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REVIEW ARTICLE

# Chemical composition and biological activities of two chemotype-oils from *Cinnamomum verum* J. Presl growing in North Brazil

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**Abstract** Chemical composition and antioxidant and antifungal action of the oils from leaves and wood bark of two chemotypes of *Cinnamomum verum* J. Presl were evaluated. Plants were sampled in the cities of São Luís and Santa Inês, state of Maranhão, Brazil. GC–MS and GC-FID, DPPH radical scavenging, and in vitro test against the phytopathogenic fungus *Colletotrichum musae* were used to perform these analyses. *Cinnamomum verum* is worldwide known as Cinnamon, highlighted for its extensive use in the cooking of diverse cultures of the world, and as a medicinal plant to treat environmental viral diseases. In the leaf oil of São Luís chemotype, eugenol (93.6%) was the main constituent, while in Santa Inês chemotype, it was benzyl benzoate (95.3%). In the bark wood oil of São Luís chemotype, (*E*)-cinnamaldehyde (89.3%) was the main constituent, while in Santa Inês chemotype, they were benzyl benzoate (23.3%), linalool (14.0%), (*E*)-caryophyllene (9.1%), caryolan-8-ol (7.2%) and borneol (4.7%). Leaf oils from both chemotypes showed strong to moderate antifungal activity, reaching 100% efficacy in eugenol-containing oils and above 70% in benzyl benzoate oils. In the antioxidant evaluation, the chemotype with a high eugenol content presented an inhibitory concentration higher than 80%, compared to Trolox. The leaf oils of the two *C. verum* chemotypes showed significant antifungal and antioxidant potential, considering their economic use as a functional and nutraceutical food supplement.

**Keywords** Cinnamon oils · Eugenol · Benzyl benzoate · Chemical variability · Antifungal effect · Antioxidant activity

## Introduction

*Cinnamomum* belongs to Lauraceae. It is represented by trees and shrubs and comprises about 250 species which are distributed in tropical and subtropical regions of Southeast Asia, Australia, and North, Central and South America (Jayaprakasha et al. 2003; Wang et al. 2009). *Cinnamomum verum* J. Presl (syn. *Camphora mauritiana* Lukman, *Cinnamomum zeylanicum* Blume, *Laurus cinnamomum* L.) (Missouri Botanical Garden, www.tropicos.org/Name/17800682), is a native species grown mostly in Sri Lanka, India, and Seychelles and Madagascar islands. It is worldwide known as Cinnamon, has been highlighted for its extensive use in the cooking of diverse cultures of the world, as well as to possess aromatic, digestive, stimulant, antibacterial, astringent, antioxidant, and antinociceptive pharmacological properties (Wang et al. 2009; Gupta 2010). The species was introduced in Brazil during the slavery period, and it is commonly known as Canela, Canela-da-Índia, or Canela-do-Ceilão, popularly used as a stimulant, tonic, carminative and anti-spasmodic (Pio Corrêa 1984).

Concerning the *C. verum* oil, some reports have shown diversity in its composition, displaying some chemical

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types. The leaf and bark oils of specimens of *C. zeylanicum* growing in Sri Lanka, India, Fiji Islands and Malaysia presented eugenol and cinnamaldehyde content, respectively, as the principal constituents (Senanayake et al. 1978; Raina et al. 2001; Mallavarapu and Rao 2007; Patel et al. 2007; Jantan et al. 2008; Subki et al. 2013; Chakraborty et al. 2015). Besides, benzyl benzoate (Nath et al. 1996), linalool (Jirovetz et al. 2001), and cinnamaldehyde, cinnamyl acetate, and cinnamyl benzoate (Boniface et al. 2012) have been identified as the main compounds in the leaf and bark oils from other Cinnamon specimens occurring in India and Africa, respectively.

A number of biological properties have been attributed to *C. verum* leaf and bark oils, including the antimicrobial (El-Baroty et al. 2010; Boniface et al. 2012) antifungal (Simic et al. 2004; Jantan et al. 2008), mosquitocidal (Samarasekera et al. 2005), antioxidant (Simic et al. 2004; Schmidt et al. 2006), and cytotoxic activities (Unlu et al. 2010).

The substitution of synthetic pesticides for natural products less toxic to humans has stimulated their use in the control of phytopathogens. Alternatives to reduce pests and diseases in agriculture are the oils and extracts of medicinal plants, which has increased in recent years and proving to be potential fungicidal and fungistatic agents, as well as contributing to the activation of plant defense mechanisms. In Brazil, the action of essential oils on phytopathogenic fungi that attacks economically important crops is still little known, and this knowledge can contribute alternatively to the control of some diseases, as well as in the development of new products. In this regard, one example is the post-harvest sanitary control of bananas.

Banana is cultivated on a large scale in many locations of Brazil due its nutritional value and export potential. Storage of banana is made difficult by the growth of fungi, as *Colletotrichum musae*, which causes anthracnose disease. Banana producers are looking for new alternative post-harvest treatments that are pesticides free and acceptable to consumers.

Antioxidants from natural sources have received attention from researchers. Efforts have been made to identify compounds which can prevent oxidative body damage and be formulated as new functional foods and nutraceuticals (Hashemi et al. 2017). The leaf and bark oils of *C. zeylanicum* and eugenol, its main constituent, were tested in vitro models of peroxynitrite-induced nitration and lipid peroxidation, showing a significant antioxidant property in both models, higher than Trolox (Chericoni et al. 2005). The *C. zeylanicum* leaf oil demonstrated significant scavenger activity against the DPPH radical, at concentrations lower than the eugenol (Schmidt et al. 2006). Also, eugenol showed a most potent radical-scavenging activity in comparison to butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), α-tocopherol, and Trolox (Gülçin 2011).

The objective of this work was to determine the variability in the composition of the essential oils of leaf and bark wood of two *C. verum* specimens, sampled in the municipalities of Santa Inês (SI) and São Luís (SL), Maranhão state, and to test their antifungal and antioxidant action, with a view to its economic utilization as functional food and nutraceutical.

## Materials and methods

### Chemicals

The reagents and solvents, dimethyl sulfoxide (DMSO), ethanol, 1,1-diphenyl-2-picrylhydrazyl (DPPH), tris hydrochloride (tris-HCl), and 6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (Trolox) were all from Sigma-Aldrich, USA. The potato dextrose agar medium was from Millipore, USA.

### Plant material and collection data

The *C. verum* leaves and barks wood were collected from municipalities of Santa Inês (SI) (3° 41′ 0″ S/45° 23′ 12″ W) and São Luís (SL) (02° 31′ 47″ S/44° 18′ 10″ W), State of Maranhão, both at 9 am, January 2014. Samples of the two specimens were sent to the João Murça Pires Herbarium, at the Museu Emílio Goeldi (MPEG), city of Belém (PA), and identified by comparison with an authentic sample (MG 165477) previously deposited.

### Essential oil extraction

The leaves and barks (50 g, each) of *C. verum* were ground and submitted to hydrodistillation using a Clevenger-type apparatus (3 h), after drying at room temperature (3 days). The oils were dried over anhydrous sodium sulfate, and their yields were calculated by the plant dry weight. The moisture content of the samples was calculated using an Infrared Moisture Balance for water loss measurement. The procedure was performed in duplicate.

### Oil composition analysis

Analysis of the oils were carried on a GC–MS Thermo-Electron, model Focus DSQ II, under the following conditions: DB-5 ms (30 m × 0.25 mm; 0.25 mm film thickness) fused-silica capillary column; programmed temperature, 60–240 °C (3 °C/min); injector temperature, 250 °C; carrier gas, helium, adjusted to a linear velocity of 32 cm/s (measured at 100 °C); injection type, split (1.0 μL), from 1:1000 hexane solution; split flow was adjusted to yield a 20:1 ratio; septum sweep was a constant

10 mL/min; EIMS, electron energy, 70 eV; temperature of the ion source and connection parts, 200 °C. The quantitative data regarding the volatile constituents were obtained by peak area normalization using a FOCUS GC/FID operated under similar conditions for the GC–MS, except the carrier gas (nitrogen). The retention index was calculated for all the volatiles constituents using a homologous series of *n*-alkanes ($C_8$–$C_{32}$, Sigma-Aldrich), according to Van den Dool and Kratz (1963). The oil components were identified by comparing their retention indices and mass spectra (molecular mass and fragmentation pattern) with those existing in the GC–MS system libraries and literature spectra (Adams 2007; NIST 2011; Modello 2011).

### Antifungal assay

The leaf oils of *C. verum* (Cvl-SL and Cvl-SI) were tested against the fungus *C. musae* (Berk. & M.A. Curtis) Arx, a plant pathogen that causes severe damage in a ripe banana. The isolate of *C. musae* (MGSS85) was obtained from the mycology collection of Laboratório de Fitopatologia, Universidade Estadual do Maranhão, São Luís, MA. The oils were dissolved in DMSO (50% v/v) and incorporated to the PDA culture medium at concentrations 0.5, 1.0, 2.0, 3.0 and 4.0 µL/mL. The media (20 mL) containing the samples was poured into separately Petri dishes and inoculated in the center with a 6 mm diameter disk containing the fungal mycelia. The plates were incubated in a BOD incubator, under a 12 h photoperiod and 25 °C. Negative control was composed by plates containing the media and fungus mycelia, but without the oil. The effect of the oil on the mycelial growth (mm) was determined by measuring the radial growth of the fungus in intervals from the 1st to 11th day, after the inoculation. The in vitro fungitoxic activity was expressed by the inhibition percentage of mycelial growth, calculated by the equation, $(I\%) = [(NC - TP)/TP] \times 100$, where NC and TP are the mycelial growth of the negative control and the treated plate, respectively. The experimental design was completely randomized with five treatments and six replications. Three replicates were performed and the data were also evaluated by mycelial growth rate index (MGRI), expressed in mm/day and calculated by the equation, $MGRI = (D - Db)/n$, where D and Db are the diameters of the current day and the previous day, respectively, and *n* the number of days of incubation (Nascimento et al. 2013).

### Antioxidant assay

A stock solution of DPPH (1,1-diphenyl-2-picrylhydrazyl, 0.5 mM) was prepared in ethanol. The solution was diluted to approximately 60 µM, measuring an initial absorbance of $0.62 \pm 0.02$, at 517 nm and room temperature. The radical scavenging activity was expressed as milligrams of Trolox equivalent per gram of oil (mg TE/g), and it was calculated for the leaf oils of *C. verum* (Cvl-SL and Cvl-SI). The reaction mixture was composed of 900 µL of tris-HCl (100 mM, pH = 7.4), 40 µL of ethanol, 50 µL of Tween 20 solution (0.5% m/v), 10 µL of Trolox in ethanol at concentrations of 0.25, 0.375, 0.50, 0.75, 1.00 and 1.25 mg/mL, followed by 1 mL of DPPH. The absorbance was measured at the start of the reaction, every 5 min during the first 20 min and, then, at 10 min intervals until the constant absorbance value. The DPPH inhibition percentage was calculated by the equation, $IDPPH\% = [1 - (AbsA/AbsB)] \times 100$, where AbsA and AbsB are the absorbance values of the sample and the control (blank) at the end of the reaction, respectively. The Trolox equivalent was obtained by replacing the Trolox solution with 10 µL of oil sample and it was calculated by the equation, $TE = (A - B)/(A - C) \times 25/1000 \times 250.29/1000 \times 1000/10 \times D$, where A, B and C are the blank, sample and Trolox absorbance values in the reaction end, and D is the dilution factor (da Silva et al. 2010).

### Statistical analysis

All data were submitted to analysis of variance (ANOVA) and compared by Tukey's test at 5% probability, using the Prisma 4.0 software. Results were expressed as mean ± standard deviation. All samples in each experiment were performed in triplicate.

## Results and discussion

### Oil yield and composition

The average values of oil yields were determined in triplicate, and they are presented in Table 1. Leaf oils yield was higher when compared to previous samples of *C. verum* (Wang et al. 2009; Chakraborty et al. 2015; Boniface et al. 2012). On the other hand, the bark wood oils yields obtained for the two analyzed specimens were lower in comparison with other reported works (Li et al. 2013; Unlu et al. 2010). The yield and composition of essential oils can be influenced by genetic and environmental factors, among them, the age and plants growth stage. It has been seen that younger plants show higher activity while growing, with an increase in their metabolism.

The oil compositions of leaves (Cvl-SL and Cvl-SI) and wood barks (Cvb-SL and Cvb-SI) for two analyzed specimens are shown in Table 1. In total, forty-four constituents were identified. In general, the phenylpropanoid compounds predominated in the cinnamon oils analyzed, with

**Table 1** Constituents of the leaf (Cvl-SL and Cvl-SI) and bark (CVb-SL and CVb-SI) oils from the specimens of *C. verum* of São Luís and Santa Inês (MA)

| *Cinnamomum verum* | | São Luís chemotype | | Santa Inês chemotype | | |
|---|---|---|---|---|---|---|
| Oil yields (%) | | 2.2 | 0.7 | 2.4 | | 0.7 |
| Oil constituents (%) | $RI_{Calc}$ | $RI_{Lit}$ | Cvl-SL | Cvb-SL | Cvl-SI | Cvb-SI |
| α-Thujene | 924 | 924 | 0.7 | 0.1 | 0.6 | 0.2 |
| Camphene | 942 | 946 | 0.1 | 0.1 | 0.2 | 0.2 |
| Benzaldehyde | 953 | 952 | | 0.1 | 0.05 | |
| Sabinene | 968 | 969 | 0.1 | 0.1 | 0.3 | 0.1 |
| α-Phellandrene | 999 | 1002 | 0.6 | 0.1 | | 0.1 |
| *p*-Cymene | 1017 | 1020 | 0.05 | 0.3 | 0.05 | 0.2 |
| 1,8-Cineole | 1022 | 1026 | 0.2 | | | 2.9 |
| *β*-Phellandrene | 1025 | 1025 | | 1.5 | 0.5 | |
| *cis*-Linalool oxide (furanoid) | 1063 | 1067 | | | | 0.05 |
| *trans*-Linalool oxide (furanoid) | 1079 | 1084 | 0.05 | 0.05 | 0.05 | 0.1 |
| Linalool | 1092 | 1095 | 0.2 | 1.8 | 1.1 | 14.0 |
| *endo*-Fenchol | 1112 | 1114 | | | | 0.1 |
| *cis-p*-Menth-2-en-1-ol | 1117 | 1118 | | | | 0.05 |
| *trans-p*-Menth-2-en-1-ol | 1134 | 1136 | | 0.05 | | |
| Camphor | 1139 | 1141 | | | 0.05 | 6.8 |
| Camphene hydrate | 1143 | 1145 | | 0.05 | | 0.05 |
| Borneol | 1163 | 1165 | 0.05 | 0.05 | 0.1 | 4.7 |
| Terpinen-4-ol | 1172 | 1174 | | 0.4 | 0.05 | 1.1 |
| α-Terpineol | 1184 | 1186 | 0.1 | 0.5 | 0.1 | 2.8 |
| (*Z*)-Cinnamaldehyde | 1213 | 1217 | | 0.1 | | |
| (*E*)-Cinnamaldehyde | 1263 | 1267 | 0.6 | 89.3 | 0.3 | 0.4 |
| *iso*-Bornyl acetate | 1278 | 1283 | | | | 0.05 |
| *δ*-Elemene | 1329 | 1335 | | | | 0.1 |
| Eugenol | 1351 | 1356 | 93.6 | 2.8 | 0.8 | 0.3 |
| Hydrocinnamyl acetate | 1361 | 1366 | | 0.1 | | 0.1 |
| α-Copaene | 1369 | 1374 | | 0.1 | 0.05 | |
| *β*-Elemene | 1384 | 1389 | 0.05 | | | 0.1 |
| (*E*)-Caryophyllene | 1413 | 1417 | 1.4 | 0.4 | 0.05 | 9.1 |
| *trans*-α-Bergamotene | 1428 | 1432 | 0.05 | | | 0.1 |
| (*E*)-Cinnamyl acetate | 1439 | 1443 | 0.2 | 0.7 | 0.1 | 3.1 |
| α-Humulene | 1448 | 1452 | 0.2 | 0.1 | 0.05 | 1.9 |
| *ar*-Curcumene | 1475 | 1479 | 0.1 | | 0.05 | 0.05 |
| *γ*-Gurjunene | 1474 | 1475 | 0.1 | | 0.05 | 0.1 |
| Germacrene A | 1506 | 1508 | | | | 0.1 |
| Caryolan-8-ol | 1569 | 1571 | 0.4 | 0.1 | 0.05 | 7.2 |
| Caryophyllene oxide | 1581 | 1582 | | 0.5 | | 0.5 |
| Viridiflorol | 1590 | 1592 | | 0.9 | | 0.9 |
| Humulene epoxide II | 1605 | 1608 | | 4.1 | | 4.1 |
| *β*-Atlantol | 1608 | 1608 | | 0.9 | | 0.9 |
| *allo*-Aromadendrene epoxide | 1637 | 1639 | | 3.0 | | 3.0 |
| α-Muurolol (= Torreyol) | 1640 | 1644 | | 0.6 | | 0.6 |
| 14-hydroxy-9-*epi*-(*E*)-Caryophyllene | 1663 | 1668 | | 2.1 | | 2.1 |
| Germacra-4(15),5,10(14)-trien-1-α-ol | 1681 | 1685 | | 0.1 | | 0.1 |
| Benzyl benzoate | 1755 | 1759 | | 0.4 | 95.3 | 23.3 |
| Monoterpene hydrocarbons | | | 1.55 | 2.20 | 1.65 | 0.80 |

**Table 1** continued

| Oil constituents (%) | $RI_{Calc}$ | $RI_{Lit}$ | Cvl-SL | Cvb-SL | Cvl-SI | Cvb-SI |
|---|---|---|---|---|---|---|
| Oxygenated monoterpenes | | | 0.60 | 2.90 | 1.45 | 32.70 |
| Sesquiterpene hydrocarbons | | | 1.90 | 0.60 | 0.25 | 11.55 |
| Oxygenated sesquiterpenes | | | 0.40 | 0.10 | 0.05 | 19.40 |
| Phenylpropanoids | | | 94.40 | 93.50 | 96.55 | 27.20 |
| Total | | | 98.85 | 99.30 | 99.95 | 91.65 |

$RI_{Calc}$ = Calculated Retention Index (Rxi-5 ms column); $RI_{Lit}$ = Literature Retention Index (Adams 2007; Mondello 2011; NIST 2011)

an average value of 94.8%, except for the wood bark of the specimen harvested in Santa Inês, whose percentage was only 27.2%, below the value observed for the oxygenated monoterpenes, which was 32.7%, due to the significant percentual of linalool, camphor and others. For the leaf oil of São Luís specimen, eugenol (93.6%) was the principal component. For the wood bark oil of São Luís specimen, (*E*)-cinnamaldehyde (89.3%) was the major constituent. Benzyl benzoate (95.3%) was the main component in the leaf oil of Santa Inês specimen. In the wood bark oil of Santa Inês specimen, benzyl benzoate (23.3%), linalool (14.0%), (*E*)-caryophyllene (9.1%), caryolan-8-ol (7.2%) and camphor (6.8%) were the main constituents.

The leaf (Cvl-SL) and wood bark (Cvb-SL) oils of the *C. verum* specimen collected in the city of São Luís (MA), with the predominance of eugenol and (*E*)-cinnamaldehyde, respectively, are comparable to those previously described for specimens sampled in Sri Lanka, India, Fiji Islands and Malaysia, which showed the same principal constituents (Senanayake et al. 1978; Raina et al. 2001; Mallavarapu and Rao 2007; Patel et al. 2007; Jantan et al. 2008; Subki et al. 2013; Chakraborty et al. 2015). Similarly, the leaf (Cvl-SI) and bark (Cvb-SI) oils of the *C. verum* specimen harvested in Santa Inês (MA), with significant percentages of benzyl benzoate and linalool, were very like to those previously reported for specimens existing in India and Africa, with the same main compounds (Nath et al. 1996; Jirovetz et al. 2001). Considering the results with the cinnamon oils sampled in the cities of São Luís and Santa Inês, the similarity with the composition of the oils previously reported and the significant presence of new constituents such as (*E*)-caryophyllene, camphor and caryolan-8-ol, it was assumed the existence of at least two *C. verum* chemotypes, with the occurrence in Maranhão state, Brazil.

## Antifungal activity

The *C. verum* oil (Cvl-SL), resulting from the specimen collected in the city of São Luís (MA), and eugenol, its main constituent, displayed total inhibition of the mycelial growth of *C. musae*, in all oil concentrations tested. On the other hand, the *C. verum* oil (Cvl-SI) extracted from the Santa Inês (MA) specimen, rich on benzyl benzoate, displayed a 100% inhibition only at concentrations above 3.0 µL/mL. The benzyl benzoate standard showed a 55% maximum inhibition at 4.0 µL/mL (Table 2).

Colletotrichum species are known as the significant plant pathogens worldwide, spreading the anthracnose disease in many crop plants and leading to significant yield loss (Rabari et al. 2017). Some studies on antifungal activity of Cinnamomum oils and its main compounds have been reported as an alternative to control post-harvest diseases. Jantan et al. (2008) correlated high levels of cinnamaldehyde, eugenol, geraniol, benzyl benzoate, and methyl cinnamate, in combination with their minor volatile components, as responsible for the significant antifungal activity of cinnamon oils.

In vitro antifungal activities of Cinnamon oils, (*E*)-cinnamaldehyde and eugenol were evaluated during conidial germination and mycelial growth of *Colletotrichum gloeosporioides*, the causal agent of anthracnose in pepper fruit. Mycelial growth displayed a high inhibition when treated by the indirect vapor of the oil samples reducing the lesion diameter on the C. gloeosporioides-inoculated immature green pepper fruits at similar levels. In vitro conidial germination, it was most drastically inhibited by vapor treatments with cinnamon oil and (E)-cinnamaldehyde (Hong et al. 2015).

The antifungal property and potential mechanism of the clove oil, rich in eugenol (78.0%), were studied in vitro and in vivo against *C. gloeosporioides*, isolated from sweet cherry (*Prunus avium* L.). The values of minimal inhibitory concentration (MIC) in the air (by fumigation) and contact phases were 80 and 300 µL/L, respectively. Furthermore, the microscopy analysis of *C. gloeosporioides* after exposure to clove oil showed a deleterious morphological and ultrastructural alterations. These observations confirmed the disruption of the fungal cell wall and endomembrane system, resulting in an increase of permeability and causing the loss of the intracellular constituents (Wang et al. 2019).

Essential oils from leaves of *Cinnamomum cassia* composed by (*E*)-cinnamaldehyde (66.3%) and benzyl benzoate (10.2%) and oils from the bark of *C. zeylanicum*,

**Table 2** Effect of *C. verum* oil leaves on the fungus *Colletotrichum musae* (in vitro Micelial Growth Inhibition)

| Concentration (μL/mL) | Mycelial growth inhibition (%) | | | |
|---|---|---|---|---|
| | Cvl-SL | Eugenol | Cvl-SI | Benzyl benzoate |
| 0.5 | 100.0 ± 0.0a | 100.0 ± 0.0a | 66.7 ± 11.2b | 44.2 ± 7.9c |
| 1.0 | 100.0 ± 0.0a | 100.0 ± 0.0a | 77.9 ± 5.4b | 47.5 ± 11.5c |
| 2.0 | 100.0 ± 0.0a | 100.0 ± 0.0a | 85.24 ± 8.3b | 49.3 ± 9.55c |
| 3.0 | 100.0 ± 0.0a | 100.0 ± 0.0a | 100.0 ± 0.0a | 44.0 ± 7.6b |
| 4.0 | 100.0 ± 0.0a | 100.0 ± 0.0a | 100.0 ± 0.0a | 55.0 ± 10.8b |

Values with different letters are statistically different (Tukey's test, $p < 0.05$)

rich in (*E*)-cinnamaldehyde (64.1%) and linalool (10.3%), were tested against *C. gloeosporioides* extracted from an infected mango. The fungal suspension was spread on potato dextrose agar and tested with 5 μL of these different oils. The values of percentages of inhibition were of 72.7% to *C. cassia*, and 65.3% to *C. zeylanicum*, respectively (Rabari et al. 2017).

Effects of cinnamon bark and clove bud essential oils were investigated, in vitro, on the *Colletotrichum acutatum* mycelial growth, in conidial germination, in appressoria formation, and, in vivo, on strawberry fruit anthracnose incidence. The oil samples inhibited mycelial growth, showed a fungistatic effect at a concentration of 667 μL/L, and wholly prevented conidial germination at the lowest concentrations of 1.53 and 76.5 μL/L of air fumigation, respectively. Also, the treatments with oils had disabled the appressoria formation at a concentration of 1.53 μL/L of air fumigation. On inoculated strawberry fruit, only cinnamon bark oil reduced the anthracnose incidence at 76.5 μL/L, by air fumigation (Duduk et al. 2015). Furthermore, leaf oils from *C. zeylanicum*, rich in eugenol (76.9%), and bark oils, rich in cinnamaldehyde (50.5%) and cinnamyl acetate (8.7%), were previously tested against *C. musae*. The values of minimum inhibitory concentration (MIC) and minimum lethal concentration (MLC) displayed ranges of 0.03 to 0.05% (v/v) and 0.04 to 0.07% (v/v), respectively (Ranasinghe et al. 2002).

## Antioxidant activity

The DPPH antioxidant test was used for the sole purpose of evaluating and comparing the different *C. verum* chemotypes existing in the state of Maranhão, Brazil. Leaf oils tested in the DPPH assay displayed different ranges of inhibition after 30 min of reaction. Due to its reactivity, the oil extracted from the São Luís (Cvl-SL) specimen and the eugenol standard were diluted in the proportion of 1:10 (oil:ethanol). However, the leaf oil obtained from the Santa Inês (Cvl-SI) specimen and the benzyl benzoate standard were tested pure in the reactional mixture. The percentage of inhibition of DPPH radicals was used to calculate the Trolox Equivalent Antioxidant Capacity (TEAC, mg TE/mL). The highest antioxidant activity was observed to Cvl-SL oil and eugenol, its main constituent, with TEAC values of 1438.1 ± 5.6 and 1456.8 ± 8.0 mg TE/mL, respectively. On the other hand, the Cvl-SI oil displayed a low activity, at 165.2 ± 2.6 mg TE/mL, about nine times less than Cvl-SL oil. Benzyl benzoate standard, also the main constituent of Cvl-SI oil, was considered inactive, at 47.0 ± 3.3 mg TE/mL (Fig. 1).

The antioxidant capacity of oils from *Cinnamomum* species and its main constituents have been reported using various methods and mechanism of actions. The bark oil of *C. zeylanicum* rich in eugenol (46.5%) and cinnamaldehyde (32.7%), and eugenol standard, showed potent activities in two in vitro models of peroxynitrite-induced nitration and lipid peroxidation with half-maximal inhibition concentration (IC50) values lower than ascorbic acid and Trolox, two reference standards (Chericoni et al. 2005). In other study, a *C. zeylanicum* leaf oil, rich in eugenol (74.9%) and including *β*-caryophyllene (4.1%) and benzyl benzoate (3.0%), demonstrated scavenger activity against the DPPH radical at concentrations which are lower than the concentrations of the standards eugenol, butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA). Also, this oil showed a significant inhibitory effect

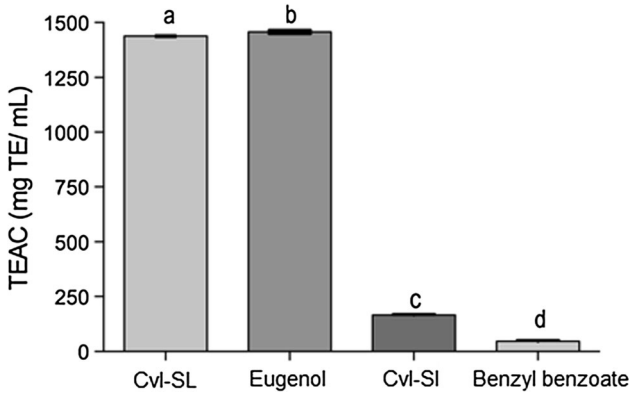


**Fig. 1** Antioxidant capacity of leaf oils of *C. verum* and their main constituents (mean ± standard deviation, $n = 3$). Different letters mean a statistical difference among the samples, determined by Tukey's test ($p < 0.05$)

on hydroxyl radicals, acting as an iron ion chelator, inhibiting the formation of conjugated dienes and the generation of secondary products of the lipid peroxidation efficiently, at a concentration equivalent to that of the standard BHT (Schmidt et al. 2006).

Leaf oils of *C. walaiwarense*, unexplored wild cinnamon from India, displayed high amount of benzyl benzoate (65.0 to 89.8%). The DPPH and ABTS assays evaluated the free radical scavenging potential of the oils and the standard benzyl benzoate. Benzyl benzoate ($IC_{50}$, 10.0 mg/mL) was about three times less active than the oils ($IC_{50}$ $\approx$ 3.7 mg/mL) of *C. walaiwarense* (Sriramavaratharajan and Murugan 2018). Some commercial oils of clove bud, rich in eugenol (76.1%), and jasmine absolute, rich in benzyl acetate (32.3%) and benzyl benzoate (22.9%), as well as the standards of eugenol, benzyl acetate and benzyl benzoate, were submitted to antioxidant assays by different methods. Clove bud oil, jasmine absolute, and eugenol were active in the $\beta$-carotene bleaching test and as scavengers of ABTS and DPPH radicals. However, the standards benzyl acetate and benzyl benzoate were inactive in all assays (Wang et al. 2017).

## Conclusion

Considering the results with the cinnamon oils sampled in the cities of São Luís and Santa Inês, the similarity with the composition of the oils previously reported and the significant presence of new constituents, such as (*E*)-caryophyllene, camphor and caryolan-8-ol, it was assumed the existence of at least two *C. verum* chemotypes, with the occurrence in Maranhão state, Brazil. *C. verum* leaf oil from São Luís and the standard eugenol, its main constituent, displayed total inhibition of the mycelial growth of *C. musae*, in all oil concentrations tested. *C. verum* oil from Santa Inês, rich on benzyl benzoate, displayed a 100% inhibition only at concentrations above 3.0 µL/mL. The highest antioxidant activity was observed to *C. verum* oil from São Luís and the eugenol standard. *C. verum* oil from Santa Inês displayed a low activity, about nine times less than the *C. verum* oil from São Luís, while benzyl benzoate standard was considered inactive.

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**Compliance with ethical standards**

**Conflict of interest** The authors declare that they have no conflict of interest.

**Ethical approval** This article does not contain any studies with human or animal subjects.

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