Insect Sci.** v. 19, n. 6, 21. https://doi.org/10.1093/jisesa/iez110

Nerio L. S., Olivero-Verbel, J., Stashenko, E. Repellent activity of essential oils: a review. Bioresour Technol. 101, 372-8. https://doi.org/10.1016/j.biortech.2009.07.048.

Nurnina, N., Muis, A., 2022. Egg laying and damage by fall armyworm, *Spodoptera frugiperda* J. E Smith on maize variety HJ 21 at screen house. **IOP Conference Series**: Earth and Environmental Science, 1107. https://doi.org/10.1088/1755-1315/1107/1/012005

Okuma, D.M., Bernardi, D., Horikoshi, R.J., Bernardi, O., Silva, A.P., Omoto, C., 2018. Inheritance and fitness costs of *Spodoptera frugiperda* (Lepidoptera: Noctuidae) resistance to spinosad in Brazil. **Pest Manag. Sci.** v. 74, p. 1441–1448. https://doi.org/10.1002/ps.4829

Oliveira, N.C., Rodrigues, P.A.P., Cônsoli, F.L., 2023. Host-Adapted Strains of *Spodoptera frugiperda* Hold and Share a Core Microbial Community Across the Western Hemisphere. **Microbial Ecology**, v.85, n. 4, p.1552-1563. https://doi.org/10.1007/s00248-022-02008-6

Olmedo, R., Herrera, J. M., Lucini, E . I., Zunino, M. P. et al., 2015. Aceite esencial de *Tagetes filifolia* contra *Tribolium castaneum* y su relación con la actividad acetilcolinesterasa y peroxidación de lípidos. **AgriScientia**, 32. https://doi.org/10.31047/1668.298x.v32.n2.16562

Parra, J.R.P. Técnicas de criação de insetos para programas de controle biológico. Piracicaba, ESALQ/FEALQ, 137p. 2001.

Parreira, D.S., Alcántara-de la Cruz, R., Zanuncio, J.C. et al., 2018. Essential oils cause detrimental effects on biological parameters of Trichogramma galloi immatures. J Pest Sci 91, 887–895. https://doi.org/10.1007/s10340-017-0945-x

Parreira, D. S., Alcántara-de la Cruz, R. , Dimaté, F. A. R., Batista, L. D., Ribeiro, R. C., Ferreira, G. A. R., Zanuncio, J. C. 2019. Bioactivity of tem essential oils on the biological parameters of *Trichogramma pretiosum* (Hymenoptera: Trichogrammatidae) adults. **Industrial Crops and Products**, v. 127 – 11 - 15. https://doi.org/10.1016/j.indcrop.2018.10.063

Pinheiro, L.S., Gatti, V.C.M., de Oliveira, J.T., da Silva, J.N., Silva, V.F.A., Silva, P.A., 2021. Características agro econômicas do milho: uma revisão. **Natural Resources**, v.11, n.2, p.13-21. http://doi.org/10.6008/CBPC2237-9290.2021.002.0003

Piri, A., Sahebzadeh, N., Zibaee, A., Sendi, J.J., Shamakhi, L., Shahriari, M., 2020. Toxicity and physiological effects of ajwain (*Carum copticum*, Apiaceae) essential oil and its major constituents against *Tuta absoluta* (Meyrick) (Lepidoptera: Gelechiidae). **Chemosphere**, v. 256. https://doi.org/10.1016/j.chemosphere.2020.127103

Poorjavad, N., Goldansaz, S.H., Dadpour, H. et al., 2014 Effect of Ferula assafoetida essential oil on some biological and behavioral traits of Trichogramma embryophagum and T. evanescens. **BioControl** 59, 403–413. https://doi.org/10.1007/s10526-014-9583-x

Ruttanaphan, T., Pluempanupat, W., Aungsirisawat, C., Boonyarit, P., et al., 2019. Effect of Plant Essential Oils and Their Major Constituents on Cypermethrin Tolerance Associated

Detoxification Enzyme Activities in *Spodoptera litura* (Lepidoptera: Noctuidae), **Journal of Economic Entomology**, 112. https://doi.org/10.1093/jee/toz126

Saran, A., fernández, L., minig, M., reinhard, M.B., merini, L.J. 2019. Repellent activity of essential oils from native plants and their blend for *Tribolium castaneum* control in store grains. **Semiárida UNLPam**. v. 29, p. 43-51. https://doi.org/10.19137/semiarida.2019(01).43-51

Silva de Assis, H. C., 1998. **Der einsatz von biomarkern zur summarischen erfassung von Gewässerverschmutzungen**. 99 f. 1998. Tese de Doutorado apresentada na Universidade Técnica de Berlim, Alemanha.

Silveira, R.M., Carvalho, A.F.U., Bünger, M.O., Gomes, M.M., da Costa, I.R, 2022. How Much do the Environmental Conditions Interfere with the Essential Oils of *Eugenia* spp. L. (Myrtaceae)? **J. Braz. Chem. Soc.** v. 33, n. 3, p. 274-280. https://doi.org/10.21577/0103-5053.20210146

Souza, M.T., Souza, M.T., Bernardi, D., Melo, D.J., Zarbin, P.H.G., Zawadneak, M.A.C., 2021. Insecticidal and oviposition deterrent efects of essential oils of *Baccharis* spp. and histological assessment against *Drosophila suzukii* (Diptera: Drosophilidae). **Sci. Rep.** v. 11. https://doi.org/10.1038/s41598-021-83557-7

Tavares, W. S., Cruz, I., Petacci, F., Assis Júnior, S. L., et al., 2009. Potential use of Asteraceae extracts to control *Spodoptera frugiperda* (Lepidoptera: Noctuidae) and selectivity to their parasitoids *Trichogramma pretiosum* (Hymenoptera: Trichogrammatidae) and *Telenomus remus* (Hymenoptera: Scelionidae). **Industrial Crops and Products**, 30. https://doi.org/10.1016/j.indcrop.2009.07.007

Tunç, I., Erler, F., Dagli, F., Çalis, Ö., 1997. Insecticidal activity of acetone vapours. **Journal of Stored Products Research**,33. https://doi.org/10.1016/S0022-474X(96)00021-5

Turchen, L.M., Piton, L.P., Dall'Oglio, E.L. et al. Toxicity of Piper aduncum (Piperaceae) Essential Oil Against Euschistus heros (F.) (Hemiptera: Pentatomidae) and Non-Effect on Egg Parasitoids. **Neotrop Entomol** 45, 604–611 (2016). https://doi.org/10.1007/s13744-016-0409-7

Usseglio, V.L., Dambolena, J.S., Zunino, M.P., 2023. Can Essential Oils Be a Natural Alternative for the Control of *Spodoptera frugiperda*? A Review of Toxicity Methods and Their Modes of Action. **Plants**, v. 12, n. 1. https://doi.org/10.3390/plants12010003

Velasques, J., Cardoso, M.H., Abrantes, G., Frihling, B.E., Franco, O.L., Migliolo, L., 2017. The rescue of botanical insecticides: A bioinspiration for new niches and needs. **Pestic Biochem Physiol**. http://dx.doi.org/10.1016/j.pestbp.2017.10.003

Wang Y, Zhang LT, Feng YX, Zhang D, Guo SS, Pang X, Geng ZF, Xi C, Du SS (2019) Comparative evaluation of the chemical composition and bioactivities of essential oils from four spice plants (Lauraceae) against stored- product insects. **Ind. Crops Prod**. 140: 111640 https://doi.org/10.1016/j.indcrop.2019.111640

Zachrisson, B., Santana, A., Gupta, M. Effects of Essential Oils from Two Species of Piperaceae on Parasitized and Unparasitized Eggs of *Oebalus insularis* (Heteroptera: Pentatomidae) by *Telenomus podisi* (Hymenoptera: Platygastridae). **Natural Product Communications**, 2019. https://doi.org/10.1177/1934578X1901400122

Zimmermann, R.C., Aragão, C.E.C., de Araújo, P.J.P., Benatto, A., Chaaban, A., Martins, C.E.N., do Amaral, W., et al., 2021. Insecticide activity and toxicity of essential oils against two stored-product insects. **Crop Prot.** v. 144. https://doi.org/10.1016/j.cropro.2021.105575

## CONCLUSÃO GERAL

Devido à grande biodiversidade de plantas nativas encontradas na Floresta Atlântica, é possível encontrar moléculas a partir da extração de metabólitos secundários, que expressam grande potencial de controle de pragas agrícolas. Os óleos essenciais (OEs) das plantas nativas da Floresta Atlântica estudadas nesse trabalho, apresentaram potencial inseticida para o controle de *S. frugiperda.*

Descobrimos que o OE de *D. brasiliensis* e o OE de *E. muticus* exibem potencial significativo no controle de *S. frugiperda,* devido à sua toxicidade e seus efeitos em diferentes mecanismos relacionados a enzimas de biotransformação, enzimas do sistema nervoso, além de causar danos a biomoléculas.

Os OEs do gênero *Baccharis* também apresentaram atividade inseticida para *S. frugiperda*, com evidências de ação em sítios do sistema nervoso e causaram danos por peroxidação lipídica. Além disso, as espécies *B. calvescens* e *B. milleflora* apresentaram seletividade para o parasitoide de ovos *T. remus*.

Observamos que todos os OEs testados nessa pesquisa apresentaram potencial inseticida, e isso aponta para uma tendência, em que esses OEs sejam alternativas promissoras aos inseticidas sintéticos em programas de manejo de *S. frugiperda*. No entanto, mais estudos voltados para formulações, viabilidade econômica e segurança ambiental se fazem necessários, visando o desenvolvimento de inseticidas botânicos comerciais.

## CONSIDERAÇÕES FINAIS

O uso de substâncias naturais na agricultura, foi o precursor da maioria dos estudos voltados para a fitossanidade, pois desde que o homem deixou de ser nômade, surtos de pragas e doenças são comuns no meio agrícola. O uso de óleos essenciais (OEs) no controle de pragas agrícolas tem potencial para integrar-se a sistemas de manejo de pragas, tanto na agricultura convencional, quanto na agricultura orgânica e agroecológica, promovendo um controle mais sustentável e de menor impacto ambiental.

Esse estudo é entendido como um estudo de base, ao que também podemos chamar de pesquisa básica, onde identificamos, a partir de OEs extraídos de plantas nativas da Floresta Atlântica, substâncias que apresentam elevado potencial inseticida, no entanto, sabemos que os OEs são compostos que, na sua essência, apresentam alta volatilidade, e esse, atualmente, é um dos grandes entraves de estudos e pesquisas utilizando OEs em situações de campo.

Dada essa limitação, sugerimos que futuras pesquisas se concentrem no desenvolvimento de tecnologias que aumentem a estabilidade dos OEs e prolonguem sua atividade no ambiente. Entre as estratégias promissoras, estão a incorporação dos óleos essenciais em emulsões ou em sistemas de micro e nanoencapsulados. Essas técnicas podem encapsular as moléculas dos OEs em estruturas que limitam a volatilidade e protegem o composto ativo das condições externas, garantindo uma liberação controlada e prolongada, além disso, a nanoencapsulação permite direcionar o OE para locais específicos, o que pode otimizar o efeito inseticida e reduzir a quantidade de produto utilizado.

Outro ponto que consideramos relevante para que os avanços se traduzam em alternativas viáveis no que diz respeito à utilização dos OEs no setor agrícola, são os estudos de viabilidade econômica. É necessário avaliar o custo-benefício do uso dos óleos essenciais em larga escala, visto que a produção e o processamento dos OEs, assim como o desenvolvimento das tecnologias de dispersão, exigem investimentos que devem ser analisados frente à eficácia, durabilidade e à aceitação dos produtos pelo mercado.

Adicionalmente, para garantir a segurança ambiental e a sustentabilidade dos OEs a longo prazo, faz-se necessário que futuras pesquisas avaliem o impacto dos OEs nas cadeias tróficas e nos ecossistemas em que serão aplicados. Nesses estudos, seria importante considerar os efeitos dos OEs e seus compostos encapsulados sobre organismos não-alvo, incluindo inimigos naturais, polinizadores e outros elos essenciais das redes tróficas.

Por fim, ressaltamos que estudos visando a interação entre a segurança ecológica e a eficácia dos OEs contribuirão para soluções agrícolas que respeitem tanto a saúde ambiental quanto a eficiência produtiva.

## REFERÊNCIAS BIBLIOGRÁFICAS


ABDELGALEIL, S. A. M., GAD, H. A., RAMADAN, G. R. M., EL-BAKRY, A. M., EL-SABROUT, A. M. Monoterpenes: chemistry, insecticidal activity against stored product insects and modes of action—a review. **Int. J. Pest Manag**. 2021. https://doi.org/10.1080/09670874.2021.1982067

ABDELGALEIL, S.A.M., AL-NAGAR, N.M.A., ABOU-TALEB, H.K., SHAWIR, M.S Effect of monoterpenes, phenylpropenes and sesquiterpenes on development, fecundity and fertility of *Spodoptera littoralis* (Boisduval). **Int J Trop Insect Sci**, v. 42, 2022. https://doi.org/10.1007/s42690-021-00539-y

ABDOUL-LAFIT, F. M., AINANE, A., ABDOUL-LAFIT, T. M., AINANE, T. Chemical study and evaluation of insectical properties of African *Lippia citriodora* essential oil. **Journal of Biopesticides** 13: 2020.

ADAMS, R. P. Identification of Essential Oil Components by Gas Chromatography/ Mass Spectroscopy. 4th ed., Carol Stream: Allured Publishing, 2007. 804 p.

ADORJAN, B., BUCHBAUER, G. Biological properties of essential oils: an updated review. **Flavour Fragr. J**. 25, 2010. https://doi.org/10.1002/ffj.2024

AHMAD, S., PARDINI, R.S., 1990. Mechanisms for regulating oxygen toxicity in phytopha gous insects. **Free Radic. Biol. Med**. 8, 401–413.

AINANE, A., ABDOUL-LAFIT, F. M., ABDOUL-LAFIT, T. M., AINANE, T. Evaluation of biological activities of two essential oils as a safe environmental bioinsecticides: case of *Eucalyptus globulus* and *Rosmarinus officinalis*. Scientific Review – Engineering and Environmental Sciences 29: 2020. https://doi.org/10.22630/PNIKS.2020.29.4.47

ALAM, S. B., DIB, M. E. A., DJABOU, N., TABTI, B., BENYELLES, N. G., COSTA, J., MUSELLI, A. Essential Oils as Biocides for the Control of Fungal Infections and Devastating Pest (*Tuta absolute*) of Tomato (*Lycopersicon esculentum* Mill.). **Chem. Biodiversity** 4. 2017. https://doi.org/10.1002/cbdv.201700065

ALCÂNTARA, P.B. & BUFARAH, G. 1982. Plantas forrageiras: gramíneas & leguminosas. 1 ed., Nobel, São Paulo.

AL-GHANIM, K. A., KRISHNAPPA, K., PANDIYAN, J., NICOLETTI, M. et al. Insecticidal Potential of *Matricaria chamomilla's* Essential Oil and Its Components (E)--Farnesene, Germacrene D, and-Bisabolol Oxide A against Agricultural Pests, Malaria, and Zika Virus Vectors. **Agriculture** 2023, 13, 779. https://doi.org/10.3390/agriculture13040779

AL-NAGAR, N.M.A., ABOU-TALEB, H.K., SHAWIR, M.S., ABDELGALEIL, S.A.M. Comparative toxicity, growth inhibitory and biochemical effects of terpenes and phenylpropenes on *Spodoptera littoralis* (Boisd.). **J. Asia Pac. Entomol.** v. 23, 2020. https://doi.org/10.1016/j.aspen.2019.09.005

AMARAL, W., DESCHAMPS, C., BIZZO, H. R., PINTO, M. A. S., BIASI, L. A., SILVA, L. E. Essential Oil Yield and Composition of Native Tree Species from Atlantic Forest, South of Brazil. **J. Essent. Oil-Bear**. 20, 2017. https://doi.org/10.1080/0972060X.2017.1346484

AMOABENG, B.W., JOHNSON, A.C., GURR, G.M. Natural enemy enhancement and botanical insecticide source: a review of dual use companion plants. Appl. Entomol. Zool. 2019. https://doi.org/10.1007/s13355-018-00602-0

ANEC - Associação Nacional dos Exportadores de Cereais – Brasil em destaque: **Rumo ao recorde para as exportações de soja e milho**. Disponível em: https://periodicos.fgv.br/agroanalysis/article/view/90110/84578 Acesso em: 18 set. 2024.

ANESE, S., GAMBARRA, W. P. T., GRISI, P. U., GUALTIERI, S. C. J. Insecticidal action of *Drimys brasiliensis* Miers on black citrus aphid. **Rev. Ciênc. Agron**. 49, 2018. https://doi.org/10.5935/1806-6690.20180055

ARIAS, O., CORDEIRO, E., CORRÊA, A.S., DOMINGUES, F. A., GUIDOLIN, A.S., OMOTO, C. Population genetic structure and demographic history of *Spodoptera frugiperda* (Lepidoptera: Noctuidae): implications for insect resistance management programs. **Pest Manag. Sci**., 75, 2019. https://doi.org/10.1002/ps.5407

AUNGTIKUN, J., SOONWERA, M., SITTICHOK, S. Insecticidal synergy of essential oils from *Cymbopogon citratus* (Stapf.), *Myristica fragrans* (Houtt.), and *Illicium* *verum* Hook. f. and their major active constituents. **Ind. Crops Prod**. 164, 2021. https://doi.org/10.1016/j.indcrop.2021.113386

AWAD, M., HASSAN, N. N., ALFUHAID, N. A., AMER, A., et al. Insecticidal and biochemical impacts with molecular docking analysis of three essential oils against *Spodoptera littoralis* (Lepidoptera: Noctuidae). **Crop Protection**, 180, 2024. https://doi.org/10.1016/j.cropro.2024.106659

BARBEHENN, R. V. Gut-based antioxidant enzymes in a polyphagous and a graminivorous grasshopper. **J Chem Ecol**. 28, 2002. https://doi.org/10.1023/a:1016288201110

BABENDREIER, D., AGBOYI, L. K., BESEH, P., OSAE, M. et al. The E cacyofAlternative, Environmentally Friendly Plant Protection Measures for Control of Fall Armyworm, *Spodoptera frugiperda*, in Maize. **Insects**, 11, 2020. https://doi.org/10.3390/insects11040240

BAI, L., JIAO, M. L., ZANG, H. Y., GUO, S. S., WANG, Y., SANG, Y. L., DU, S. S. Chemical composition of essential oils from four *Rhododendron* species and their repellent activity against three stored-product insects. **Environ Sci Pollut Res**. 26, 2019. https://doi.org/10.1007/s11356-019-05577-1

BAI, Y., LIU, X., BALDWIN, I. T. Using Synthetic Biology to Understand the Function of Plant Specialized Metabolites. **Annual Review of Plant Biology**, 75, 2024. https://doi.org/10.1146/annurev-arplant-060223-013842

BAKKALI, F., AVERBECK, S., AVERBECK, D., IDAOMAR, M. Biological effects of essential oils – a review. **Food Chem Toxicol.**, 46, 2008. https://doi.org/10.1016/j.fct.2007.09.106.

BARROS, E.M.; TORRES, J.B.; BUENO, A.F. Oviposition, Development and Reproduction of *Spodoptera frugiperda* (J.E.Smith) (Lepidoptera: Noctuidae) Fedo n Differents Hosts of Economic Importance. **Neotropical Entomology**, v. 39, 2010. DOI: https://doi.org/10.1590/S1519-566X2010000600023

BASAID, K., CHEBLI, B., MAYAD, E.H., FURZE, J.N. et al. Biological activities of essential oils and lipopeptides applied to control plant pests and diseases: a review, **Int. J. Pest Manag.**, 67, 2021. https://doi.org/10.1080/09670874.2019.1707327

BASILE, S., BADALAMENTI, N., RICCOBONO, O., GUARINO, S., et al., Chemical Composition and Evaluation of Insecticidal Activity of *Calendula incana* subsp. maritima and *Laserpitium siler* subsp. siculum Essential Oils against Stored Products Pests. **Molecules**, 2022, 27, 588. https://doi.org/10.3390/molecules27030588

BATISTA, C. B.; DE LIMA, I. P.; ARRUDA, R.; LIMA, M. R. Downscaling the Atlantic Forest biodiversity hotspot: Using the distribution of bats to find smaller hotspots with conservation priority. **Biological Conservation**, 263, 2021. DOI: https://doi.org/10.1016/j.biocon.2021.109331

BARLOW, J. et al. Anthropogenic disturbance in tropical forests can double biodiversity loss from deforestation. **Nature**, 535, 2016. DOI: https://doi.org/10.1038/nature18326

BARROS, E. M., TORRES, J. B., BUENO, A. F. Oviposition, development and reproduction of *Spodoptera frugiperda* (JE Smith) (Lepidoptera: Noctuidae) fed on different hosts of economic importance. **Neotrop. Entomol**. 39, 2010. https://doi.org/10.1590/S1519-566X2010000600023

BENELLI, G.; PAVELA, R.; PETRELLI, R.; CAPPELLACCI, L. et al. The essential oil from industrial hemp (*Cannabis sativa* L.) by-products as an effective tool for insect pest management in organic crops. **Industrial and Crops Products**, v. 122, 2018. https://doi.org/10.1016/j.indcrop.2018.05.032

BENELLI, G., PAVELA, R., MAGGI, F., WANDJOU, J. G. N. et al. Insecticidal activity of the essential oil and polar extracts from *Ocimum gratissimum* grown in Ivory Coast: Efficacy on insect pests and vectors and impact on non-target species. **Industrial Crops and Products**, 132, 2019. https://doi.org/10.1016/j.indcrop.2019.02.047

BENELLI, G., PAVONI, L., ZENI, V., RICCIARDI, R., COSCI, F., CACOPARDO, G., GENDUSA, S. Developing a Highly Stable *Carlina acaulis* Essential Oil Nanoemulsion for Managing *Lobesia botrana*. **Nanomaterials** 10, 2020. https://doi.org/10.3390/nano10091867

BERNAL, J. S., MELANCON, J. E., ZHU-SALZMAN, K. Clear advantages for fall armyworm larvae from feeding on maize relative to its ancestor Balsas teosinte may not be reflected in their mother's host choice. **Entomol Exp Appl**. 155, 2015. https://doi.org/10.1111/eea.12299

BESTEN, A. M., NUNES, D. S., GRANATO, D., SENS, S. L., WISNIEWSKI, A., SIMIONATTO, E. L., SCHARF, D. R. Chemical Composition of Essential Oils from Cladodes and Inflorescences from Male and Female Specimens of *Baccharis milleflora*. **J. Essent. Oil-Bear**. 2014 .https://doi.org/10.1080/0972060X.2014.890078

BHATTACHARYA, S. Cultivation of Essential Oils (2016). In: **Essential Oils in Food Preservation, Flavor and Safety**, Ed: Preedy, V.R. Elsevier, 2016.

BHUSAL, S., CHAPAGAIN, E. Threats of fall armyworm (*Spodoptera frugiperda*) incidence in Nepal and it's integrated management-A review. **Journal of Agriculture and Natural Resources**, 3, 2020. https://doi.org/10.3126/janr.v3i1.27186

BIBIANO, C. S., ALVES, D. S., FREIRE, B. C., BERTOLUCCI, S. K. V., CARVALHO, G. A. Toxicity of essential oils and pure compounds of Lamiaceae species against *Spodoptera frugiperda* (Lepidoptera: Noctuidae) and their safety for the nontarget organism *Trichogramma pretiosum* (Hymenoptera: Trichogrammatidae). **Crop Protection**, 158, 2022. https://doi.org/10.1016/j.cropro.2022.106011

BOLZAN, A.; PADOVEZ, F.O.E.; NASCIMENTO, A.R.B.; KAISER, I.S. et al. Selection and characterization of the inheritance of resistance of *Spodoptera frugiperda* (Lepidoptera: Noctuidae) to chlorantraniliprole and cross-resistance to Other diamide insecticides. **Pest Management Science**, v. 75, 2019. https://doi.org/10.1002/ps.5376

BORGES, L.P.; AMORIM, V.A. Secondary Plant Metabolites. **Revista Agrotecnologia**, v.11, 2020.

BRADFORD, M. M. A Rapid and Sensitive Method for the Quantitation of Microgram Quantities of Protein Utilizing the Principle of Protein-Dye Binding. Anal. Biochem. 72, 1976. https://doi.org/10.1006/abio.1976.9999.

BURTET, L. M.; BERNARDI, O.; MELO, A.A.; PES, M.P. et al. Managing fall armyworm, *Spodoptera frugiperda* (Lepidoptera: Noctuidae), with Bt maize and insecticides in Southern Brazil. **Pest Management Science**, v. 73, 2017. https://doi.org/10.1002/ps.4660

CACCIABUE, M. et al. *Elionurus muticus* from north of Argentina: evaluation of the antibacterial activity of three essencial oil chemotypes. **Biocell**, 29 2005.

CÂMARA, I. G. **Breve história da conservação da Mata Atlântica**. In: Galindo-Leal, C.; Câmara, I.G. (eds.). Mata Atlântica: biodiversidade, ameaças e perspectivas. Fundação SOS Mata Atlântica/Conservação Internacional, São Paulo/Belo Horizonte. p. 31-42, 2005.

CAMPOLO, O., PUGLISI, I., BARBAGALLO, R. N., CHERIF, A. et al. Side effects of two citrus essential oil formulations on a generalist insect predator, plant and soil enzymatic activities. **Chemosphere**, 257, 2020. https://doi.org/10.1016/j.chemosphere.2020.127252

CAMPOS, A.C.T., RADUNZ, L.L., RADÜNZ, A.L., MOSSI, A.J., DIONELLO, R.G. Atividade repelente e inseticida do óleo essencial de carqueja doce sobre o caruncho do feijão. **Rev. Bras. Eng. Agríc. Ambient**., 18, 2014. https://doi.org/10.1590/1807-1929/agriambi.v18n08p861-865

CANTÓ-TEJERO, M., CASAS, J. L., MARCOS-GARCÍA, M. A., PASCUAL-VILLALOBOS, M. J. et al. Essential oils-based repellents for the management of *Myzus persicae* and *Macrosiphum euphorbiae*. **Journal of Pest Science**, 95, 2022. https://doi.org/10.1007/s10340-021-01380-5

CARVALHO, R. A., OMOTO, C., FIELD, L. M., WILLIAMSON, M. S., BASS, C. Investigating the molecular mechanisms of organophosphate and pyrethroid resistance in the fall armyworm *Spodoptera frugiperda*. PLOS ONE, 8, 2013. https://doi.org/10.1371/journal.pone.0062268

CASSEL, E., VARGAS, R.M.F., MARTINEZ, N., LORENZO, D., DELLACASS, E. Steam distillation modeling for essential oil extraction process. **Industrial and Crops Products**, v. 29, 2009. https://doi.org/10.1016/j.indcrop.2008.04.017

CASTELO BRANCO, A.F.V.; LIMA, P.V.P.S.; MEDEIROS FILHO, E.S. et al. Avaliação da perda da biodiversidade na Mata Atlântica. **Ciência Florestal**, v. 31, 2021. https://doi.org/10.5902/1980509853310

CASTRO, P. R. C.; KLUGE, R. A.; PERES, L. E. P. **Manual de fisiologia vegetal** (teoria e prática). Ed. Agronomica Ceres, Piracicaba, 2005. 650p.

CASTRO, Y. C., ROJAS, C. G., CEDEÑO, C. V., VELÁSQUEZ, V. V. Development of a laboratory rearing methodology for the corn worm *Spodoptera frugiperda* (Smith) (Lepidoptera: Noc tuidae) as a possible host for bio-controller insects of agricultural interest. **Tecnología en marcha**, 22, 2009.

CELAYA, L.S., LE VRAUX, M.A., HEIT, C. I., VITURRO, C.I., MARTINA, P. F. Phytochemical and Biological Profile of Essential Oils of *Elionurus muticus* (Spreng.) Growing in Northeastern Argentina. Chem. Biodiversity 20, 2023. doi: https://doi.org/10.1002/cbdv.202201105

CHAABAN, A., MARTINS, C.E.N., BRETANHA, L.C., MICKE, G.A. et al. Insecticide activity of *Baccharis dracunculifolia* essential oil against *Cochliomyia macellaria* (Diptera: Calliphoridae). **Nat. Prod. Res.**, 32, 2018. https://doi.org/10.1080/14786419.2017.1392947

CHAGONDA, L.S., MAKANDA, C., CHALCHAT, J.C. The essential oils of wild and cultivated *Cymbopogon validus* (Stapf) Stapf ex Burtt Davy and *Elionurus muticus* (Spreng.) Kunth from Zimbabwe. Flavour Fragr. J. 15, 2000. https://doi.org/10.1002/(SICI)1099-1026(200003/04)15:2<100::AID-FFJ874>3.0.CO;2-Y

CHASE, M.A. Primeiro livro de gramíneas: noções sobre a estrutura com exemplos da flora brasileira. 1 ed., Instituto de Botânica, São Paulo. 1991.

CHAUDHARI, A.K., SINGH, V.K., KEDIA, A., DAS, S., DUBEY, N.K. Essential oils and their bioactive compounds as eco-friendly novel green pesticides for management of storage insect pests: prospects and retrospects. Environ. Sci. Pollut. Res. 28, 2021. https://doi.org/10.1007/s11356-021-12841-w

CHEN, Y., LUO, J., ZHANG, N., YU, W., JIANG, J., DAI, G. Insecticidal activities of *Salvia hispanica* L. essential oil and combinations of their main compounds against the beet armyworm *Spodoptera exigua*. **Ind Crops Prod**, 162, 2021. https://doi.org/10.1016/j.indcrop.2021.113271

CHEN, Y.; NGUYEN, D.T.; SPAFFORD, H.; HERRON, G.A. A high-throughput multilocus-amplicon sequencing panel to monitor insecticide resistance in fall armyworm (FAW) *Spodoptera frugiperda* (Lepidoptera:Noctuidae). **Pest Management Science**, v. 80, 2024. https://doi.org/10.1002/ps.7883

CHIZZOLA, R. **Regular Monoterpenes and Sesquiterpenes (Essential Oils)**. In: Ramawat, K., Mérillon, JM. (eds) Natural Products. Springer, Berlin, Heidelberg. 2013. https://doi.org/10.1007/978-3-642-22144-6_130

CIPRIANO, R.R., DUARTE, M.C.T., TOMAZZOLI, M.M., MAIA, B.H.N.S., DESCHAMPS, C. Yield, composition and biological activities of *Eugenia uniflora* L. essential oil according to seasonality. **J. Essent. Oil Res.**, 35, 2023. https://doi.org/10.1080/10412905.2023.2192210

COÊLHO, Jackson Dantas. MILHO: v. 9, n. 342, junho, 2024. **Caderno Setorial ETENE**, Fortaleza, v. 9, n. 343, 2024. Disponível em: https://www.bnb.gov.br/revista/cse/article/view/2728. Acesso em: 5 ago. 2024.

COLMENAREZ, Y.C., BABENDREIER, D., FERRER WURST, F.R. et al. The use of T*elenomus remus* (Nixon, 1937) (Hymenoptera: Scelionidae) in the management of *Spodoptera* spp.: potential, challenges and major benefits. CABI Agric Biosci 3, 2022. DOI: https://doi.org/10.1186/s43170-021-00071-6

COLPO, J. F., JAHNKE, S.M., FÜLLER, T. Potencial inseticida de óleos de origem vegetal sobre *Grapholita molesta* (Busck) (Lepidoptera: Tortricidae). Rev. Bras. Pl. Med., Campinas, 16(2), 182-188, 2014. https://doi.org/10.1590/S1516-05722014000200003

CONAB - COMPANHIA NACIONAL DE ABASTECIMENTO. Acompanhamento da safra brasileira de grãos 2023/2024. 6º. Levantamento. Disponível em: https://www.conab.gov.br/info-agro/safras/graos Acesso em: 18/09/2024.

CORTEZ-VEGA, A., JOFRÉ-BARUD, F., ANDINO, N., GÓMEZ, M. P., LÓPEZ, M. L. Toxicological interactions between spinosad and essential oils in the Mediterranean fruit fly, *Ceratitis capitata*. **J App Entomol** 147, 2023. https://doi.org/10.1111/jen.13175

CRESCENTE, G., BOUYMAJANE, A., CASCONE, G., SQUILLACI, G. et al. Essential Oils: An Overview of Extraction Methods and Food Applications. Curr. Nutraceuticals, 4, 2023. https://doi.org/10.2174/2665978604666230601104713

CROTEAU, R.; KUTCHAN, T. M.; LEWIS, N.G. Natural Products – Secondary Metabolites. In: **Biochemistry & Molecular Biology of Plants**, B. Buchanan, W. Gruissem, R. Jones, Eds. 2000, American Society of Plant Physiologists.

CRUZ, I., FIGUEIREDO, M., SILVA, R. B., SILVA, I. F., PAULA, C. S., FOSTER, J. E. Using sex pheromone traps in the decision-making process for pesticide application against fall armyworm (*Spodoptera frugiperda*) (Smith) (Lepidoptera: Noctuidae) larvae in maize. **Int. J. Pest Manag**. 58, 2012. https://doi.org/10.1080/09670874.2012.655702

CRUZ, B. P., CASTRO, E. M., CARDOSO, M. G., SOUZA, K. F., et al. Comparison of leaf anatomy and essential oils from *Drimys brasiliensis* Miers in a montane cloud forest in Itamonte, MG, Brazil. Botanical Studies 55: 2014. https://doi.org/10.1186/s40529-014-0041-y

CRUZ, R. A., PARREIRA, D. S., DIMATÉ, F. A. R., BATISTA, L. D. et al. Effects of essential oils on biological attributes of *Trichogramma galloi* adults. **Journal of Asia-Pacific Entomology**, 24, 2021. https://doi.org/10.1016/j.aspen.2021.04.002

CUARTAS, P., BARRERA, G., BARRETO, E., VILLAMIZAR, L. Characterisation of a Colombian granulovirus (Baculoviridae: Betabaculovirus) isolated from *Spodoptera frugiperda* (Lepidoptera: Noctuidae) larvae. **Biocontrol Sci. Technol**. 24, 2014. https://doi.org/10.1080/09583157.2014.933312

DAWAR, K., KHAN, A., MIAN, I. A., KHAN, B. et al. Maize productivity and soil nutrients variations by the application of vermicompost and biochar. **Plos One**, 2022. https://doi.org/10.1371/journal.pone.0267483

De MENEZES, C.W.G., CARVALHO, G.A., ALVES, D.S. et al. Biocontrol potential of methyl chavicol for managing *Spodoptera frugiperda* (Lepidoptera: Noctuidae), an important corn pest. **Environ Sci Pollut Res**. 27, 2020. https://doi.org/10.1007/s11356-019-07079-6

De-OLIVEIRA, A.C., Ribeiro-Pinto, L.F., Paumgartten, F.J. In vitro inhibition of CYP2B1 monooxygenase by β-myrcene and other monoterpenoid compounds. **Toxicol. Lett**. 92, 1997. https://doi.org/10.1016/s0378-4274(97)00034-9

De OLIVEIRA, E.R., ALVES, D.S., CARVALHO, G.A., DE OLIVEIRA, B.M.R.G. et al. Toxicity of *Cymbopogon flexuosus* essential oil and citral for *Spodoptera frugiperda*. Cienc. e Agrotecnologia 42, 2018. https://doi.org/10.1590/1413-70542018424013918

DHIFI, W., BELLILI, S., JAZI, S., BAHLOUL, N., MNIF, W. Essential Oils' Chemical Characterization and Investigation of Some Biological Activities: A Critical Review. **Medicines**, 3, 2016. https://doi.org/10.3390/medicines3040025

DINIZ, M. F., ANDRADE-NÚÑES, M.J., DALLMEIER, F., SÁNCHES-CUERVO, A.M. Habitat assessment for threatened species in the cross-border region of the Atlantic Forest. **Landsc Ecol** (2023) 38:2241–2260. https://doi.org/10.1007/s10980-023-01689-9

DUQUE, J. E., URBINA, D. L., VESGA, L. C., ORTIZ-RODRÍGUEZ, L. A. et al. Insecticidal activity of essential oils from American native plants against *Aedes aegypti* (Diptera: Culicidae): an introduction to their possible mechanism of action. **Scientific Reports**, 2023. https://doi.org/10.1038/s41598-023-30046-8

DUTRA, K.A., WANDERLEY TEIXEIRA, V., CRUZ, G.S., SILVA, C.T.S. et al. Morphological and immunohistochemical study of the midgut and fat body of *Spodoptera frugiperda* (J.E. Smith) (Lepidoptera: noctuidae) treated with essential oils of the genus *Piper*. **Biotech. Histochem**. 94, 2019. https://doi.org/10.1080/10520295.2019.1599144

ECCEL, C., ZIMMERMANN, R. C., GIRALDI, G. T., et al. *Baccharis* essential oils from the Atlantic Forest as sources of natural pesticides. **Ind Crops Prod** 215, 2024. https://doi.org/10.1016/j.indcrop.2024.118589

ELBEHERY, H.H., IBRAHIM, S.S. Potential fumigant toxicity of essential oils against *Sitotroga cerealella* (Olivier) (Lepidoptera: Gelechiidae) and its egg parasitoid *Trichogramma evanescens* (Hymenoptera: Trichogrammatidae). **Sci Rep** 14, 2024. https://doi.org/10.1038/s41598-024-56611-3

ELLMAN, G. L., COURTNEY, K. D., ANDRES, JR. V., FEATHERSTONE, R. M. A new and rapid colorimetric determination of acetylcholinesterase activity. Biochem. Pharmacol. 7, 1961. https://doi.org/10.1016/0006-2952(61)90145-9

ERB, K. et al. Unexpectedly large impact of forest management and grazing on global vegetation biomass. **Nature** 553, 2018. https://doi.org/10.1038/nature25138

ERB, M., KLIEBENSTEIN, D. J. Plant Secondary Metabolites as Defenses, Regulators, and Primary Metabolites: The Blurreb Functional Trichotomy. Plant Physiol. 184, 2020. https://doi.org/10.1104/pp.20.00433

ERCAN, F. S., BAS, H., AZARKAN, S. Y. In silico detection of Cucurbitacin-E on antioxidant enzymes of model organism *Galleria mellonella* L. (Lepidoptera: Pyralidae) and variation of antioxidant enzyme activities and lipid peroxidation in treated larvae. Beni-Suef University Journal of Basic and Applied Sciences, 11, 2022. https://doi.org/10.1186/s43088-022-00310-3

ERENSTEIN, O., JALETA, M., SONDER, K. *et al.* Global maize production, consumption and trade: trends and R&D implications. **Food Sec**. 14, 2022. https://doi.org/10.1007/s12571-022-01288-7

FAKOREDE, M. A. B., BADU-APRAKU, B., KAMARA, A. Y., MENKIR, A. et al. Maize revolution in West and Central Africa: An overview. In *Maize revolution in West and Central Africa*, ed. B. Badu-Apraku, M.A.B. Fakorede, M. Ouédraogo, R.J. Carsky, and A. Menkir, 3–15. Proceedings of a Regional Maize Workshop, IITA-Cotonou, 14–18 May 2001.

FARIAS, J. R., ANDOW, D. A, HORIKOSHI, R. J., SORGATTO, R, J. et al. Field-evolved resistance to Cry1F maize by *Spodoptera frugiperda* (Lepidoptera: Noctuidae) in Brazil. Crop Prot. 64:150–58, 2014. https://doi.org/10.1016/j.cropro.2014.06.019

FARIA, R.D., CABRAL, I.R., DOS SANTOS OLIVEIRA, T.A., THIESEN, L.V. et al. Essential oils from *Cordia verbenacea* and *Elionurus latiflorus* and their binary mixture: Bioactivity against the Mexican bean weevil and an aflatoxin-producing fungal species. Ind. Crops Prod. 206, 2023. https://doi.org/10.1016/j.indcrop.2023.117674

FELTON, G. W., SUMMERS, C. B. Antioxidant system in insects. **Arch Insect Biochem Physiol**. 29, 1995 DOI: https://doi.org/10.1002/arch.940290208.

FERGANI, Y., ELBANNA, H., HAMAMA, H. Genotoxicity of Some Plant Essential Oils in Cotton Leafworm, *Spodoptera Littoralis* (Lepidoptera: Noctuidae): the Potential Role of Detoxification Enzymes. **Egypt. J. Zool.**, 73, 2020. https://doi.org/10.21608/ejz.2020.28358.1029

FERNANDES, T.O.M., QUEIROZ, T.B., ROCHA, S.M.G., DA FONSECA, F.S.A. et al. Seasonal variation in the essential oil from  Jacq. accessions. **Bol. latinoam. Caribe Plantas Med. Aromát.**, 20, 2021. https://doi.org/10.37360/blacpma.21.20.6.48

FERREIRA, G. H. C., SANTOS, M. L., MONNERAT, R., ANDRADE, M. A. et al. Ovicidal and Deleterious Effects of Cashew (*Anacardium occidentale*) Nut Shell Oil and Its Fractions on *Musca domestica*, *Chrysomya megacephala*, *Anticarsia gemmatalis* and *Spodoptera frugiperda*. Chem. Biodivers. 16, 2019. https://doi.org/10.1002/cbdv.201800468

FERREIRA, I.J.M.; CAMPANHARO, W.A.; FONSECA, M.G. et al. Potential aboveground biomass increase in Brasilian Atlantic Forest fragments with climate change. **Global Change Biology**, v. 29, 2023. DOI: https://doi-org.ez22.periodicos.capes.gov.br/10.1111/gcb.16670

FIGUEIREDO MLC, DELLA LUCIA TMC, CRUZ I. Effect of *Telenomus remus* Nixon (Hymenoptera: Scelionidae) density on control of Spodoptera frugiperda (Smith) (Lepidoptera: Noctuidae) egg masses upon release in a maize field. **Rev. Bras. Milho Sorgo** 1, 2002. DOI: https://doi.org/10.18512/1980-6477/rbms.v1n02p%25p

FIGUEIREDO, M. L. C., CRUZ, I., DA SILVA, R. B., FOSTER, J.E. Biological control with *Trichogramma pretiosum* increases organic maize productivity by 19.4%. **Agron. Sustain. Dev.** 35, 2015. DOI: https://doi.org/10.1007/s13593-015-0312-3

FILOMENO, C. A., BARBOSA, L. C. A., TEIXEIRA, R. R., PINHEIRO, A. L. et al. *Corymbia* spp. and *Eucalyptus* spp. essential oils have insecticidal activity against *Plutella xylostella*. **Ind. Crops Prod**. 109, 2017. https://doi.org/10.1016/j.indcrop.2017.08.033

FLAMINI, G., TEBANO, M., CIONI, P.L., CECCARINI, L., RICCI, A.S., LONGO, I. Comparison between the conventional method of extraction of essential oil of Laurus nobilis L. and a novel method which uses microwaves applied in situ, without resorting to an oven. **Journal of Chromatography A**, 2007. https://doi.org/10.1016/j.chroma.2007.01.031

FORMAN, H.J.; ZHANG, H.; RINNA, A. Glutathione: Overview of its protective roles, measurement, and biosynthesis. **Mol. Asp. Med**. 2009, 30, 1–12. https://doi.org/10.1016/j.mam.2008.08.006

FRANCESCATO, L. N.; DEUSCHLE, R. A. N.; MALLMANN, C. A.; ALVES, S. H.; HEIZMANN, B. M. Atividade antimicrobiana de *Senecio heterotrichius* DC (Asteraceae). **Revista Brasileira de Ciências Farmacêuticas**, 43, 2007.

FRANCO, M.J.V; ALBIERO, A.L.M. Estruturas secretoras em folha e caule de *Esenbeckia febrifuga* (A.St.-Hil.) A. Juss. ex Mart. e *Esenbeckia grandiflora* Mart. (Rutaceae). **Hoehnea** 45(3): 468-483, 2018. http://dx.doi.org/10.1590/2236-8906-75/2017

FRITZ, G.J. **Keepers of Louisiana's levees: Early mound builders and forest managers**. In Rethinking agriculture: Archaeological and ethnoarchaeological perspectives, ed. T.P. Denham, J. Iriarte, and L. Vrydaghs, 189–209, 2007.

FÜLLER, T.N., TESSELE, C., BARROS, I.B.I., BARBOSA NETO, J.F. Phenotypical, phytochemical and molecular characterization of "capim-carona" [*Elionurus muticus* (Spreng.) Kuntze] populations. **Rev. Bras. Plantas Med**. 12, 2010. https://doi.org/10.1590/S1516-05722010000300003

FÜLLER, T.N., BERTRAND, C., ANTONELLO, B., WESP, C. et al. Chemical diversity of wild populations of *Elionurus muticus* (Spreng.) and the allelopathic effect of its essential oil. **J. Essent. Oil Res**. 29, 2017. https://doi.org/10.1080/10412905.2017.1313786

FÜLLER, T.N., BERTRAND, C., SIMON, A., DE BARROS, I.B.I. et al. *Elionurus muticus* as an alternative source of citral from pampa biome, Brazil. **J. Oleo Sci**. 63, 2014. https://doi.org/10.5650/jos.ess13234

GAD, H. A., RAMADAN, G. R. M., EL-BAKRY, A. M., EL-SABROUT, A. M., ABDELGALEIL, S. A. M. Monoterpenes: Promising natural products for public health insect control – A review. **Int. J. Trop. Insect Sci**. 42, 2022. https://doi.org/10.1007/s42690-021-00692-4

GARCIA, A.G.; FERREIRA, C.P.; GODOY, W.A. et al. A computational model to predict the population dynamics of *Spodoptera frugiperda*. **Journal of Pest Science**, v. 92, 2019. DOI: https://doi.org/10.1007/s10340-018-1051-4

GAO, R., YUAN, Z., ZHAO, Z., GAO, X. Mechanism of pyrogallol autoxidation and determination of superoxide dismutase enzyme activity. **Bio Electrochem Bioenergy**, 45, 1998. https://doi.org/10.1016/S0302-4598(98) 00072-5.

GARAY, J., BRENNAN, T., BON, D. Review: Essential Oils A Viable Pest Control Alternative. **Int. J. Ecotoxicol. Ecobiol**. 5, 2020. https://doi.org/10.11648/j.ijee.20200502.11

GARLET, C.G., GUBIANI, P.S., PALHARINI, R.B., MOREIRA, R.P., Godoy, D.N. et al. Field-evolved resistance to chlorpyrifos by *Spodoptera frugiperda* (Lepidoptera: Noctuidae): Inheritance mode, cross-resistance patterns, and synergism. **Pest Manag. Sci.**, 77, 2021. https://doi.org/10.1002/ps.6576

GIRALDI, G. T., AMARAL, W., ZIMMERMANN, R. C., MAZAROTTO, E. J. et al. Insecticidal activity, toxicity and biochemical alterations of *Drimys brasiliensis* essential oil against *Spodoptera frugiperda*. **Journal of Pest Science**, 2024. https://doi.org/10.1007/s10340-024-01827-5

GIUNTI, G.; CAMPOLO, O.; LAUDANI, F.; PALMERI, V. et al. Essential oil-based nanoinsecticides: ecological costs and commercial potential. In: **Development and Commercialization of Biopesticides** – Cost and Benefits. Ed: Opender Koul, 2023. https://doi.org/10.1016/B978-0-323-95290-3.00002-9

GOMES, M. R. F., SCHUH, R. S., BEMVENUTI, A. L. J., DORNELES, G. G. et al. Biological assessment (antiviral and antioxidant) and acute toxicity of essential oils from *Drimys angustifolia* and *D. brasiliensis*. Brazilian Journal of Pharmacognosy, 23, 2013. https://doi.org/10.1590/S0102-695X2012005000142

GOMES, M. R. F., DORNELES, G. G., SCHUH, R. S., JACQUES, A. L. B. et al. Chemical composition of essential oils of *Drimys angustifolia* Miers and *Drimys brasiliensis* Miers and their repellency to drywood termite *Cryptotermes brevis* (Isoptera: Kalotermitidae). Journal of Basic and Applied Pharmaceutical Sciences 35, 2014.

GRAF JÚNIOR, A. L., FONTOURA, S. B., ANDRADE, G. C., COSTA, J. S., ITAKO, A. T., SOLDI, C. Essential oil from cataia leaves (*Drimys brasiliensis*) on the mycelial growth of Alternaria porri. Green Magazine of Agroecology and Sustainable Development 16, 2021.

GRECCO, S.S., GIMENES, L., FERREIRA, M.J.P., ROMOFF, P., FAVERO, O.A., ZALEWSKI, C.A., LAGO, J.H.G. Triterpenoids and phenolic derivatives from *Baccharis uncinella* DC. (Asteraceae). **Biochem. Syst. Ecol.** 38, 1234–1237, 2010a. https://doi.org/10.1016/j.bse.2010.12.005

GRECCO, S.S., REIMÃO, J.Q., TEMPONE, A.G., SARTORELLI, P., ROMOFF, P., FERREIRA, M.J.P., FÁVERO, O.A., LAGO, J.H.G. Isolation of an antileishmanial and antitrypanosomal flavanone from the leaves of *Baccharis retusa* DC. (Asteraceae). **Parasitol. Res.** 106, 1245–1248, 2010b. https://doi.org/10.1007/s00436-010-1771-8

GRECCO S.S., REIMÃO J.Q., TEMPONE A.G., SARTORELLI P., CUNHA R.L.O.R., ROMOFF P., FERREIRA M.J.P., FÁVERO O.A., LAGO J.H.G. In vitro antileishmanial and antitrypanosomal activities of flavanones from *Baccharis retusa* DC. (Asteraceae). **Experimental Parasitology**. 130, 141–145, 2012. https://doi.org/10.1016/j.exppara.2011.11.002

GUAN, F., ZHANG, J., SHEN, H., WANG, X. et al. Whole-genome sequencing to detect mutations associated with resistance to insecticides and Bt proteins in *Spodoptera frugiperda*. **Insect Sci.**, 28, 2020. https://doi.org/10.1111/1744-7917.12838

GUENGERICH, F.P. Cytochrome P450 and chemical toxicology. **Chem Res Toxicol**. 21, 2008. https://doi.org/10.1021/tx700079z.

GUERRA, A.; REIS, L. K.; BORGES, F. L. G. et al. Ecological restoration in Brazilian biomes: Identifying advances and gaps. **Forest Ecology and Management**, v. 458, 2020. https://doi.org/10.1016/j.foreco.2019.117802

GUERRERO, A., MALO, E.A., COLL, J., QUERO, C. Semiochemical and natural product-based approaches to control Spodoptera spp. (Lepidoptera: Noctuidae). **J. Pest Sci**, 87, 2014. https://doi.org/10.1007/s10340-013-0533-7

GUTIÉRREZ-MORENO R, MOTA-SANCHEZ D, BLANCO CA, WHALON ME, TERÁN-SANTOFIMIO H, et al. Field-evolved resistance of the fall armyworm (Lepidoptera: Noctuidae) to synthetic insecticides in Puerto Rico and Mexico. **J. Econ. Entomol**. 112, 2019. https://doi.org/ 10.1093/jee/toy372

HALLIWELL, B., GUTTERIDGE, J. M. C. **Free Radicals in Biology and Medicine**, 5th edn (Oxford, 2015; online edn, Oxford Academic, 22 Oct. 2015. https://doi.org/10.1093/acprof:oso/9780198717478.001.0001

HANS, A.L.; SAXENA, S. Plant Bioprospecting for Biopesticides and Bioinsecticides. In: **Bioprospecting of Plant Biodiversity for Industrial Molecules**. Ed: Santosh Kumar Upadhyay, Sudhir P. Singh, 2021. https://doi.org/10.1002/9781119718017

HARRISON, R.D., THIERFELDER, C., BAUDRON, F., CHINWADA, P. et al. Agro-ecological options for fall armyworm (*Spodoptera frugiperda* JE Smith) management: Providing low-cost, smallholder friendly solutions to an invasive pest. **J. Environ. Manage.**, 243, 2019. https://doi.org/10.1016/j.jenvman.2019.05.011

HARTMANN, T. **Diversity and variability of plant secondary metabolism: a mechanistic view**. In: Städler, E., Rowell-Rahier, M., Bauer, R. (eds) Proceedings of the 9th International Symposium on Insect-Plant Relationships. Series Entomologica, vol 53. Springer, Dordrecht. 1996. https://doi.org/10.1007/978-94-009-1720-0_42

HASHEM, A.S., AWADALLA, S.S., ZAYED, G.M. et al. Pimpinella anisum essential oil nanoemulsions against *Tribolium castaneum*—insecticidal activity and mode of action. **Environ Sci Pollut Res** 25, 2018. https://doi.org/10.1007/s11356-018-2068-1

HAYES, J. D., McLELLAN, L. I. Glutathione and Glutathione Dependent-Enzymes Represent a Co-Ordinately Regulated Defence against Oxidative Stress, **Free Radical Research**, 31, 1999. http://dx.doi.org/10.1080/10715769900300851

HEINZMANN, B.M.; SPITZER, V.; SIMÕES, C.M.O. Óleos voláteis. In: Simões, C. M. O.; Schenkel, E. P.; Mello, J. C. P.; Mentz, L. A.; Petrovick, P. R. **Farmacognosia**: da planta ao medicamento. Simões C. M. O et al. Porto Alegre: Artmed, 2017.

HESS, S.C. et al. Evaluation of seasonal changes in chemical composition and antibacterial activity of *Elyonurus muticus* (Sprengel) O. Kuntze (Gramineae). **Química Nova**, v.30, n.2, p.370-3, 2007.

HIKAL et al. Botanical insecticide as simple extractives for pest control. **Cogent Biology**, 3, 2017. https://doi.org/10.1080/23312025.2017.1404274

HU, J., WANG, W., DAI, J., ZHU, L. Chemical composition and biological activity against *Tribolium castaneum* (Coleoptera: Tenebrionidae) of *Artemisia brachyloba* essential oil. Ind. Crops Prod. 128, 2019. https://doi.org/10.1016/j.indcrop.2018.10.076

HUMMELBRUNNER, L. A., ISMAN, M. B. Acute, sublethal, antifeedant, and synergistic effects of monoterpenoid essential oil compounds on the tobacco cutworm, *Spodoptera litura* (Lep., Noctuidae). J. Agr. FoodChem. 49, 2001. https://doi.org/10.1021/jf000749t

HURLEY, T.M.; MITCHELL, P.D. The value of insect management to US maize, soybean and cotton farms. **Pest Management Science**, v. 76, 2020. https://doi.org/10.1002/ps.5974

HUSSAIN, A. G., WENNMANN, J. T., GOERGEN, G., BRYON, A. et al. Viruses of the fall armyworm *Spodoptera frugiperda*: a review with prospects for biological control. **Viruses**, 13, 2021. https://doi.org/10.3390/v13112220

HYLDGAARD M, MYGIND T, MEYER RL. Essential oils in food preservation: mode of action, synergies, and interactions with food matrix components. **Front Microbiol**. 2012. 10.3389/fmicb.2012.00012. PMID: 22291693; PMCID: PMC3265747.I

IBGE – Instituto Brasileiro de Geografia e Estatística. Mapa da área de aplicação da Lei nº 11.428 de 2006, 2008.

IMLAY, J.A., LINN, S. DNA damage and oxygen radical toxicity. **Science**, 240, 1988. https://doi.org/10.1126/science.3287616

IQBAL, W., KHAN, A., JAMAL, A., RADICETTI, E. et al. Optimizing Maize Productivity and Soil Fertility: Insights from Tillage, Nitrogen Management, and Hydrochar Applications. **Land**, 13, 2024. https://doi.org/10.3390/land13081329

IRIARTE, J. **New perspectives on plant domestication and the development of agriculture in the New World**. In: Rethinking agriculture: Archaeological and ethnoarchaeological perspectives, ed. T.P. Denham, J. Iriarte, and L. Vrydaghs, 167–188, 2007.

ISMAN, M. B. Plant essential oils for pest and disease management. **Crop Protection**, 19, 2000. https://doi.org/10.1016/S0261-2194(00)00079-X

ISMAN, M.B. Botanical Insecticides, Deterrents, and Repellents in Modern Agriculture and an Increasingly Regulated World. **Annual Review Entomology**, v. 51, 2006. https://doi.org/10.1146/annurev.ento.51.110104.151146

ISMAN, M. B. Commercial development of plant essential oils and their constituents as active ingredients in bioinsecticides. **Phytochem Rev**. 2019. https://doi.org/10.1007/s11101-019-09653-9

ISMAN, M.B. Bioinsecticides based on plant essential oils: a short overview. **Z. Naturforsch**, v. 75, 2020. https://doi.org/10.1515/znc-2020-0038

ISMAN, M.B.. Botanical insecticides in the twenty-first century-fulfilling their promise? **Annu. Rev. Entomol**. 65, 2020a. https://doi.org/10.1146/annurev-ento-011019-025010

IVANO, L.R.P.F.M.; FREITAS, J.F.; NETTO, M.F. Óleos essenciais na indústria cosmética e medicina alternativa: benefícios e desafios para uso responsável. **Revista Contemporânea**, 3, 2023. https://doi.org/10.56083/RCV3N10-084

JACOB, R.F., MASON, R.P. Lipid peroxidation induces cholesterol domain formation in model membranes. **J. Biol. Chem**. 280, 2005. https://doi.org/10.1074/jbc.M507587200

JAHANIAN, H.; KAHKESHANI, N.; SANEI-DEHKORDI, A.; ISMAN, M.B. et al. *Rosmarinus officinalis* as natural insecticide: a review. **International Journal of Pest Management**, 2022. https://doi.org/10.1080/09670874.2022.2046889

JANG, M., KIM, J., YOON, K.A., LEE, S.H. et al. Biological activity of Myrtaceae plant essential oils and their major components against *Drosophila suzukii* (Diptera: Drosophilidae). Pest Manag. Sci. 73, 2017. https://doi.org/10.1002/ps.4430

JANKOWSKA, M., ROGALSKA, J., WYSZKOWSKA, J., STANKIEWICZ, M. Molecular targets for components of essential oils in the insect nervous system—a review. **Molecules**, 23, 2018. https://doi.org/10.3390/molecules23010034

JIANG, Z., HUNT, J. V., WOLFF, S. P. Ferrous ion oxidation in the presence of xylenol orange for detection of lipid hydroperoxide in low density lipoprotein. Anal. Biochem. 202, 1992. https://doi.org/10.1016/0003-2697(92)90122-N

JUDD, W.S., CAMPBELL, C.S., KELLOGG, E.A., STEVENS, P.F. & DONOGHUE, M.J. Sistemática vegetal: um enfoque filogenético. 3 ed., Artmed, Porto Alegre. 2009.

JULIO, A.H.F., GIGLIOLLI, A.A.S., CARDOSO, K.A.K., DROSDOSKI, S.D. et al. Multiple resistance to pirimiphos-methyl and bifenthrin in Tribolium castaneum involves the activity of lipases, esterases, and laccase2. Comp. Biochem. Physiol. Part C Toxicol. Pharmacol. 195, 2017. https://doi.org/10.1016/j.cbpc.2017.01.011

KAUR, K., CHEEMA, H. K., JINDA, J., GARG, T. et al. Categorization of resistance against the fall armyworm, *Spodoptera frugiperda* (J.E. Smith) in select maize inbred lines. **Crop Protection**, 178, 2024. https://doi.org/10.1016/j.cropro.2024.106581

KEEN, J. H., HABIG, W. H., JAKOBY, W. B. Mechanism for the several activities of glutathione. **J. Biol. Chem**. 251: 6183–6188, 1976.

KENIS, M., BENELLI, G., BIONDI, A., CALATAYUD, P. A., DAY, R., DESNEUX, N., et al. Invasiveness, biology, ecology, and management of the fall armyworm, *Spodoptera frugiperda*. **Entomol. Gen**. 43, 2023. https://doi.org/10.1127/entomologia/2022/1659

KIM, S.W., KANG, J., PARK, I.K. Fumigant toxicity of Apiaceae essential oils and their constituents against Sitophilus oryzae and their acetylcholinesterase inhibitory ac tivity. **J. Asia Pac. Entomol**. 16, 2013. https://doi.org/10.1016/j.aspen.2013.07.002

KIM, S.W., KANG, J., PARK, I.K. Fumigant toxicity of Apiaceae essential oils and their constituents against Sitophilus oryzae and their acetylcholinesterase inhibitory activity. **J. Asia. Pac. Entomol**. 16, 2013. https://doi.org/10.1016/j.aspen.2013.07.002

KIM, J., KIM, H., BEUCHAT, L. R., RYU, J. H. Synergistic antimicrobial activities of plant essential oils against *Listeria monocytogenes* in organic tomato juice. **Food Control** 125, 2021. https://doi.org/10.1016/j.foodcont.2021.108000

KIM, S., YOON, J., TAK, J.H. Synergistic mechanism of insecticidal activity in basil and mandarin essential oils against the tobacco cutworm. **J Pest Sci**, 94, 2021. https://doi.org/10.1007/s10340-021-01345-8

KIRAN, S., PRAKASH, B. Toxicity and biochemical efficacy of chemically characterized Rosmarinus officinalis essential oil against Sitophilus oryzae and Oryzaephilus surinamensis. **Ind. Crops Prod**. 74, 2015. https://doi.org/10.1016/j.indcrop.2015.05.073

KIRAN, S., PRAKASH, B. Toxicity and biochemical efficacy of chemically characterized Rosmarinus officinalis essential oil against Sitophilus oryzae and Oryzaephilus surinamensis. **Ind. Crops Prod**. 74, 2015. https://doi.org/10.1016/j.indcrop.2015.05.073

KIRAN, S., KUJUR, A., PATEL, L., RAMALAKSHMI, K., PRAKASH, B. Assessment of toxicity and biochemical mechanisms underlying the insecticidal activity of chemically characterized *Boswellia carterii* essential oil against insect pest of legume seeds. **Pestic. Biochem. Physiol**. 139, 2017. https://doi.org/10.1016/j.pestbp.2017.04.004

KOYAMA, S.; HEINBOCKEL, T. The Effects of Essential Oils and Terpenes in Relation to Their Routes of Intake and Application. **Int. J. Mol. Sci.**, 21, 2020. https://doi.org/10.3390/ijms21051558

KREIS, W.; MUNKERT, J.; PÁDUA, R.M. Biossíntese de metabólitos primários e secundários. In: Simões, C. M. O.; Schenkel, E. P.; Mello, J. C. P.; Mentz, L. A.; Petrovick, P. R. **Farmacognosia**: da planta ao medicamento. Simões C. M. O et al. Porto Alegre: Artmed, 2017.

KUMAR, P., MISHRA, S., MALIK, A., SATYA, S. Compositional analysis and insecticidal activity of *Eucalyptus globulus* (family:Myrtaceae) essential oil against housefly (*Musca domestica*). **Acta Trop**. 122, 2012. https://doi.org/10.1016/j.actatropica.2012.01.015

KUMAR, S., MAHAPATRO, G.K., YADAV, D.K., TRIPATHI, K. et al. Essential oils as green pesticides: An overview. **Indian J. Agric. Sci**. 92, 2022. https://doi.org/10.56093/ijas.v92i11.122746

KUMAR, S. et al. Essential oil as green pesticides: An overview. **Indian Journal of Agricultural Sciences** 92 (11): 1298–1305, 2022. https://doi.org/10.56093/ijas.v92i11.122746

KURDELAS R.R, LÓPEZ S, LIMA B, FERESIN G.E, ZYGADLO J, ZACCHINO S, LÓPEZ M.L, TAPIA A, FREILE M.L. Chemical composition, anti-insect and antimicrobial activity of *Baccharis darwinii* essential oil from Argentina, Patagonia. **Industrial Crop and Products**, 40, 2012. https://doi.org/10.1016/j.indcrop.2012.03.024L

LACERDA, L. F. et al. Biological basis for adoption of an isoline of *Telenomus remus* (Hymenoptera: Scelionidae) for an augmentative biological-control program for Spodoptera frugiperda (Lepidoptera: Noctuidae). **Journal of Insect Science**, 23, 2023. DOI: https://doi.org/10.1093/jisesa/iead045

LAGO, L. H. G.; ROMOFF P.; FÁVERO O. A. Chemical composition of the essential oils from leaves of six species of the genus *Baccharis* of São Paulo rainforest. **Química Nova**. 31, 2008.

LAGO, J. H. G., CARVALHO, L. A. C., SILVA, F. S., TOYAMA, D. O. et al. Chemical Composition and Anti- Inflammatory Evaluation of Essential Oils from Leaves and Stem Barks from *Drimys brasiliensis* Miers (Winteraceae). **J. Brazil. Chem. Soc**. 21, 2010. https://doi.org/10.1590/S0103-50532010000900024

LEAL, A.L.A.B., BEZERRA, C.F., FERREIRA E SILVA, A.K., DA SILVA, L.E. et al. Seasonal variation of the composition of essential oils from *Piper cernuum* Vell and *Piper rivinoides* Kunth, ADMET study, DFT calculations, molecular docking and dynamics studies of major components as potent inhibitors of the heterodimer methyltransferase complex NSP16-NSP10 SARS COV-2 protein. **J. Biomol. Struct. Dyn.**, 41, 2022. https://doi.org/10.1080/07391102.2022.2107072

LEE, S.E., LEE, B.H., CHO, W.S., PARK, B.S., KIM, J.G., CAMPBELL, B.C. Fumigant toxicity of volatile natural products from Korean species and medicinal plants to wards the rice weevil, Sitophilus oryzae (L). **Pest Manag. Sci.** 57, 2001. https://doi.org/10.1002/ps.322

LI, S.G., LI, M.Y., HUANG, Y.Z., HUA, R.M., et al. Fumigant activity of Illicium verum fruit extracts and their effects on the acet ylcholinesterase and glutathione S-transferase activities in adult Sitophilus zeamais. **J. Pest. Sci.** 86, 2013. https://doi.org/10.1007/s10340-013-0520-z

LIAO, M., XIAO, J. J., ZHOU, L. J., YAO, X. et al. Chemical composition, insecticidal and biochemical effects of *Melaleuca alternifolia* essential oil on the *Helicoverpa armigera*. **J App Entomol** 00, 2017. https://doi.org/10.1111/jen.12397

LILLIG, C.H.; BERNDT, C. Preface. Cellular functions of glutathione. **Biochim. Biophys. Acta**, 1830, 2013. https://doi.org/10.1016/j.bbagen.2013.02.019

LIMA, R. A. F.; OLIVEIRA, A.A.; PITTA, G.R. et al., The erosion of biodiversity and biomass in the Atlantic Forest biodiversity hotspot. **Nature Communications**, v. 11, 2020. https://doi.org/10.1038/s41467-020-20217-w

LIRA, E.C.; BOLZAN, A.; NASCIMENTO, A, R.B.; AMARAL, F.S.A.; KANNO, R.H. et al. Resistance of *Spodoptera frugiperda* (Lepidoptera:Noctuidae) to spinetoram: inheritance and cross-resistance to spinosad. **Pest Management Science**, v. 76, 2020. https://doi.org/10.1002/ps.5812

LIU, H., GUO, S. S., LU, L., LI, D. et al. Essential oil from *Artemisia annua* aerial parts: composition and repellent activity against two storage pests. Nat. Prod. Res. 35, 2021. https://doi.org/10.1080/14786419.2019.1599887

LIU, Z., LI, Q.X., SONG, B. Pesticidal Activity and Mode of Action of Monoterpenes. J. Agric. Food Chem. 70, 2022. https://doi.org/10.1021/acs.jafc.2c00635

LOPEZ-MARTINEZ, G., ELNITSKY, M.A., BENOIT, J.B., LEE JR., R.E., DENLINGER, D.L. High resistance to oxidative damage in the Antarctic midge Belgica antarctica, and developmentally linked expression of genes encoding superoxide dismutase, catalase and heat shock proteins. **Insect Biochemistry and Molecular Biology** 38, 2008. https://doi.org/10.1016/j.ibmb.2008.05.006

LUKASIK, I., 2007. Changes in activity of superoxide dismutase and catalase within cereal aphids in response to plant o-dihydroxyphenols. **J. Appl. Entomol**. 131, 209–214. https://doi.org/10.1111/j.1439-0418.2006.01136.x

MACIEL, R.M.A.; LUSKI, P.G.G.; SUTIL, W.P.; GONÇALVEZ, J. et al. The use of baculovirus Spodoptera SfMNPV alone and combined with herbicides and adjuvant to control *Spodoptera frugiperda* (Smith, 1797) (Lepidoptera: Noctuidae). **Biological Control**, v.188, 2024. https://doi.org/10.1016/j.biocontrol.2023.105408

MAHAJAN, R. S., BHAMARE, V. K. Residual toxicity of insecticides to egg parasitoids of *Spodoptera frugiperda* (J E SMITH). **Indian Journal of Entomology**, 85, 2023. https://doi.org/10.55446/IJE.2023.1203

MAKSIC. J.; VENANCIO, I.M.; SHIMIZU, M.H. et al. Brazilian biomes distribution: Past and future. **Palaeogeography, Palaeoclimatology, Palaeoecology**, v. 585, 2022. https://doi.org/10.1016/j.palaeo.2021.110717

MANFRON, J., RAMAN, V., KHAN, I. A., FARAGO, P. V. Essential Oils of *Baccharis*: Chemical Composition and Biological Activities. In: Fernandes, GW, Oki, Y., Barbosa, M. (eds) Baccharis. Springer, Cham. 2021. https://doi.org/10.1007/978-3-030-83511-8_10

MARANGONI, C.; MOURA, N.F.; GARCIA, F.R.M. Utilização de Óleos Essenciais e Extratos de Plantas no Controle de Insetos. **Revista de Ciências Ambientais**, v. 6, n.2, p. 95 a 112, 2012.

MARCHIORO, C. A., FOERSTER, L. A. Performance of the Wheat Armyworm, *Pseudaletia sequax* Franclemont, on Natural and Artificial Diets. **Neotrop. Entomol**. 41, 2012. https://doi.org/10.1007/s13744-012-0046-8

MARSCHALL, H. R., JIANG, S. Y. Tourmaline Isotopes: No Element Left Behind. Elements 7, 2011. https://doi.org/10.2113/gselements.7.5.313

MARUTHADURAI, R., RAMESH, R. Occurrence, damage pattern and biology of fall armyworm, *Spodoptera frugiperda* (J.E. smith) (Lepidoptera: Noctuidae) on fodder crops and green amaranth in Goa, India. **Phytoparasitica**, 48, 2020. https://doi.org/10.1007/s12600-019-00771-w

MAYANGLAMBAM, S., RAJASHEKAR, Y. Antifeedant effects of crofton weed, *Ageratina adenophora* extracts and their phytochemical compounds against three cabbage insect pest species. **Entomologia Experimentalis et Applicata** 71, 2023. https://doi.org/10 .1111/eea.13309

MENG, J.Y., ZHANG, C.Y., ZHU, F., WANG, X.P., LEI, C.L. Ultraviolet light-induced oxidative stress: effects on antioxidant response of Helicoverpa armigera adults. J. **Insect Physiol**. 55, 2009. https://doi.org/10.1016/j.jinsphys.2009.03.003

MITTERMEIER, R. A.; GIL, P. R.; HOFFMANN, M.; PILGRIM, J.; BROOKS, T.; MITTERMEIER, C. G.; LAMOUREX, J. & FONSECA, G. A. B. **Hotspots revisited**. CEMEX, México City, 2004. 392p.

MOJARAB-MAHBOUBKAR, M., SENDI, J. J., ALIAKBAR, A. Effect of *Artemisia annua* L. essential oil on toxicity, enzyme activities, and energy reserves of cotton bollworm *Helicoverpa armigera* (Hübner) (Lepidoptera: Noctuidae). **J. Plant Prot. Res**. 55, 2015. https://doi.org/10.1515/jppr-2015-0049

MONAGHAN, P., METCALFE, N.B., TORRES, R. Oxidative stress as a mediator of life history trade-offs: mechanisms, measurements, and interpretations. **Ecol. Lett**. 12, 2009. https://doi.org/10.1111/j.1461-0248.2008.01258.x

MONTEZANO, D. G., SPECHT, A., SOSA-GÓMEZ, D., ROQUE-SPECHT, V. F. et al. Host plants of *Spodoptera frugiperda* (Lepidoptera: Noctuidae) in the Americas. **African Entomology**, 26, 2018. https://doi.org/10.4001/003.026.0286

MOSCARDINI, V.F.; MARQUES, L.H.; SANTOS, A.C.; ROSSETO, J. et al. Efficacy of *Bacillus thuringiensis* (Bt) maize expressing Cry1F, Cry1A.105, Cry2Ab2 and Vip3Aa20 proteins to manage the fall armyworm (Lepidoptera: Noctuidae) in Brazil. **Crop Protection**, v. 137, 2020. https://doi.org/10.1016/j.cropro.2020.105269

MOUNGTHIPMALAI, T., SOONWERA, M. Adulticidal activity against houseflies (*Musca domestica* L.; Muscidae: Diptera) of combinations of *Cymbopogon citratus* and *Eucalyptus globulus* essential oils and their major constituents. **Int. J. Agric. Technol**. 19, 2023.

MOUSTAFA, M.A.M., AWAD, M.; AMER, A., HASSAN, N.N., et al., Insecticidal Activity of Lemongrass Essential Oil as an Eco-Friendly Agent against the Black Cutworm *Agrotis ipsilon* (Lepidoptera: Noctuidae). **Insects** 2021, 12, 737. https://doi.org/10.3390/insects12080737

MOUSTAFA, M.A.M., HASSAN, N.N., ALFUHAID, N. A., AMER, A. et al., Insights into the toxicity, biochemical activity, and molecular docking of *Cymbopogon citratus* essential oils and citral on *Spodoptera littoralis* (Lepidoptera: Noctuidae**). Journal of Economic Entomology**, 116, 2023. https://doi.org/10.1093/jee/toad093

MURARO, D.S., ABBADE NETO, D.O., KANNO, R.H., KAISER, I.S. et al. Inheritance patterns, cross-resistance and synergism in *Spodoptera frugiperda* (Lepidoptera: Noctuidae) resistant to emamectin benzoate. **Pest Manag. Sci.**, 77, 2021. https://doi.org/10.1002/ps.6545

MURCIA-MESEGUER, A., ALVES, T.J.S., BUDIA, F., ORTIZ, A. et al. Insecticidal toxicity of thirteen commercial plant essential oils against *Spodoptera exigua* (Lepidoptera: Noctuidae). Phytoparasitica 46, 2018. https://doi.org/10.1007/s12600-018-0655-9

MURÚA, M. G., VERA, M. A., MICHEL, A., CASMUZ, A. S. et al. Performance of field-collected *Spodoptera frugiperda* (Lepidoptera: Noctuidae) strains exposed to different transgenic and refuge maize hybrids in Argentina. **J. Insect Sci.**, 19, 2019. https://doi.org/10.1093/jisesa/iez110

MYERS, N., MITTERMEIER, R. A., MITTERMEIER, C.G., FONSECA, G. A. B. & KENT, J. Biodiversity hotspots for conservation priorities. **Nature**, 403, 2000. https://doi.org/10.1038/35002501

NIASSY S, AGBODZAVU MK, KIMATHI E, MUTUNE B, ABDEL-RAHMAN EFM, SALIFU D, et al. Bioecology of fall armyworm *Spodoptera frugiperda* (J. E. Smith), its management and potential patterns of seasonal spread in Africa. **Plos One**, 16, 2021. https://doi.org/ 10.1371/journal.pone.0249042

NINKUU, V., ZHANG, L., YAN, J., FU, Z. et al. Biochemistry of Terpenes and Recent Advances in Plant Protection. Int. J. Mol. Sci. 22, 2021. https://doi.org/10.3390/ijms22115710

NIST Mass Spectral Library, v11, National Institute of Standards and Technology, Gaithersburg, 2011.

NURNINA, N., MUIS, A. Egg laying and damage by fall armyworm, *Spodoptera frugiperda* J. E Smith on maize variety HJ 21 at screen house. **IOP Conference Series**: Earth and Environmental Science, 1107. 2022. https://doi.org/10.1088/1755-1315/1107/1/012005

OKUMA, D. M., BERNARDI, D., HORIKOSHI, R. J., BERNARDI, O., SILVA, A. P., OMOTO, C. Inheritance and fitness costs of *Spodoptera frugiperda* (Lepidoptera:

Noctuidae) resistance to spinosad in Brazil. **Pest Manag. Sci**. 74, 2017. https://doi.org/10.1002/ps.4829

OLIVEIRA R.N., REHDER V.L.G., OLIVEIRA A.S.S., MONTANARI JÚNIOR Í., CARVALHO J.E., RUIZ A.L.T.G., JERALDO V.L.S., LINHARES A.X., ALLEGRETTI S.M. Anthelmintic activity in vitro and in vivo of *Baccharis trimera* (Less) DC against immature and adult worms of *Schistosoma mansoni*. **Experimental Parasitology**. 139, 2014. https://doi.org/10.1016/j.exppara.2014.02.010

OLIVEIRA, L.Z.; GASPER, A.L.; VIBRANS, A.C. Potential new areas for conservation of key botanical families in the subtropical Atlantic Forest. **Biodiversity and Conservation**, v. 30, 2021. https://doi-org.ez22.periodicos.capes.gov.br/10.1007/s10531-021-02280-x

OLIVEIRA, N.C., RODRIGUES, P.A.P., CÔNSOLI, F.L. Host-Adapted Strains of *Spodoptera frugiperda* Hold and Share a Core Microbial Community Across the Western Hemisphere. **Microbial Ecology**, 85, 2023. https://doi.org/10.1007/s00248-022-02008-6

OLMEDO, R., HERRERA, J.M., LUCINI, E.I., ZUNINO, M.P. et al. Essential oil of *Tagetes filifolia* against the flour beetle *Tribolium castaneum* and its relation to acetylcholinesterase activity and lipid peroxidation. **AgriScientia** 32, 2015. 10.31047/1668.298x.v32.n2.16562

OMUUT, G.; MOLLEL, H.G.; KANYESIGYE, D.; AKOHOUE, F. et al. Genetic analyses and detection of point mutations in the acetylcholinesterase-1 gene associated with organophosphate insecticide resistance in fall armyworm (*Spodoptera frugiperda)* populations from Uganda. **BMC Genomics**, v. 24, 2023. https://doi-org.ez22.periodicos.capes.gov.br/10.1186/s12864-022-09093-4

OOTANI, M. A., AGUIAR, R. W., RAMOS, A. C. C., BRITO, D. R. et al. Use of Essential Oils in Agriculture. **Journal of Biotechnology and Biodiversity**, 4, 2013.

OVERTON, K., MAINO, J. L., DAY, R., UMINA, P. A. et al. Global crop impacts, yield losses and action thresholds for fall armyworm (*Spodoptera frugiperda*): A review. **Crop Protection**, 145, 2021. https://doi.org/10.1016/j.cropro.2021.105641

PAGARE, S., BHATIA, M., TRIPATHI, N., PAGARE, S. et al. Secondary Metabolites of Plants and their Role: Overview. **Current Trends in Biotechnology and Pharmacy**, 9, 2015.

PAN, Z., LIU, S., CHEN, Y.C., WANG, Y.D. et al. As natural phytocide: Biomarker assessment of *Litsea cubeba* (Lour.) Persoon essential oil against *Drosophila suzukii* Matsumura (Diptera: Drosophilidae.). **Ind. Crops Prod**. 187, 2022. https://doi.org/10.1016/j.indcrop.2022.115421

PARK, Y.L.; TAK, J.H. Essential Oils for Arthropod Pest Management in Agricultural Production Systems. In: **Essential Oils in Food Preservation, Flavor and Safety**, Ed: Preedy, V.R. Elsevier, 2016.

PARKINSON, A., OGILVIE, B. W. **Biotransformation of xenobiotics**. In C. D. Klaassen (Ed.), Casarett and Doull's Toxicology: The Basic Science of Poisons. 8th ed. 2008.

PARRA, J. R. P. Insect breeding techniques for biological control programs. Piracicaba, ESALQ/FEALQ, 137p. 2001.

PARREIRA, D. S., CRUZ, R. A., ZANUNCIO, J. C., LEMES, P. G. et al. Essential oils cause detrimental effects on biological parameters of *Trichogramma galloi* immatures. **Journal of Pest Science**, 2017. https://doi.org/10.1007/s10340-017-0945-x.

PARREIRA, D. S., ALCÁNTARA-DE la CRUZ, R., DIMATÉ, F. A. R., BATISTA, L. D. et al. Bioactivity of tem essential oils on the biological parameters of *Trichogramma pretiosum* (Hymenoptera: Trichogrammatidae) adults. **Industrial Crops and Products**, 127, 2019. https://doi.org/10.1016/j.indcrop.2018.10.063

PASSERO, L.F.D., BONFIM-MELO, A., CORBETT, C.E.P., LAURENTI, M.D., TOYAMA, M.H., TOYAMA, D.O., ROMOFF, P., FÁVERO, O.A., GRECCO, S.S., ZALEWSKY, C.A., LAGO, J.H.G. Anti-leishmanial effects of purified compounds from aerial parts of *Baccharis uncinella* DC. (Asteraceae). **Parasitol. Res**. 108, 2011. https://doi.org/10.1007/s00436-010-2091-8

PAVELA, R. History, Presence and Perspective of Using Plant Extracts as Commercial Botanical Insecticides and Farm Products for Protection against Insects – a Review. **Plant Protect. Sci**. 52, 2016. https://doi.org/10.17221/31/2016-PPS

PAVELA, R., SEDLÁK, P. Post-application temperature as a factor influencing the insecticidal activity of essential oil from *Thymus vulgaris*. **Ind Crops Prod** 113, 2018. https://doi.org/10.1016/j.indcrop.2018.01.021

PHILIPPOU, D., FIELD, L., MOORES, G. Metabolic enzyme(s) confer imidacloprid resistance in a clone of *Myzus persicae* (Sulzer) (Hemiptera: Aphididae) from Greece. **Pest Manag. Sci**. 66, 2010. https://doi.org/10.1002/ps.1888

PICKSON, R. B., GUI, P., CHEN, A., BOATENG, E. Empirical analysis of rice and maize production under climate change in China. **Environmental Science and Pollution Research**, 29, 2022. https://doi.org/10.1007/s11356-022-20722-z

PINHEIRO, L.S., GATTI, V.C.M., DE OLIVEIRA, J.T., DA SILVA, J.N. et al. Características agro econômicas do milho: uma revisão. **Natural Resources**, 11, 2021. http://doi.org/10.6008/CBPC2237-9290.2021.002.0003

PIPERNO, D. R., RANERE, A. J., HOLST, I. IRIARTE, J. et al. Starch grain and phytolith evidence for early ninth millennium B.P. maize from the Central Balsas River Valley, Mexico. **PNAS**, 2009. https://doi.org/10.1073pnas.0812525106

PIRI, A., SAHEBZADEH, N., ZIBAEE, A., SENDI, J. J. et al. Toxicity and physiological effects of ajwain (*Carum copticum*, Apiaceae) essential oil and its major constituents against *Tuta absolute* (Meyrick) (Lepidoptera: Gelechiidae). **Chemosphere**, 256, 2020. https://doi.org/10.1016/j.chemosphere.2020.127103

PITRE, H. N. Relationship of fall armyworm (Lepidoptera: Noctuidae) from Florida, Honduras, Jamaica, and Mississippi: susceptibility to insecticides with reference to migration. **Fla. Entomol**, 71, 1988. https://doi.org/10.2307/3494893

PLATA-RUEDA, A., FIAZ, M., BRÜGGER, B. P., CAÑAS, V. et al. Lemongrass essential oil and its components cause effects on survival, locomotion, ingestion, and histological changes of the midgut in *Anticarsia gemmatalis* caterpillars. **Toxin Reviews**, https://doi.org/10.1080/15569543.2020.1861468

POGUE, G. M. A world revision of the genus *Spodoptera* Guenée (Lepidoptera: Noctuidae). Memoirs of the American Entomological Society 43:1-202. 2002.

POMARI-FERNANDES A, DE FREITAS BUENO A, OLIVEIRA DE FREITAS BUENO R C, MENEZES A JR., PRADO FERNANDES FONSECA AC. Releasing number of *Telenomus remus* (Nixon) (Hymenoptera: Platygastridae) against *Spodoptera frugiperda* Smith (Lepidoptera: Noctuidae) in corn, cotton and soybean. **Cienc. Rural**, 43, 2013. https://doi.org/10.1590/S0103-84782013005000013

POMARI-FERNANDES A, DE FREITAS BUENO A, DE BORTOLI SA, FAVETTI BM. Dispersal capacity of the egg parasitoid *Telenomus remus* Nixon (Hymenoptera: Platygastridae) in maize and soybean crops. **Biol. Control**, 126, 2018. https://doi.org/10.1016/j.biocontrol.2018.08.009

POORJAVAD, N., GOLDANSAZ, S.H., DADPOUR, H. et al. Effect of *Ferula assafoetida* essential oil on some biological and behavioral traits of *Trichogramma embryophagum* and T. evanescens. **BioControl** 59, 2014. https://doi.org/10.1007/s10526-014-9583-x

POPHAM, H. J. R., ROWLEY, D. L., HARRISON, R. L. Differential insecticidal properties of *Spodoptera frugiperda* multiple nucleopolyhedrovirus isolates against corn-strain and rice-strain fall armyworm, and genomic analysis of three isolates. **J. Invertebr. Pathol**. 183, 2021. https://doi.org/10.1016/j.jip.2021.107561

PORTO, J.V.A.; REZENDE, F.P.C.; NUCCI, H.H.P.; ROEL, A.R. et al. Deep neural networks with attention mechanisms for *Spodoptera frugiperda* pupae sexing. **Smart Agricultural Technology**, v. 4, 2023. https://doi.org/10.1016/j.atech.2023.100200

QUEIROZ, A.P.; FAVETTI, B.M.; LUSKI, P.G.G.; GONÇALVEZ, J. et al. Telenomus remus (Hymenoptera: Platygastridae) parasitism on *Spodoptera frugiperda* (Lepidoptera: Noctuidae) eggs: different parasitoid and host egg ages. **Semina**: Ciências Agrárias, v. 40, 2019. https://doi.org/10.5433/1679-0359.2019v40n6Supl2p2933

RAHIMI, V., HAJIZADEH, J., ZIBAEE, A., SENDI, J.J. Effect of Polygonum persicaria (Polygonales: Polygonaceae) extracted agglutinin on life table and antioxidant re sponses in Helicoverpa armigera (Lepidoptera: Noctuidae) larvae. **J. Econ. Entomol**. 111, 2018. https://doi.org/10.1093/jee/toy006

REBOURG, .C., CHASTANET, .M., GOUESNARD, B. et al. Maize introduction into Europe: the history reviewed in the light of molecular data. **Theor Appl Genet**, 106, 2003.

https://doi.org/10.1007/s00122-002-1140-9

REGNAULT-ROGER, C.; VINCENT, C.; THOR, J. Essential oils in insect control: low-risk products in a high-stakes world. **Annual Review Entomology**, v. 57, 2012. https://doi.org/10.1146/annurev-ento-120710-100554

REIS, S.L., MANTELLO, A.G., MACEDO, J.M., GELFUSO, E.A. et al. Typical monoterpenes as insecticides and repellents against stored grain pests. Molecules 21, 2016. https://doi.org/10.3390/molecules21030258

RENOZ, F., DEMETER, S., DEGAND, H., NICOLIS, S. C. et al. The modes of action of *Mentha arvensis* essential oil on the granary weevil *Sitophilus granarius* revealed by a label-free quantitative proteomic analysis. **J Pest Sci**, 95, 2022. https://doi.org/10.1007/s10340-021-01381-4

REZENDE, C.L.; SCARANO, F.R.; ASSAD, E.D. et al. From hotspot to hopespot: An opportunity for the Brazilian Atlantic Forest. **Perspectives in Ecology and Conservation**, v. 16, 2018. https://doi.org/10.1016/j.pecon.2018.10.002

RIBEIRO, V. L. S., ROLIM, V., BORGIGNON, S., HENRIQUES, A. T. et al. Chemical composition and larvicidal properties of the essential oils from *Drimys brasiliensis* Miers (Winteraceae) on the cattle tick *Rhipicephalus (Boophilus) microplus* and the brow dog tick *Rhipicephalus sanguineus*. Parasitol. Res. 102, 2008. https://doi.org/10.1007/s00436-007-0799-x

RIBEIRO, M.C.; METZGER, J.P.; MARTENSEN, A.C. et al. The Brazilian Atlantic Forest: Much is left, and how is the remaining forest distributed? Implications for conservation. **Biological Conservation**, v. 142, 2009. https://doi.org/10.1016/j.biocon.2009.02.021

RÍOS, J.L. Essential Oils: What They Are and How the Terms Are Used and Defined 2016. In: **Essential Oils in Food Preservation, Flavor and Safety**, Ed: Preedy, V.R. Elsevier, 2016.

ROSA, A. P. A., TRECHA, C. O., ALVES, A. C., GARCIA, L. et al. Biologia e tabela de vida de fertilidade de *Spodoptera frugiperda* (J.E. SMITH) em linhagens de milho. **Arq. Inst. Biol.**, São Paulo, v.79, n.1, p.39-45, jan./mar., 2012

RUSSO, M.L.; JARBER, L.R.; SCORSETTI, A.C.; VIANNA, F. et al. Effect of entomopathogenic fungi introduced as corn endophytes on the development, reproduction, and food preference of the invasive fall armyworm *Spodoptera frugiperda*. **Journal of Pest Science**, v. 94, 2021. https://doi.org/10.1007/s10340-020-01302-x

RUTTANAPHAN, T., PLUEMPANUPAT, W., AUNGSIRISAWAT, C., BOONYARIT, P., et al., Effect of Plant Essential Oils and Their Major Constituents on Cypermethrin Tolerance Associated Detoxification Enzyme Activities in *Spodoptera litura* (Lepidoptera: Noctuidae), **Journal of Economic Entomology**, 112, 2019. https://doi.org/10.1093/jee/toz126

SABINI, L.I. et al. Study of the cytotoxic and antifungal activity of the essencial oil of *Elyonurus muticus* against *Candida* spp. **Molecular Medicinal Chemistry**, v.11, p.31-3, 2006.

SAMPAIO, F. et al. A new biocontrol agent against old enemies: The potential of *Trichogramma foersteri* for the control of *Spodoptera frugiperda* and *Spodoptera eridania*. **Biological Control**, v. 192, p. 1-8, 2024. https://doi.org/10.1016/j.biocontrol.2024.105504.

SANCHA, N. U.; BOYLE, S.A.; MCLNTYRE, N.E. Identifying structural connectivity priorities in eastern Paraguay's fragmented Atlantic Forest. **Scientific Reports**, v. 11, 2021. https://doi.org/10.1038/s41598-021-95516-3

SANCHES, A.; SALES, C. Expressivo aumento nas exportações brasileiras de milho impõe mudanças na dinâmica do mercado nacional. **Centro de Estudos Avançados em Economia Aplicada** (CEPEA-USP), set, 2022. Disponível em: < https://www.cepea.esalq.usp.br/br/opiniao-cepea/expressivo-aumento-nas-exportacoes-brasileiras-de-milho-impoe-mudancas-na-dinamica-do-mercado-nacional.aspx#:~:text=O%20maior%20excedente%20export%C3%A1vel%20em,milh%C3%B5es%20de%20toneladas%2C%20um%20recorde.> Acesso em: 18 fev. 2024

SANTOS, A.S.; ALVES, S.M., FIGUEIREDO, F.J.C.; ROCHA NETO, O.G. Descrição de sistema e de métodos de extração de óleos essenciais e determinação de umidade de biomassa em laboratório. Belém, PA: **Comunicado técnico, 99**. Embrapa Amazônia Oriental, 2004. Disponível em: http://www.infoteca.cnptia.embrapa.br/infoteca/handle/doc/402448 Acesso em: 25 fev. 2024

SANTOS, A.S.; ALVES, S.M., FIGUEIREDO, F.J.C.; ROCHA NETO, O.G. Descrição de sistema e de métodos de extração de óleos essenciais e determinação de umidade de biomassa em laboratório. Belém, PA: **Comunicado técnico, 99**. Embrapa Amazônia Oriental, 2004. Disponível em: http://www.infoteca.cnptia.embrapa.br/infoteca/handle/doc/402448 Acesso em: 25 fev. 2024

SANTOS, T. G.; DOGNINI, J.; BEGNINI, I. M.; REBELO, R. A.; VERDI, M.; GASPER, A. L. DALMARCOD, E. M. Chemical Characterization of Essential Oils from *Drimys angustifolia* Miers (Winteraceae) and Antibacterial Activity of their Major Compounds. **J. Braz. Chem. Soc**., 24, 2013. https://doi.org/10.1590/S0103-50532013000100020

SANTOS, A. A., WANDERLEY-TEIXEIRA, V., CRUZ, G. S., DUTRA, K. A. et al. Essential oil toxicity on biological and reproductive parameters of Alabama argillacea (Hübner) (Lepidoptera: Erebidae). **Acta Histochemica**, 123, 2021. https://doi.org/10.1016/j.acthis.2021.151714

SARAN, A., FERNÁNDEZ, L., MINIG, M., REINHARD, M.B., MERINI, L.J. Repellent activity of essential oils from native plants and their blend for *Tribolium castaneum* control in store grains. **Semiárida UNLPam**. 29, 2019. https://doi.org/10.19137/semiarida.2019(01).43-51

SCHRIPSEMA, J., LEMOS, M.A., DAGNINO, D. *et al.* Carqueja (*Baccharis* sect. *Caulopterae*), a critical review of its history, phytochemistry and medicinal use: problems of ethnopharmacology in Latin America. **Phytochem Ver**, 18, 2019. https://doi.org/10.1007/s11101-019-09616-0

SEMMAR, N. **Variational Factors and Regulation Processes of Secondary Metabolites**. In: Secondary Metabolites in Plant Stress Adaptation. Signaling and Communication in Plants. Springer, Cham. 2024. https://doi.org/10.1007/978-3-031-52595-7_2

SENTHIL-NATHAN, S. Physiological and biochemical effect of neem and other Meliaceae plants secondary metabolites against lepidopteran insects. **Front. Physiol**. 4, 2013. https://doi.org/10.3389/fphys.2013.00359

SEO, S.M., KIM, J., KANG, J., KOH, S.H. et al. Fumigant toxicity and acetylcholinesterase inhibitory activity of 4 Asteraceae plant essential oils and their constituents against Japanese termite (Reticulitermes speratus Kolbe). **Pestic. Biochem. Physiol**. 113, 2014. https://doi.org/10.1016/j.pestbp.2014.06.001

SHAHRIARI, M., ZIBAEE, A., SAHEBZADEH, N., SHAMAKHI, L. Effects of α-pinene, trans-anethole, and thymol as the essential oil constituents on antioxidant system and acetylcholine esterase of *Ephestia kuehniella* Zeller (Lepidoptera: Pyralidae). **Pestic. Biochem. Phys.** 150, 2018. https://doi.org/10.1016/j.pestbp.2018.06.015

SHAHRIARI, M., ZIBAEE, A., SHAMAKHI, L., SAHEBZADEH, N. et al. Bio-efficacy and physiological effects of *Eucalyptus globulus* and *Allium sativum* essential oils against *Ephestia kuehniella* Zeller (Lepidoptera: Pyralidae). **Toxin Rev**. 39, 2020. https://doi.org/10.1080/15569543.2018.1554588

SHEEHAN, D., MEADE, G., FOLEY, V. M., DOWD, C. A. Structure, function and evolution of glutathione transferases: implications for classification of non-mammalian members of an ancient enzyme superfamily. Biochem J., 15, 2001. https://doi.org/10.1042/0264-6021:3600001.

SHIFERAW, B., et al. Crops that feed the world 6. Past successes and future challenges to the role played by maize in global food security. **Food Security**, 3, 2011. 10.1007/s12571-011-0140-5.

SILVA de ASSIS, H. C. **Der einsatz von biomarkern zur summarischen erfassung von Gewässerverschmutzungen**. 99 f. 1998. Tese de Doutorado apresentada na Universidade Técnica de Berlim, Alemanha. 1998.

SILVA, C.L.T.; PAIVA, L. A.; CORREA, F.; SILVA, F.C.; PELOSI, A.P. et al. Interaction between Corn Genotypes with Bt Protein and Management Strategies for *Spodoptera frugiperda* (Lepidoptera: Noctuidae). **Florida Entomologist**, v. 12, 2019. https://doi.org/10.1653/024.102.0409

SILVA, I.H.S.; COSTA, V.H.D.; CURY, J.C.; VALICENTE, F. H. et al. The Infectivity of SfMNPV on fall armyworm is influenced by the host plant. **Revista Brasileira de Milho e Sorgo**, v. 17, 2018. https://doi.org/10.18512/1980-6477/rbms.v17n39369-379

SILVEIRA, R.M., CARVALHO, A.F.U., BÜNGER, M.O., GOMES, M.M. et al. How Much do the Environmental Conditions Interfere with the Essential Oils of *Eugenia* spp. L. (Myrtaceae)? **J. Braz. Chem. Soc.**, 33, 2022. https://doi.org/10.21577/0103-5053.20210146

SILVESTRE, W. P., VICENÇO, C. B., THOMAZONI, R. A., PAULETTI, G. F. Insecticidal activity of *Callistemon speciosus* essential oil on *Anticarsia gemmatalis* and *Spodoptera frugiperda*. **Int. J. Trop. Insect Sci** 42, 2022. https://doi-org.ez22.periodicos.capes.gov.br/10.1007/s42690-021-00648-8

SIQUEIRA-FILHO, J. A., LEME, E. M. C. **Fragmentos de Mata Atlântica do Nordeste**. Biodiversidade, conservação e suas bromélias. Andrea Jakobsson Estúdio, Rio de Janeiro, 2006. 415p.

SOARES, L.A.L.; FARIAS, M.R. Qualidade de insumos farmacêuticos ativos de origem natural. In: Simões, C. M. O.; Schenkel, E. P.; Mello, J. C. P.; Mentz, L. A.; Petrovick, P. R. **Farmacognosia**: da planta ao medicamento. Simões C. M. O et al. Porto Alegre: Artmed, 2017.

SOMBRA, K.E.S., DE AGUIAR, C.V.S., DE OLIVEIRA, S.J., BARBOSA, M.G. et al. Potential pesticide of three essential oils against *Spodoptera frugiperda* (J.e. smith) (lepidoptera: Noctuidae). **Chil. J. Agric. Res**. 80, 2020. https://doi.org/10.4067/S0718-58392020000400617

SOUZA, C.V; LORENZI, H. **Botânica Sistemática**: Guia ilustrado para identificação das famílias de fanerógamas nativas e exóticas no Brasil, baseado em APG II. 2ª edição, Editora Plantarum, Nova Odessa, SP, 2008.

SOUZA, M. T., SOUZA, M. T., BERNARDI, D., MELO, D. J. et al. Insecticidal and oviposition deterrent effects of essential oils of *Baccharis* spp. and histological assessment against *Drosophila suzukii* (Diptera: Drosophilidae). **Sci. Rep**. 11, 2021. https://doi.org/10.1038/s41598-021-83557-7

STADTMAN, E.R. Oxidation of proteins by mixed-function oxidation systems: implication in protein turnover, aging and neutrophil function. **Trends in Biochemistry Sciences**, 11, 1986. https://doi.org/10.1016/0968-0004(86)90221-5

STADTMAN, E.R., LEVINE, R.L. Free radical-mediated oxidation of free amino acids and amino acid residues in proteins. **Amino Acids** 25, 2003. https://doi.org/10.1007/s00726-003-0011-2

STEFANAZZI, N., STADLER, T., FERRERO, A. Composition and toxic, repellent and feeding deterrent activity of essential oils against the stored-grain pests *Tribolium castaneum* (Coleoptera: Tenebrionidae) and *Sitophilus oryzae* (Coleoptera: Curculionidae). **Pest Manag. Sci**. 67, 2011. https://doi.org/10.1002/ps.2102

STEHMANN et al. Plantas da Floresta Atlântica. – Rio de Janeiro: Jardim Botânico do Rio de Janeiro, 2009. 516 p. Disponível em: https://www.gov.br/jbrj/pt-br/centrais-de-conteudo/publicacoes/plantas_floresta_atlantica.pdf Acesso em: 23 mar. 2024.

STEVENSON, P.C., BELMAIN, S.R., ISMAN, M.B. Pesticidal plants: From smallholder use to commercialisation, **Plants**. 2020.

STOKSTAD, E. New crop pest takes Africa at lightning speed. **Science** 356, 2017. https://doi.org/10.1126/science.356.6337.473

STORER, N. P., BABCOCK, J. M., SCHLENZ, M., MEADE, T., THOMPSON, G. D. et al. Discovery and characterization of field resistance to Bt maize: *Spodoptera frugiperda* (Lepidoptera: Noctuidae) in Puerto Rico. **J. Econ. Entomol**. 103, 2010. https://doi.org/10.1603/ec10040

STRATAKOS, A. C.; KOIDIS, A. Methods for Extracting Essential Oils. In: **Essential Oils in Food Preservation, Flavor and Safety**, Ed: Preedy, V.R. Elsevier, 2016.

SUN X-X, HU C-X, JIA H-R, WU Q-L, SHEN X-J, et al. Case study on the first immigration of fall armyworm, *Spodoptera frugiperda* invading into China. **J. Integr. Agric**. 20, 2021. https://doi.org/10.1016/S2095-3119(19)62839-X

TABARELLI, M.; AGUIAR, A.V.; RIBEIRO, M.C. Prospects for biodiversity consercation in the Atlantic Forest: Lesson from aging human-modified landscapes. **Biological Conservation**, v. 143, 2010. https://doi.org/10.1016/j.biocon.2010.02.005

TAIZ, L.; ZEIGER, E. **Fisiologia Vegetal**, trad. Armando Molina Divan Junior, et al. 5 ed. Porto Alegre: Artmed, 2013.

TAK, J.H., ISMAN, M.B. Metabolism of citral, the major constituent of lemongrass oil, in the cabbage looper, *Trichoplusia ni*, and effects of enzyme inhibitors on toxicity and metabolism. **Pestic. Biochem. Physiol**. 133, 2016. https://doi.org/10.1016/j.pestbp.2016.03.009

TAK, J. H., JOVEL, E., ISMAN, M. B. Comparative and synergistic activity of *Rosmarinus officinalis* L. essential oil constituents against the larvae and ovarian cell line of the cabbage looper, *Trichoplusia ni* (Lepidoptera: Noctuidae). **Pest Manag. Sci**. 72, 2016. https://doi.org/10.1002/ps.4010

TAMPE, J., ESPINOZA, J., CHACÓN-FUENTES, M., QUIROZ, A., RUBILAR, M. Evaluation of *Drimys winteri* (Canelo) Essential Oil as Insecticide against *Acanthoscelides obtectus* (Coleoptera: Bruchidae) and *Aegorhinus superciliosus* (Coleoptera: Curculionidae). **Insects** 11, 2020. https://doi.org/10.3390/insects11060335

TAVARES, W. S., CRUZ, I., PETACCI, F., ASSIS JÚNIOR, S. L., et al., Potential use of Asteraceae extracts to control *Spodoptera frugiperda* (Lepidoptera: Noctuidae) and selectivity to their parasitoids *Trichogramma pretiosum* (Hymenoptera: Trichogrammatidae) and *Telenomus remus* (Hymenoptera: Scelionidae). **Industrial Crops and Products**, 30, 2009. https://doi.org/10.1016/j.indcrop.2009.07.007

TAY, W. T., MEAGHER Jr, R. L., CZEPAK, C., GROOT, A. *Spodoptera frugiperda*: Ecology, Evolution, and Management Options of an Invasive Species. **Annu. Rev. Entomol**. 68, 2023. https://doi.org/10.1146/annurev-ento-120220 102548

THEIS, N.; LERDAU, M. The Evolution of Function in Plant Secondary Metabolites. **International Journal of Plant Science**, 2015. https://doi.org/10.1086/374190.

THOMPSON, P. B. The Agricultural Ethics of Biofuels: The Food vs. Fuel Debate. **Agriculture**. 2, 2012. https://doi.org/10.3390/agriculture2040339.

TRIPATHI, A.K., PRAJAPATI, V., KUMAR, S. Bioactivity of l-carvone, d-carvone and dihydrocarvone towards three stored product beetles. **J. Econ. Entomol**., 96, 2003. https://doi.org/10.1603/0022-0493-96.5.1594

TUNÇ, I., ERLER, F., DAGLI, F., ÇALIS, Ö. InseInsecticidal activity of acetone vapours. **Journal of Stored Products Research**,33, 1997. https://doi.org/10.1016/S0022-474X(96)00021-5

TURCHEN, L.M., PITON, L.P., DALL'OGLIO, E.L. et al. Toxicity of *Piper aduncum* (Piperaceae) Essential Oil Against *Euschistus heros* (F.) (Hemiptera: Pentatomidae) and Non-Effect on Egg Parasitoids. **Neotrop Entomol** 45, 2016. https://doi.org/10.1007/s13744-016-0409-7

UNITED STATES DEPARTAMENT OF AGRICULTURE – USDA – **Corn**: Production, Supply and Distribution, 2023. Disponível em: < https://apps.fas.usda.gov/newgainapi/api/Report/DownloadReportByFileName?fileName=Grain%20and%20Feed%20Annual_Brasilia_Brazil_BR2023-0008> Acesso em 18 fev. 2024

UPADHYAY, N., SINGH, V.K., DWIVEDY, A.K., DAS, S. et al. Assessment of *Melissa officinalis* L. essential oil as an eco-friendly approach against biodeterioration of wheat flour caused by *Tribolium castaneum* Herbst. **Environ. Sci. Pollut. Res**. 26, 2019.. https://doi.org/10.1007/s11356-019-04688-z

USSEGLIO, V.L., DAMBOLENA, J.S., ZUNINO, M.P. Can Essential Oils Be a Natural Alternative for the Control of *Spodoptera frugiperda*? A Review of Toxicity Methods and Their Modes of Action. **Plants** 12, 2023. https://doi.org/10.3390/plants12010003

VALE, M.M.; TOURINHO, L.; LORINI, M.L. et al. Endemic Birds of the Atlantic Forest: trits, conservation status, and patterns of biodivessity. **Journal of Field Ornithology**, v. 39, 2018. https://doi-org.ez22.periodicos.capes.gov.br/10.1111/jofo.12256

VALLE, D., MONTELLA, I. R. Quantification methodology for enzyme activity related to insecticide resistance in *Aedes aegypti*. Brazil. Ministry of Health. Oswaldo Cruz Foundation, 1, 128. 2006.

VAN den BERG, J.; PLESSIS, H. Chemical Control and Inseticide Resistance in *Spodoptera frugiperda* (Lepidoptera: Noctuidae). **Entomological Society of America**, v. 115, 2022. https://doi.org/10.1093/jee/toac108

VAN den DOOL, H., KRATZ, P. D. A generalization of the retention index system including linear temperature programmed gas liquid partition chromatography. **J. of Chromatogr**. 11: 463-471, 1963.

VELASQUES, J., CARDOSO, M.H., ABRANTES, G., FRIHLING, B.E. et al. The rescue of botanical insecticides: A bioinspiration for new niches and needs. **Pestic Biochem Physiol**., 143, 2017. https://doi.org/10.1016/j.pestbp.2017.10.003

VICENÇO, C. B., SILVESTRE, W. P., MENEGOL, I. R., CARRARO, M. C., PAULETTI, G. F. Insecticidal Activity of *Lavandula dentata* L. Essential Oil on *Anticarsia gemmatalis* (Hübner, 1818). **Braz. Arch. Biol. Technol**. 64, 2021. https://doi.org/10.1590/1678-4324-2021210327

VIEIRA, N. F., POMARI-FERNANDES, A., LEMES, A. A. F., VACARI, A. M. et al. Cost of production of *Telenomus remus* (Hymenoptera: Platygastridae) grown in natural and alternative hosts. **J. Econ. Entomol**. 110, 2017. https://doi.org/10.1093/jee/tox271

WANG, Y., OBERLEY, L.W., MURHAMMER, D.W. Evidence of oxidative stress following the viral infection of two lepidopteran insect cell lines. **Free Radic. Biol. Med**., 31, 2001. https://doi.org/10.1016/S0891-5849(01)00728-6

WANG, Y., ZHANG, L. T., FENG, Y. X., ZHANG, D. et al. Comparative evaluation of the chemical composition and bioactivities of essential oils from four spice plants (Lauraceae) against stored- product insects. **Ind. Crops Prod**. 140, 2019. https://doi.org/10.1016/j.indcrop.2019.111640

WANG, F., XUE, J., XIE, R., MING, B. et al. Assessing Growth and Water Productivity for Drip-Irrigated Maize under High Plant Density in Arid to Semi-Humid Climates. **Agriculture**, 12, 2022. https://doi.org/10.3390/agriculture12010097

WARBURTON, M.L.; WOOLFOLK, S.W.; SMITH, J.S.; HAWKINS, L.K. Genes and genetic mechanisms contributing to fall armyworm resistance in maize. **The Plant Genome**, v. 16, 2023. https://doi.org/10.1002/tpg2.20311

YANG, Y., ISMAN, M.B., TAK, J.H. Insecticidal activity of 28 essential oils and a commercial product containing *Cinnamomum cassia* bark essential oil against *Sitophilus zeamais* Motschulsky. **Insects** 11, 2020. https://doi.org/10.3390/insects11080474

YEDOMON, B.H., SAVES, I., MTIMET, N., RAOELISON, E.G. et al. *Elionurus tristis* Essential Oil: GC-MS Analysis and Antioxidant and Antituberculosis Activities. **Nat. Prod. Commun**. 12, 2017. https://doi.org/10.1177/1934578x1701200436

YEOM, H.J., JUNG, C.S., KANG, J., KIM, J. et al. Insecticidal and acetylcholine esterase inhibition activity of *Asteraceae* plant essential oils and their constituents against adults of the German cockroach (*Blattella germanica*). **J. Agric. Food Chem**. 63, 2015. https://doi.org/10.1021/jf505927n

YOUNG, J. R., McMILLAN, W. W. Differential feeding by two strains of fall armyworm larvae on carbaryl treated surfaces. **J. Econ. Entomol**. 72, 1979.

ZACHRISSON, B., SANTANA, A., GUPTA, M. Effects of Essential Oils from Two Species of Piperaceae on Parasitized and Unparasitized Eggs of *Oebalus insularis* (Heteroptera: Pentatomidae) by *Telenomus podisi* (Hymenoptera: Platygastridae). **Natural Product Communications**, 2019. https://doi.org/10.1177/1934578X1901400122

ZAPATA, N., BUDIA, F., VINUELA, E., MEDINA, P. Bioactivity of essential oils from leaves and bark of *Laurelia sempervirens* and *Drimys winteri* against *Acyrthosiphon pisum*. **Pest Manag Sci** 66, 2010. https://doi.org/10.1002/ps.2018

ZHANG, L. B., FENG, M. G. Antioxidant enzymes and their contributions to biological control potential of fungal insect pathogens. **Appl. Microbiol. Biotechnol**. 102, 2018. https://doi.org/10.1007/s00253-018-9033-2

ZEM, L. M., ZUFFELATO-RIBAS, K. C., RADOMSKI, M. I., KOEHLER, H. S., DESCHAMPS, C. *Drimys brasiliensis* essential oil as a source of drimenol. **Holos**, 32, 2016. https://doi.org/10.15628/holos.2016.3192

ZIMMERMANN, R. C., ARAGÃO, C. E. C., ARAÚJO, P. J. P., BENATTO, A. et al. Insecticide activity and toxicity of essential oils Against two store-products insects. **Crop Prot**. 144, 2021. https://doi.org/10.1016/j.cropro.2021.105575

# ANEXOS

ANEXO I – Inscrição do projeto no Sistema Nacional do Patrimônio Genético e do Conhecimento Tradicional Associado (SisGen)

**Ministério do Meio Ambiente**
**CONSELHO DE GESTÃO DO PATRIMÔNIO GENÉTICO**
**SISTEMA NACIONAL DE GESTÃO DO PATRIMÔNIO GENÉTICO E DO CONHECIMENTO TRADICIONAL ASSOCIADO**

**Atestado de Regularidade de Acesso**
**Cadastro nº AE4C4BF**

O Conselho de Gestão do Patrimônio Genético, no exercício da competência conferida pelo inciso IV do § 1º do art. 6º da Lei nº 13.123/2015, atesta que o acesso ao Patrimônio Genético, referente ao cadastro abaixo identificado e resumido, cumpriu os requisitos da Lei nº 13.123/2015 e seus regulamentos até a data de emissão deste atestado.

| | |
|---|---|
| Número do cadastro: | **AE4C4BF** |
| Usuário: | **Universidade Federal do Paraná** |
| CPF/CNPJ: | **75.095.679/0001-49** |
| Objeto do Acesso: | **Patrimônio Genético** |
| Finalidade do Acesso: | **Pesquisa** |