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Comparative Study of the Thermal Stability of Cinnamon and Oregano Essential Oils from Cinnamon and Oregano After Heat Treatment

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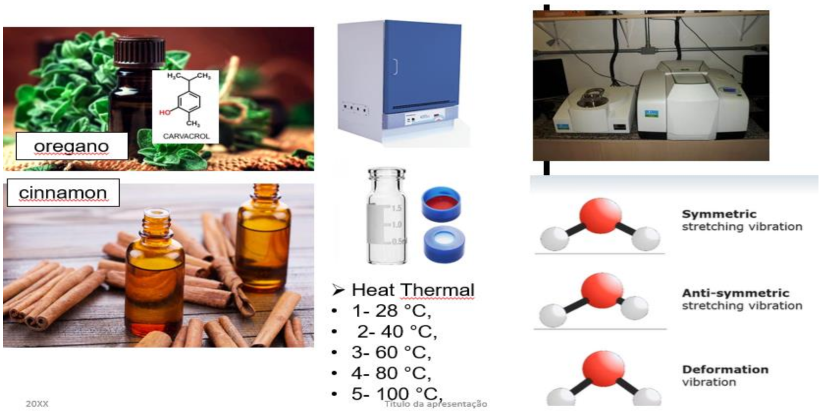
Essential oils (OEs) are extracted from aromatic plants and are complex mixtures of compounds mainly generated from terpenoids, benzenes, aromatic rings, and phenolic acids. They possess various features that make them valuable as raw materials in diverse industrial and agricultural fields. The main objective of this work was to research, compare, and optimize the thermochemical stability of commercial cinnamon (*Cinnamomum verum*) and oregano (*Origanum vulgare*) OEs at room temperature and after treatment at temperatures of 40 °C, 60 °C, 80 °C, and 100 °C for one hour. Each heated OE was considered a sample and was stored in two systems (open and closed) during heating. Forty-two compounds were identified in cinnamon OE, while thirty-five compounds were characterized in oregano OE, with the aid of Fourier transform infrared spectroscopy (FTIR-ATR) to examine the functional groups. Thermal stability and enthalpy variations were studied using thermogravimetric analysis (TG), derivative thermogravimetric analysis (DTG), and differential scanning calorimetry (DSC). The findings indicated that cinnamon essential oil demonstrated greater thermal stability against thermovolatilization compared to oregano essential oil. Importantly, the results also suggested that storing the samples in closed containers significantly slows the thermal decomposition of their constituents. This research underscores the importance of thermal stability and proper storage conditions for preserving the quality and efficacy of essential oils.

Graphical abstract



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1. Introduction

Consciously, has increased society's interest in consuming products that use essential oils in their manufacture has significantly increased. Essential oils (OEs) are multifunctional natural compounds that can be applied to various manufactured products, such as food, beverages, agricultural products, personal hygiene products, cosmetics and pharmaceuticals, with the aim of delaying oxidation and contamination by microorganisms. Some of the best properties of essential oils include excellent resistance to bacterial proliferation and antioxidant activity, making them an alternative to replacing synthetic or artificial substances that release toxins [1,2].

Essential oils are very volatile [3,4]. Chemical composition of essential oils varies among species and plant parts extracted. Physical-chemical properties of OEs can be influenced by a set of factors such as soil cultivation, climatic conditions, extraction and storage methodology [5]. Major compounds in essential oils are derived from terpenes, such as monoterpenes, hydrocarbons (α-pirene, β-pirene, p-cymene), sesquiterpenes (β-caryophyllene), linalool, terpinem-4-ol, and phenols (carvacrol, thymol). This mixture of these existing multicomponents helps in control oxidation, pathogenic bacterial proliferation and free radicals, consistently enhancing the resistance of products produced with essential oils, such as food, antibiotics and pharmaceuticals, to antimycobacterial activity such as *Salmonella cholerasuis, Listeria monocytogenes, Staphylococcus aureus* and *Escherichia coli*. Given the qualities already mentioned, aplication of essential oils have becomes as a sustainable alternative for development of commercial products.

Cinnamon is a spice with a aroma pleasant that provides a mildly spicy, sweet flavor and has been used for centuries by various cultures around world. Cinnamon essential oil was obtained from diferentes parts of the tree belonging to the genus Cinnamon, and the Lauraceae Family. Essential oil can be extracted by steam distillation of the bark and leaves Cinnamon essential oil extracted from leaves, mostly composed of carvacrol and thymol [6,7]. Cinnamon OEs are widely used in the food, beverage, perfumery, and pharmaceutical industries [8].

Previous studies [9,10] described oregano (*Origanum vulgare L.*) as a very versatile plant with diverse therapeutic properties (antiseptic, carminative, antispasmodic, and anti-inflammatory). Oregano is recognized worldwide as one of the most aromatic plants. Oregano OEs are composed mainly of phenolics that are responsible for antimicrobial activity [11,12], rich in carvacrol. This compound is recognized by the Food and Drug Administration (FDA) from EUA as a dietary supplement that attests to natural intoxicates according to the strict American standards of control and qualities detailed in the Regulation of the United States Code of Federal Regulations 172.515 [13].

Currently, Brazil is one of the main importers of cinnamon and oregano essential oils worldwide due to the favorable environmental conditions for the cultivation of these raw materials [14]. Thermal treatment of essential oils has the function of deteriorating contaminating microorganisms, delaying harmful microbiological and metabolic processes and intensifying enzymatic inactivation [15].

The main objective of this work was to study the effects of controlled heating on the thermal behavior and chemical composition of commercial cinnamon and oregano OEs previously treated within the temperature range from room temperature to 100°C and stored in open and closed systems. Therefore, was possible to compare the thermal stabilities of the oils and optimize the thermal treatment temperature which resulted in greater resistance to thermal effects and physicochemical changes in oil composition as well the best storage conditions.

2. Material and Methods

Samples

Cinnamon and oregano essential oils (Laszlo) were purchased commercially. The batches were 1378 and 1613, with validities established in the deadlines in June 2021 and October 2021, respectively. OEs were extracted by steam distillation. Measures were carried out before the oils' expiration date.

Heat treatment

Samples were stored into vials containing 1.0 ml of OEs, being five sealed vials and five open vials. Each sample was exposed to treatments in dry incubator with temperature controlled, at operating temperatures at 40°C, 60°C, 80°C and 100°C for an hour. The control samples were exposed on the bench at room temperature at 28°C during same period the treatments. Then, all the vials were sealed hermetically and cooled in the refrigerator at 7°C. This methodology was reproduced in triplicate. Next, the samples were labeled with captions C (cinnamon), O (oregano), A (open) or F (closed) relating to storage conditions and numbered 1, 2, 3, 4 and 5 relatives to local outside temperature ,28°C, 40°C, 60°C, 80°C and 100°C, respectively.

Chemical characterization

Chemical characterization was performed on a gas chromatograph coupled to a mass spectrometer (GC-MS), Thermo brand equipment, Focus GC model, in which a BD5-MS capillary column with dimensions of 30 meters in length, 25 mm in internal diameter and 25μm in thickness was used. Injector temperature was 230°C, operating in a helium atmosphere. Chromatographic conditions for the tests with OE cinnamon and oregano were as follows initial temperature, 60°C, programmed controlled heating rate from 3°C min^{-1} until 220°C was reached. The injected volume was 1μL. A mixture of linear alkanes (C4 to C20) was injected into the chromatography unit under the same conditions used for the analysis of essential oils for retention index calculations with linear temperature programming. Identification of OEs was carried out based on the ADAMS library (2017).

Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectra were obtained using the Fourier transform infrared spectrometer with an attached reflectance accessory (FTIR-ART) to detect changes in the functional groups of OEs that underwent thermal heating. All absorbance spectra were collected on a spectrophotometer (model Cary 630 Agilent) in the range from 3500-500 cm^{-1}.

After the crystal surface was removed, 10μL of the sample was injected in ATR. Spectral profiles were obted with the aid of the *software* Microlab PC (Agilent) with a resolution of 4 cm^{-1}. The method used was described by Ruschel *et al.* (2014) with modifications. Interpretations of the spectra were carried out according to Lopes Fascio (2004). Analyses were carried out at the Chromatographic and Spectroscopic.

Analysis of thermal stability by TG and DTG

Commercial oil samples were introduced into open platinum rhodium crucibles in a simultanOEus thermal analyzer (STA6000 PerkinElmer, USA) heated from 25 °C to 250 °C in nitrogen atmosphere (N_2, White MartinsTM, Brazil 99.999% purity) with a flow rate of 30 $ml.min^{-1}$, and a heating rate of 20 $°C.min^{-1}$ to study the evolution of thermal degradation performance in the stages of decomposition.

Experiment found of three main temperatures were that describe the thermal behavior, T_{onset}, T_{dec} and T_{offset}, whose results shown in graphical profiles from mathematical treatment of the first order derivative thermogravimetric of experimental curve [16].

The temperature T_{onset} determines the thermal stability of substances, this is the limiting temperature for mass variations in oils heated. OEs are very important for industrial applications because they involve thermal control through which the properties of OEs fully preserved [17].

In the peaks from each stage on the differential thermal analysis (DTG) curve, we found the thermal decomposition temperature, $T_{dec,}$which is known in the literature as the critical temperature or peak temperature [18].

At this temperature, the greatest decomposition kinetics occur, in which the OE loses or gains mass more rapidly, according to the phase transition. In OEs, mass reduction is often associated with the phenomenon of vaporization, and gravimetric increase is correlated with the phenomenon of oxidation [19]. Temperature, T_{offset} is related to the end of the decomposition stage, at which point significant changes cease due to phase transition effects in the constituents of OEs [20-23].

Differential Scanning Calorimetry (DSC)

With the aid of thermal analyzer equipment, it was possible to simultanOEusly examine the OEs by thermal analysis and differential exploratory calorimetry by subjecting the samples to the same experimental conditions. However, the DSC profile results are obtained by monitoring the energy flow as a function of temperature. Through the DSC curves, it is possible to qualitatively study analyses of vaporization phase transition (endothermic curves) and oxidation (exothermic curves) stand out.

Quantitatively, tests detect the characteristic temperatures and the enthalpy variation at which first order phase transition phenomena occur monitor (ΔH) associated with phase changes. Tests were carried out in 2021, in the Thermal and Spectrometric Analysis and Materials Laboratory at the Federal Technological University of Paraná, Campus Medianeira.

3. Results and Discussion

Chemical analysis of the cinnamon OEs samples

Chromatographic peaks were assessed by comparing the respective mass spectra with the spectra NIST (2020) and Adams (2017), identifying 42 compounds., showed in the Table 1. According to the GC-MS results the most abundant compounds found in cinnamon OE plants were cis-cinnamaldehyde (58.67%), cylamine acetate (8.88%), eugenol (12.56%), linalool (5.21%), and terpenes (1.04%).

Cinnamon OEs were identified as containing 65%oxygenated monoterpenes,22.47% oxygenated sesquiterpenes, 9.93% sesquiterpenes and 1.52%monoterpenes. When the samples were treated at different temperatures, a slight increase in the amount of oxygenated monoterpene compounds was observed. This behavior was repeated for stored open oils, but was not was observed for closed essential oils. However, with heating, a slight percentage increase in oxygenated sesquiterpene compounds was identified under both storage conditions [24]. Fluctuations of oxygenated monoterpenes and sesquiterpenes were detected with to heating and storage. Monoterpenes are characterized by bonds between carbons and hydrogens, while sesquiterpenes are formed by bonds between carbons, hydrogens and oxygens. The contact and interact of Cinnamon essential oil reacted with atmospheric oxygen may have increased the percentage of oxygenated monoterpenes and sesquiterpenes.

Determination of the functional groups present in the OEs was obtained using Fourier transform infrared spectroscopy (FTIR). Figure 1 displays infrared spectra of the cinnamon OEs in the range of 3500-500 cm^{-1}. Peaks observed in the spectra are associated with the absorption band infrareds and are the result of overlapping mixtures of excited compounds in vibrational modes [25].

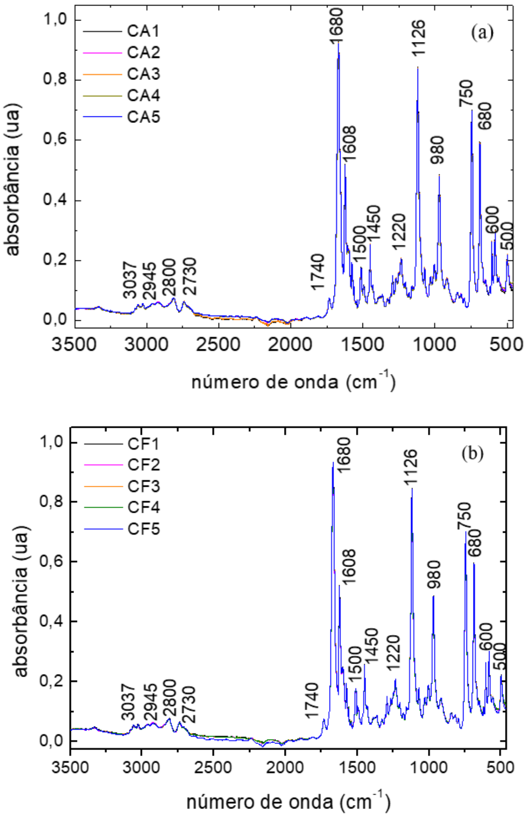


Fig. 1. FTIR spectra for cinnamon OEs treated at up to 100°C. (a) Storage in open *vials*. (b) Stored in closed vials.

Spectral analyses were used to compare the main results of OEs subjected to different applied experimental conditions. In Table 2, the main wavenumber spectral band frequency ranges, functional groups vibration modes and peak intensities are presented.

Table 1. Gas chromatography coupled with mass spectrometry of cinnamon essential oil (C) at room temperature up to 100 °C.

compounds	molecular formula	boiling temperature (°C)	terpene Class	peak IR	CA1 (%)	CA2 (%)	CA3 (%)	CA4 (%)	CA5 (%)	CF1 (%)	CF2 (%)	CF3 (%)	CF4 (%)	CF5 (%)
terpene <γ->	$C_{10}H_{16}$	183	monoterpene	1054	0.08	0.10	0.12	0.12	0.11	0.09	0.08	0.11	0.11	0.09
cimene <ρ ->	$C_{10}H_{14}$	177	monoterpene	1020	0.77	1.04	0.96	1.03	1.00	0.64	0.85	0.66	0.95	0.68
phallandrene <α->	$C_{10}H_{16}$	171-172	monoterpene	1003	0.05	0.13	0.10	0.11	0.09		0.11	0.02	0.10	0.03
phellandrene <β->	$C_{10}H_{16}$	80.74	monoterpene	1025	0.30	0.57	0.44	0.51	0.48	0.15	0.48	0.18	0.49	0.18
γ-Terpene	$C_{10}H_{16}$	183	monoterpene	1053	0.07	0.18	0.11	0.10	0.09	0.03	0.11	0.03	0.09	0.03
			subtotal		1.27	2.02	1.73	1.87	1.77	0.91	1.63	1	1.74	1.01
benzaldehyde	C_7H_6O	178,1	monoterpenand oxygenated	973	1.17	1.76	1.34	1.15	1.31		1.21	0.81	1.42	
bornOEl	$C_{10}H_{18}O$	213	monoterpenand oxygenated	1163	0.04	0.06	0.06	0.04	0.04	0.04	0.05	0.04	0.05	0.03
cinnamaldehyde (E) -	C_9H_8O	248	monoterpenand oxygenated	1283	60.21	54.80	58.07	58.64	58.33	61.66	58.41	61.31	56.52	58.8
CinOEl <1,8->	$C_{10}H_{18}O$	176-177	monoterpenand oxygenated	1028	0.85	1.20	0.97	1.02	1.09	0.51	1.04	0.56	1.11	0.57
linalool	$C_{10}H_{18}O$	198	monoterpenand oxygenated	1099	4.11	4.19	4.15	3.98	4.08	3.93	3.89	3.85	4.40	3.77
trans-linalo oxide	$C_{10}H_{18}O_2$	198-199	monoterpenand oxygenated	1087	0.01	0,02	0,04	0,04	0,03				0.02	
terpen-4-ol	$C_{10}H_{18}O$	212	monoterpenand oxygenated	1175	0.14	0.25	0.23	0.21	0.20	0.15	0.17	0.14	0.26	0.15
terpenol <α->	$C_{10}H_{18}O$	219	monoterpenand oxygenated	1190	0.18	0.29	0.25	0.24	0.22	0.15	0.23	0.17	0.27	0.18
			ssubtotal		66.71	62.57	65.11	65.32	65.30	66.44	65.00	66.88	64.05	63.50
α-muurolene	$C_{15}H_{24}$	-	sesquiterpene	1498	0.07	0.11	0.14	0.08	0.12	0.06	0.12	0.1	0.17	0.09
1H-cycloprop [and] azulene	$C_{15}H_{24}$	-	sesquiterpene	1492	0.08	0.07	0.11	0.11	0.07	0.09	0.10		0.11	0.07
cadina-1,4-diene <trans->	$C_{15}H_{24}$	245-246	sesquiterpene	1528	0.07	0.07	0.07	0.10	0.,04		0.08	0.05		
cadinene <δ->	$C_{15}H_{24}$	-	sesquiterpene	1520	1.34	1.37	1.45	1.38	0.06	1.08	1.48	1.18	0.10	1.20
copaene	$C_{15}H_{24}$	124	sesquiterpene	1374	3.72	5.32	4.07	3.77	4.05	3.66	4.04	4.35	4.82	4.48
cubebene <α->	$C_{15}H_{24}$	248	sesquiterpene	1347	0.10	0.17	0.20	0.12	0.13	0.08	0.15	0.1	0.19	0.09
E- Caryophyllene	$C_{15}H_{24}$	-	sesquiterpene	1416	3.16	3.22	3.39	3.19	3.23	3.22	3.18	2.79		3.01
germacreno D	$C_{15}H_{24}$	236.4	sesquiterpene	1477	0.19	0.04	0.06	0.06	0.06		0.07	0.04	0.06	0.10
Isoleden	$C_{15}H_{24}$	236.4	sesquiterpene	1389	0.10	0.40	0.12	0.12.	0.08	0.10	0.12	0.2	0.25	0.26
mururolene <γ->	$C_{15}H_{24}$	-	sesquiterpene	1473	0.28	0.15	0.18	0.15	0.17	0.10	0.12	0.11	0.14	0.27
trans-β-guaiene	$C_{15}H_{24}$	-	sesquiterpene	1491	0.17	0.16	0.20	0.19	0.19	0.14	0.2	0.15		0.12
			subtotal		9.28	11.08	9.99	9.27	8.2	8.53	9.66	9.07	5.84	9.69
cylamine acetate	$C_{11}H_{12}O_2$	77.06	sesquiterpene oxygenated	1447	8.60	9.82	9.56	9.46	9.40	9.49	9.51	9.02	3.39	10.57
cadin-4-en-7-ol <cis->	$C_{15}H_{26}O$	-	sesquiterpene oxygenated	1642	0.01			0.03						
Caracolene <α->	$C_{15}H_2O$	-	sesquiterpene oxygenated	1538	0.04	0.05	0.04	0.04	0.02		0.03	0.02	0.03	0.02
caryophylla-4(12),8(13)-dien-5α-ol	$C_{15}H_{24}O$	254-257	sesquiterpene oxygenated	1631	0.01			0.02						
cinnamaldeic <(E)-ρ-methoxy>	$C_{15}H_{24}O$	254-257	sesquiterpene oxygenated	1547	0.02	0.03	0.02	0.03	0.04					0.02
cubebol	$C_{15}H_{26}O$	-	sesquiterpene oxygenated	1512	0.03	0.04		0.03	1.37		0.04		0.13	0.03
cubenol <1-epi->	$C_{15}H_{26}O$	-	sesquiterpene oxygenated	1623	0.06	0.08	0.08	0.08	0.07	0.06	0.09	0.05	0.06	0.06
eugenol	$C_{10}H_{12}O_2$	254	sesquiterpene oxygenated	1360	12.91	12.69	11.96	12.43	12.27	13.09	12.48	12.63	12.29	12.83
humulene epoxide II	$C_{15}H_{24}O$	-	sesquiterpene oxygenated	1603	0.05	0.06	0.06	0.06	0.07	0.06	0.07	0.05	0.05	0.04

muurolol <epi-α->	$C_{15}H_{26}O$	303-305	sesquiterpene oxygenated	1638	0.07	0.09	0.06	0.08	0.01	0.06	0.07	0.05	0.05	0.06
caryophyllene oxide	$C_{15}H_{24}O$	254-257	sesquiterpene oxygenated	1578	0.61	0.59	0.58	0.62	0.07	0.46	0.70	0.51	0.58	0.57
spatulenol	$C_{15}H_{24}O$	-	sesquiterpene oxygenated	1573	0.03		0.04	0.04	0.66	0.03	0.05	0.03	0.03	0.03
vulgarone	$C_{15}H_{26}O$	-	sesquiterpene oxygenated	1650	0,01									
			subtotal		22.45	23.45	22.4	22.92	23.98	23.25	23.04	22.36	16.61	24.23
			sotal		99.71	99.12	99.23	99.38	99.25	99.13	99.33	99.31	88.24	98.43

Compounds cataloged according to the order of elution from the DB5-MS column; Retention Index (RI) calculated using a homologous series of n-alkanes (C10-C39) on a capillary column (DB5-MS); Identification based on comparison of NIST (2020) and ADAMS (2017) data libraries. Area (%): is the percentage of the area occupied by the compound below the chromatogram peak

Table 2. FTIR bands of cinnamon essential oil (C) heated to external temperature (28°C) and to 100 °C.

Wave number (cm^{-1})	range band Frequency (cm^{-1})	compound	functional group	peak magnitide	Vibration mode	CA1	CA2	CA3	CA4	CA5	CF1	CF2	CF3	CF4	CF5
500	750-500	C-Br	C-X (X=halogen)	strong	stretch	X	X	X	X	X	X	X	X	X	X
600	800-600	C-Cl	C-X (X=halogen)	strong	stretch	X	X	X	X	X	X	X	X	X	X
680	800-600	C-Cl	C-X (X=ihalogen)	strong	stretch	X		X	X		X	X	X	X	X
740	800-600	C-Cl	C-X (X=halogen)	strong	stretch				X						
750	800-600	C-Cl	C-X (X=halogen)	strong	stretch	X					X	X	X	X	X
800	800-600	C-Cl	C-X (X=halogen)	strong	stretch		X	X	X	X					
980	990 e 910		RCH=CH3	strong	out-of-plane angular deformation	X	X	X	X	X	X	X	X	X	X
1110	1200-1050	Tertiary alcohol	C-O alcohols and phenols	strong	stretch		X	X	X			X	X		X
1126	1200-1050	tertiary alcohol	C-O alcohols and phenols	strong	stretch	X		X	X	X	X			X	X
1220	1300-1050	Unsaturated and aromatic esters	C-O de álcoois ésteres	strong	stretch	X					X	X	X		
1250	1300-1050	Unsaturated and aromatic esters	C-O de álcoois ésteres	strong	stretch		X	X	X					X	
1420		Unsaturated and aromatic esters	C=C aromatics	weak to average	stretch					X					X
1450	1500 and 1450	Unsaturated and aromatic esters	C=C aromatics	weak to average	stretch	X		X	X	X	X	X	X	X	X
1500	1500 and 1450	Unsaturated and aromatic esters	C=C aromatics	weak to average	stretch	X	X	X	X	X	X	X	X	X	X
1608	1700-1630	N-amides	C=O de amides	strong	stretch	X	X	X			X	X	X		
1655	1700-1630	N-amides-s	C=O de amides	strong	stretch				X	X				X	X
1680	1700-1630	N-amides	C=O de amides	strong	stretch	X		X			X	X	X		X
1740	1700-1630	N-amides	C=O amides	strong	stretch	X	X	X	X		X		X	X	
2730	2820 and 2720		C-H de aldehydes	strong	sretch	X	X	X	X	X	X	X	X	X	X
2800	2820 and 2720		C-H de aldehydes	sStrong	stretch	X	X	X	X	X	X	X	X	X	X
2945	3000 and 2820		C-H de aldehydes	wWeak	stretch	X	X	X		X	X	X	X		X
3037	3400 to 3000		O-H	strong	stretch	X	X	X	X	X	X	X	X	X	X

Results suggested that there was no variation in the components belonging to the function groups for the respective out of plane angular deformation bands RCH=CH3, 980 cm^{-1}, of absorption and stretching band aromatics C=C, 1450 and 1500 cm^{-1}, aldehydes with stretching's bands, C-H, 2730 cm^{-1}, 2800 cm^{-1}, 2945 cm^{-1}, in stretch band alcohols and phenols O-H, 3037 cm^{-1}, pointing out better. The chemical stability was maintained and thermal resistance of the organic group compounds regardless of the applied heat and storage conditions the OEs.

For the ester groups, the spectra pointing out a slight attenuation of organic function with heating in vials open to the stretched band CO at 1220 cm^{-1}, however, in the closed vial system, the OEs exhibited good resistance to organic functional groups at a temperature of 60°C. This result suggested that volatilization of compounds stored in open vials may have occurred due to interactions with oxygen and heat, which may have amplied the deformation during vibration.

Different behaviors of the amines varied according to the wavenumber stretch bands C=O, 1608 cm^{-1}, 1680 cm^{-1} and 1740 cm^{-1}, suggesting that heating and storage conditions influenced the absorption. In aromatic compounds, a band corresponding to stretching C=C a peak at 1420 cm^{-1} was considered only for the 100°C treatment as was the amide C=O band at 1655 cm^{-1} at 80°C, which may indicate the formation of components with heat as an inducing agent.

For the expected stretching absorption bands in halogen groups at 700 cm $^{-1}$ and 1050 cm^{-1} amine stretching bands, SO_2 at 1350 cm^{-1}, angular strain bands of secondary amides at N-H 1470 cm^{-1}, and the amide N-replaced stretching band at C=O 1630 cm $^{-1}$, it is noteworthy that the organic functions were entirely preserved in all the samples in the closed vial group, suggesting that the samples retained thermal stability when heated.

Same preservation of functional group properties was not found in the open vial group, in which the samples showed lower thermal resistance than heated samples. Due to the interaction of the essential oil with oxygen and the constituents of the air, the heating possibly caused volatilization of the compounds and deformation of molecular bonds, leading to variations of the absorption peaks in the spectra. However, in the group of benzenes, the out of plane deformation band CH=CH- 960 cm^{-1} preserved the stability functional until 40°C in an open system and 60°C in a closed system, but the effect opposite occurred for the esters in the stretching band C-O 1420 cm^{-1}, preserving the compounds until 60°C in an open system and 40°C in a closed system. The same event occurred with aldehydes, for example, the C-H 2870 cm^{-1} stretching band preserved its functionality up to 60°C in an open system and until 80°C in a closed system. Results showed that there was possibly decomposition of the compounds from these groups upon heating.

The characteristic band corresponding to the stretching vibration at C-X 740 cm^{-1}, was found only at 100°C in an open system, as well as with the out-of-plane deformation band at CH=CH-, and 970 cm^{-1}, which maintained its functions when subjected to treatments from 60 to 100°C in an open system. Spectral results showed that the absorption peak may have shifted when subjected to different heat treatments, consequently, the application of heat dilates molecular bonds, which would indicate probable variation in the absorption peak.

Franciscato and collaborators [26] studied the composition OE commercial cinnamon provided by a local company, obtained the majority of the compounds this OE were transcinnamic acid, cis-cinnamaldehyde, benzene carboxylic acid and benzaldehyde (3.84%). Batistis and researchs [27] studied the composition of cinnamon OE (*Cinamomum cassia*) and identified the most abundant compounds as cinnamaldehyde (72.50%), methyl cinnamate (12.85%), α-methyl cinnamaldehyde (7.77%), cinnamyl alcohol (1.38%), cumene (1.23 %) and caryophyllene (0.93%) for the purpose of researching the antibacterial activity of this OE as an antiseptic. Results obtained using cinnamon OE were satisfactory for combating the antimicrobial activity of *Streptococcus mutans*.

Spectral results suggested the presence of spectral bands with medium- and high intensity elongation, among other bonds caused plane deformation. In cinnamon OEs extracted through steam distillation from the stem of this plant species cultivated in the state of Minas Gerais (MG) [26] approximately 80% of the composition of the hydrocarbon sesquiterpene α-bisabolol was detected as the predominant compound. Studies suggest that cinnamon OE has high antibacterial activity and inhibitory action against the bacteria *Escherichia coli*, *Bacillus cereus* and *Salmonella* Typhi [25, 26] which are common and harmful bacteria found in dairy products and foods. Moritz *et al*. [27] tested the antimicrobial activity of cinnamon OE on the bacteria *Lactobacillus rhamnosus* in fermented milk supplemented with cinnamon OE; the most abundant compounds were cinalmade hydens, cinnamyl and cinoele, and the results of the inhibitory analysis of the bacteria were successful.

Chemical analysis of oregano OE samples

With aid of chromatography, 34 were recognized compounds and one unidentified compound, whose majority of the components found were carvacrol (71.34%), thymol methyl ether (6.4%) and thymol (3.34%). Compounds found were showed in Table 3.

With the heating, results suggest that adequate stability was found in the percentages of monoterpenes and oxygenated monoterpenes in the storage systems (open and closed) studied. Oxygenated sesquiterpenes in the closed system treatments were conserved.

In this work, oregano OE samples were studied by FTIR to analyze the possible interactions between the functional groups of the constituent molecules. Fig. 2 shows the spectrograms of OEs treated at up to 100°C and stored in open (a) and closed (b) systems in the wavenumber range between 3500 cm^{-1} and 500 cm^{-1}.

Table 4 represent the of the central absorbing peaks. Graphs showed the existence of an aromatic ring corresponding to the 940 cm^{-1} band, suggesting that there was a stretching of the hydrogen bonds located internally in the aromatic's rings. Stretch stretching C-O 1100 cm^{-1} and 1160 cm^{-1} is associated with ether bands, phenol groups found were assigned in C-O 1200 cm^{-1} with stretch bands, the bands in C-O 1250 cm^{-1} and 1300 cm^{-1} represent stretching vibrations in unsaturated esters, spectra revealed peaks at 1500 cm^{-1} and 1600 cm^{-1} associated with the aromatic ring amine groups, the stretching bands, in the stretching chelate O-H bonds C=O, NO_2 2920 cm^{-1}, 2960 cm^{-1} and 3000 cm^{-1} and in aromatic amines the stretching band N-H 3400 cm^{-1} do not correspond to change in the characteristic components respective functional groups, suggesting chemical stability and thermal resistance organic groups of these compounds when subjected to different storage systems and the application of heat. Wide peaks at 2870 cm^{-1} and 3400 cm^{-1}

Table 3. Gas chromatography coupled with mass spectrometry (GC-MS) analysis of oregano essential oil (O) from room temperature up to 100°C.

compound	Molecular formula	boiling temperature (°C)	terpene class	peak IR	AO1 (%)	AO2 (%)	AO3 (%)	AO4 (%)	AO5 (%)	OF1 (%)	OF2 (%)	OF3 (%)	OF4 (%)	OF5 (%)
α-(10)Thujene	$C_{10}H_{16}$	151	Monoterpene	949	0.02	0.05			2.53					
canfeno	$C_{10}H_{16}$	163.6	Monoterpene	964	0.01	0.17	0.04	0.26	0.11	0.03	0.03	0.17	0.22	0.14
sabinene	$C_{10}H_{16}$	163.6	Monoterpene	979	0.14	0.09	0.12		0.06	0.09	0.15	0.05	0.06	0.06
sabinene hidarate-cis	$C_{10}H_{18}$	60.3	Monoterpene	1064,	0.01		0.04							
terpinoleno	$C_{10}H_{16}$	α: 173.5-174.8 °C; β: 173-174 °C; γ: 183 °C	Monoterpene	1013	0.08	0.51	0.26	0.66	0.45	0.19		0.48	0.57	0.49
thujene-α	$C_{10}H_{16}$	151	Monoterpene	949	0.01	0.18	0.04	0.24	0.12	0.03	0.03	0.13	0.26	0.1
methyl thymol ether	$C_{10}H_{16}$	55.3	Monoterpene	1020	1.48	8.19	6.06	8.27	7.37	4.68	4.71	8.25	7.82	7.12
α-Pinene	$C_{10}H_{16}$	159	Monoterpene	974	0.88	0.54	0.15	0.7	0.41	0.09	0.11	0.44	0.68	0.35
α-Terpiene	$C_{10}H_{16}$	173.5-174.8	Monoterpene	1933	0.04	0.05	0.06	0.07	0.05	0.05	0.04	0.06		0.06
β-mrceno	$C_{10}H_{16}$	167	Monoterpene	990	0.02	0.46	0.28	0.78	0.47	0.12	0.11	0.50	0.71	0.45
β-Pinene	$C_{10}H_{16}$	166	Monoterpene	983	0.06	0.28	0.13	0.39	0.21	0.05	0.08	0.24	0.31	0.22
γ-terpinene	$C_{10}H_{16}$	183	Monoterpene	1053	0.46	3.29	2.44	3.73	3.09	1.72	1.59	3.15	3.49	3.02
			Sub-total		2.41	13.81	9.62	15.1	14.87	7.05	6.85	13.47	14.12	12.01
carvacrol	$C_{10}H_{14}O$	236.8	Monoterpenand oxygenated	1313	81.26	69.81	71.69	65.13	69.54	76.39	75.39	69.57	65.73	68.91
decamethy yclopentasiloxane	$C_{10}H_{30}O_5Si_5$	-	Monoterpenand oxygenated	1152	0.05	0.03	0.06	0.05	0.04	0.06	0.06	0.04	0.04	0.06
fenchone	$C_{10}H_{16}O$	193.5	Monoterpenand oxygenated	1088	0.13	0.15	0.15		0.17	0.10	0.10	0.16	0.19	0.17
IsobornOEl	$C_{10}H_{18}O$	213	Monoterpenand oxygenated	1164	0.11	0.02	0.13	0.15	0.09	0.13	0.11	0.11	0.15	0.19
linalool	$C_{10}H_{18}O_2$	198	Monoterpenand oxygenated	1099	4.03	3.34	3.86	3.79	3.59	3.63	3.94	3.57	3.73	3.55
cis-oxide-linalool	$C_{10}H_{18}O_2$	198-199	Monoterpenand oxygenated	1069	0.05	0.05	0.07		0.04	0.07	0.07	0.06	0.16	0.13
terpen-4-ol	$C_{10}H_{18}O$	212	Monoterpenand oxygenated	1176	0.05		0.07	0.08	0.08	0.06	0.07	0.06	0.07	0.07
thymol	$C_{10}H_{14}O$	232.9	Monoterpenand oxygenated	1294	5.74	5.55	6.63	6.46	6.83	5.84	6.45	6.01	7.08	6.87

			Sub-total		91.42	78.95	82.66	75,66	80.38	86.28	86.19	79.58	77.15	79.95
cadinene δ	$C_{15}H_{24}$	279,7	Sesquiterpene	1520	0.01									0.02
cyclohexene, 2-ethenyl-1,3,3-trimethyl	$C_{11}H_{18}$	-	Sesquiterpene	2008	0.82	0.86	1.03	1.25	1.02	0.94	0.95	1.14	0.56	1.21
β-bisabolene	$C_{15}H_{24}$	-	Sesquiterpene	1957	0.01	0.01	0.01	0.02		0.01	0.01	0.02	0.02	0.02
ccaryophyllene- Z	$C_{15}H_{24}$	254-257	Sesquiterpene	1416	2.00	1.92	2.14	2.13	2.02	1.95	2.14	2.04		2.06
copaene	$C_{15}H_{24}$	124	Sesquiterpene	964	0.02			0.05	0.04	0.04	0.06	0.05	0.05	0.06
			Sub-total		2.86	2.79	3.18	3.45	3.08	2.94	3.16	3.25	1.11	3.37
caryophyllene oxide	$C_{15}H_{24}O$	254-257	Sesquiterpene oxygenated	1578	2.37	2.44	2.84	2.87	0.03	2.42	2.41	2.71		2.68
CinOEle 1.8-	$C_{11}H_{18}O$	172	Sesquiterpene oxygenated	1028	0.34	0,70	0,79	0,99	0,77	0,47	0.30		0,75	0,59
Dehydroabietal	$C_{20}H_{28}O$	-	Sesquiterpene oxygenated	2004	0.13	0.12	0.14	0.18	0.17	0.12	0.13		0.16	0.16
dodecamethyl-cyclopentasiloxane	$C_{12}H_{36}O_6Si_6$	-	Sesquiterpene oxygenated	1151	0.02					0.01				
estrone methyl ether	$C_{19}H_{22}O_2$	-	Sesquiterpene oxygenated		0.01	0.02	0.02	0.03	0.03		0.02	0.02		0.02
octadecamethyl-cyclononasiloxane	$C_{18}H_{54}O_9Si_9$	-	Sesquiterpene oxygenated	2281	0.04		0.01				0.02			
phenol	$C_{10}H_{14}O$	181,7	Sesquiterpene oxygenated	1313	0.10	0.16								
tetradecamethyl hexasiloxane	$C_{14}H_{42}O_5Si_6$	-	Sesquiterpene oxygenated		0.02									
Thymol-methyl ether	$C_{11}H_{16}O$	55,3	Sesquiterpene oxygenated	1021	0.27	0.33	0.36	0,56	0.34	0.30	0.35	0.36	0.45	0.41
			Sub-total		3.30	3.77	4.16	4.63	1.31	3.32	3.23	3.10	1.36	3.86
			Result		99.99	99.32	99.62	98.84	99.64	99.59	99.43	99.4	93.74	99.19

Compounds cataloged according to elution order DB5-MS column Retention Index (IR)calculated using a homologus series of n-alkanes (C10-C39) on a cappilary column (DB5-MS); Identification based on comparison of Nist (2020) and Adams (2017). Área (%): data libraries Area (%) is percentagem of área occupied by compound below the cromatogram peak.

Table 4. Bands oregano essential oil (O) at room temperature from 28°C to 100°C.

wavenumber (cm^{-1})	range band Frequency (cm^{-1})	Compound	functional group	magnitude	vibration modOE	OA 1	OA 2	OA 3	OA 4	OA 5	OF 1	OF 2	OF 3	OF 4	OF 5
540	750-500	C-Br	C-X (X=halogen)	strong	stretch	X	X	X	X	X	X	X	X	X	X
644	800-600	C-Cl	C-X (X=halogen)	strong	stretch	X	X	X	X	X	X	X	X	X	X
700	800-600	C-Cl	C-X (X=halogen)	strong	stretch	X	X				X	X	X	X	X
720	800-600	C-Cl	C-X (X=halogen)	strong	stretch			X	X						
740	800-600	C-Cl	C-X (X=halogen)	strong	stretch					X					
750	800-600	C-Cl	C-X (X=halogen)	strong	stretch	X	X	X	X	X	X	X	X	X	X
780	800-600	C-Cl	C-X (X=halogen)	strong	stretch								X	X	X
860	800-600	C-Cl	C-X (X=halogen)	strong	stretch	X	X	X	X	X	X	X	X	X	X
940	900-860	isolated H: may be present in meta-disubstituted benzene, in addition to other aromatics	aromatic ring	weak	stretch	X	X	X	X	X	X	X	X	X	X
960	970-960		CH=CH-	strong	out-of-plane angular deformation	X	X				X		X		
970	970-960		CH=CH-	strong	out-of-plane angular deformation			X	X	X		X		X	
1000	1400-1000	C-F	C-X (X=Halogen)	strong	stretch	X	X	X	X	X	X	X	X	X	X
1040	1400-1000	C-F	C-X (X=Halogen)	strong	stretch		X								
1050	1400-1000	C-F	C-X (X=Halogen)	strong	stretch	X		X	X		X		X	X	X
1100	1070-1150	C-O esters	aliphatic ethers	strong	stretch	X	X	X	X	X	X	X	X	X	X
1160	1140-1200	C-O esters	SO2	strong	stretch	X	X	X	X	X	X	X	X		X
1200	1300-1050	phenols	C-O de álcoois e phenols	strong	stretch	X	X	X	X	X	X	X	X	X	X
1250	1300-1250	unsaturated esters and aromaticss	C-O esters	strong	stretch	X	X		X	X	X	X	X	X	X
1280	1300-1250	unsaturated esters and aromatics	C-O esters	strong	stretch			X							X
1300	1300-1250	unsaturated esters and aromatics	C-O esters	strong	stretch	X	X	X	X	X	X	X	X	X	X
1350	1350-1310		SO_2	strong	stretch	X	X				X	X	X	X	X
1420	1420	CO3	C-O carboxílicos	Strong	Stretch	X	X	X			X	X			
1470	1480	secondary amines and amides	N-H	Strong	Deformação angular	X	X				X	X	X	X	X
1500	1500 and 1450		C=C aromatics	Strong	Stretch	X	X	X	X	X	X	X	X	X	X
1600	1600		C=C	Weak à média	Stretch	X	X	X	X	X	X	X	X	X	X
1630	1700-1630	N-amides -	C=O de amides	Strong	Stretch	X	X	X	X		X	X	X	X	X
2870	2820 and 2720		C-H de aldehydes	Strong	Stretch	X	X	X			X	X	X	X	
2920	3200-2500	C=O, NO_2	O-H (quelato)	Weak	Stretch	X	X	X	X	X	X	X	X		X
2960	3200-2500	C=O, NO_2	O-H (quelato)	Weak	Stretch	X	X	X	X	X	X	X	X	X	X
3000	3400 to 3000		O-H	Strong	Stretch	X	X	X	X	X	X	X	X	X	X
3400	3400	aromatic amines	N-H	Strong	Stretch	X	X	X	X	X	X	X	X	X	X

suggest overlapping bands due to interactions between compounds from groups of aromatic amines and aromatic amines with benzene, with carbon and oxygen double bonds and oxygen bonds respectively. The band at 2780 cm^{-1} corresponded to the aldehyde group, and H-C=O combined with vibrations in the aromatic ring near 2920 cm^{-1}.

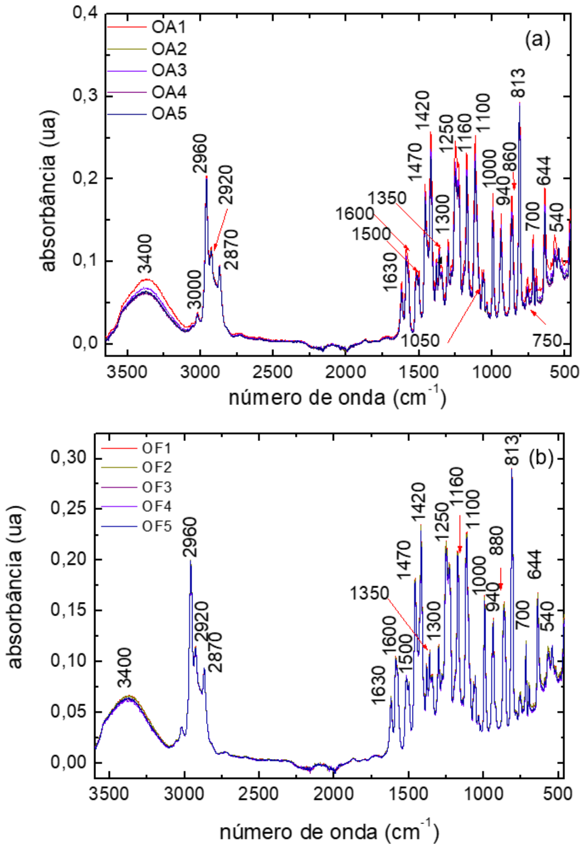


Fig. 2. FTIR spectra for oregano OEs treated at up to 100℃. (a) Storage in open *vials*. (b) Stored in closed vials.

Absorption bands at 700 cm^{-1} and 1050 cm^{-1} are attributed to stretching vibrations of halogens, whose band is centred in 1350 cm^{-1}, angular deformation band of N-H at 1470 cm^{-1}; and the amine N- replaced the stretch band at C=O, and 1630 cm^{-1} conserving the integral stability of their functions in all sealed stored samples under different heating temperatures, however, in an open system, these functional groups exhibited lower thermal resistance to temperature variation.

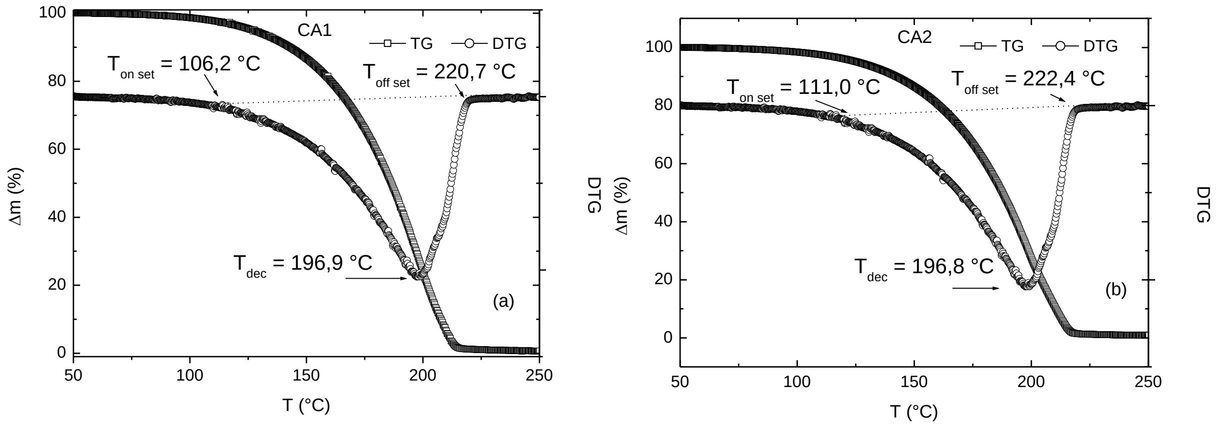
Results pointed out that heating may have elongated the molecular bonds, expanding them, as represented by the displacement of the absorption peaks. In the benzene group, the out-of-plane strain band at CH=CH, 960 cm^{-1}, maintained functional stability until 40°C in an open system and 60 °C in a closed system, but a tendence compartmental opposite was found for esters, in the what the stretching band at C-O 1420 cm^{-1}, preserving the functional stability of its components until 60°C in an open system and 40°C in a closed sample. Like for aldehydes, the C-H stretching band at 2870 cm^{-1} the functional groups were conserved until 60°C in an open system and 80°C in a closed system. Results showed that there were possibly a decomposition compounds from these groups upon the application of intense heat.

The in-band characteristic stretching vibrations at C-X 740 cm^{-1} were recognized only at 100°C in an open system, and the same trend occurred for the out-of-plane deformation band at CH=CH- 970 cm^{-1}, which conserved its functions when subjected to 60°C to 100°C in an open system. Analysis of the spectra of these groups indicated that the absorption peak may have shifted when subjected to different heat treatments. Consequently, the application of heat would have expanded and deformed the molecular bonds, indicating probable spectral band displacement.

Carvacrol is found in abundant OEs obtained from plants of specific scientific species. This compound is essential because it acts as a catalyst for antimicrobial activity, generating a harmful effect on themicrobial cell membrane [29]. In the literature, carvacrol, thymol, γ-terpinene and p-cymene were identified as the main compounds in oregano OE, while terpinen-4-ol, linalool, β-myrcene, trans-sabinene hydrate and β-caryophyllene were recognized.

Thermal behavior analysis of cinnamon OE samples

Thermogravimetric analyses of the studied OEs showed similar decomposition profiles for all the proposed treatments performed in the samples. Degration stages are highlighted in the DTG curves. In all stages, decomposition mass reduction was observed upon heating, a phenomenon that can be associated with the vaporization of compound of the OEs. DTG spectra of open (A) and closed (F) cinnamon OE plants treated at five temperatures are shown in Figures 3 and 4.



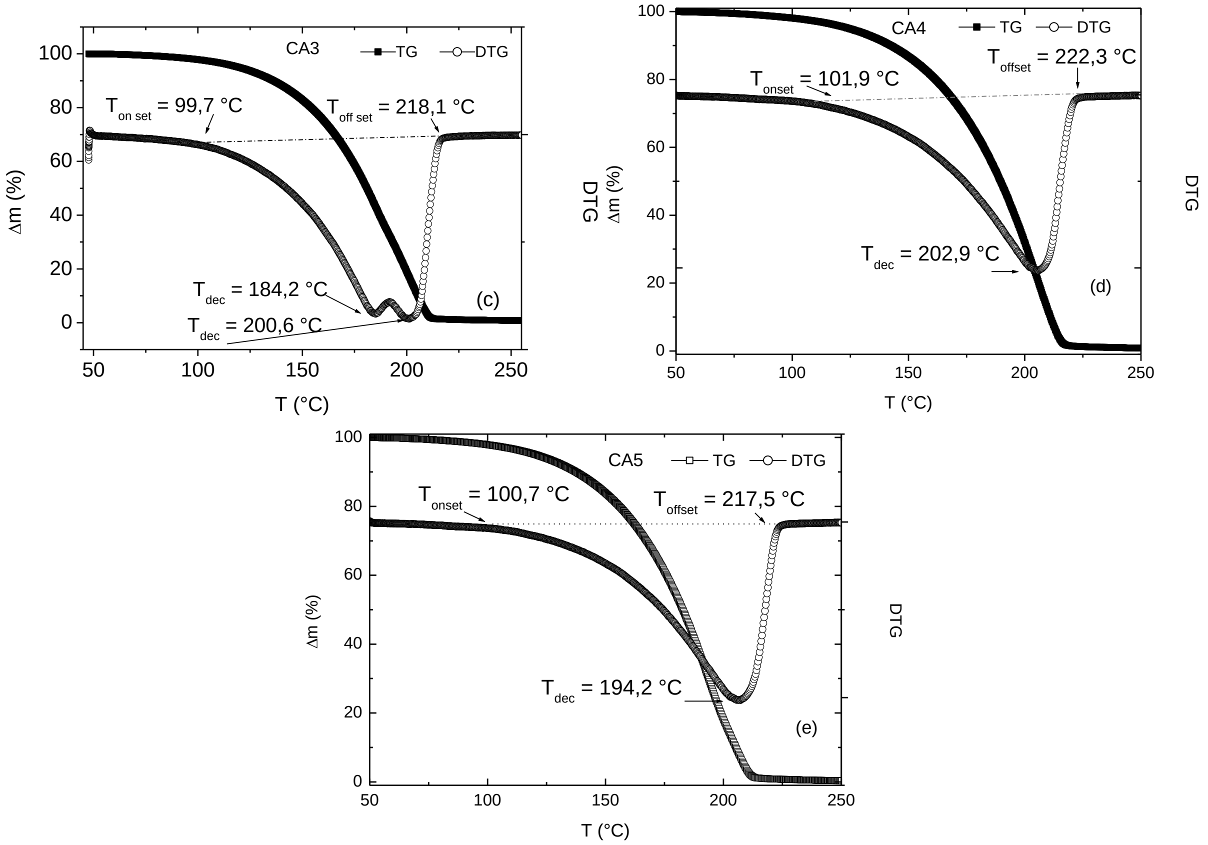
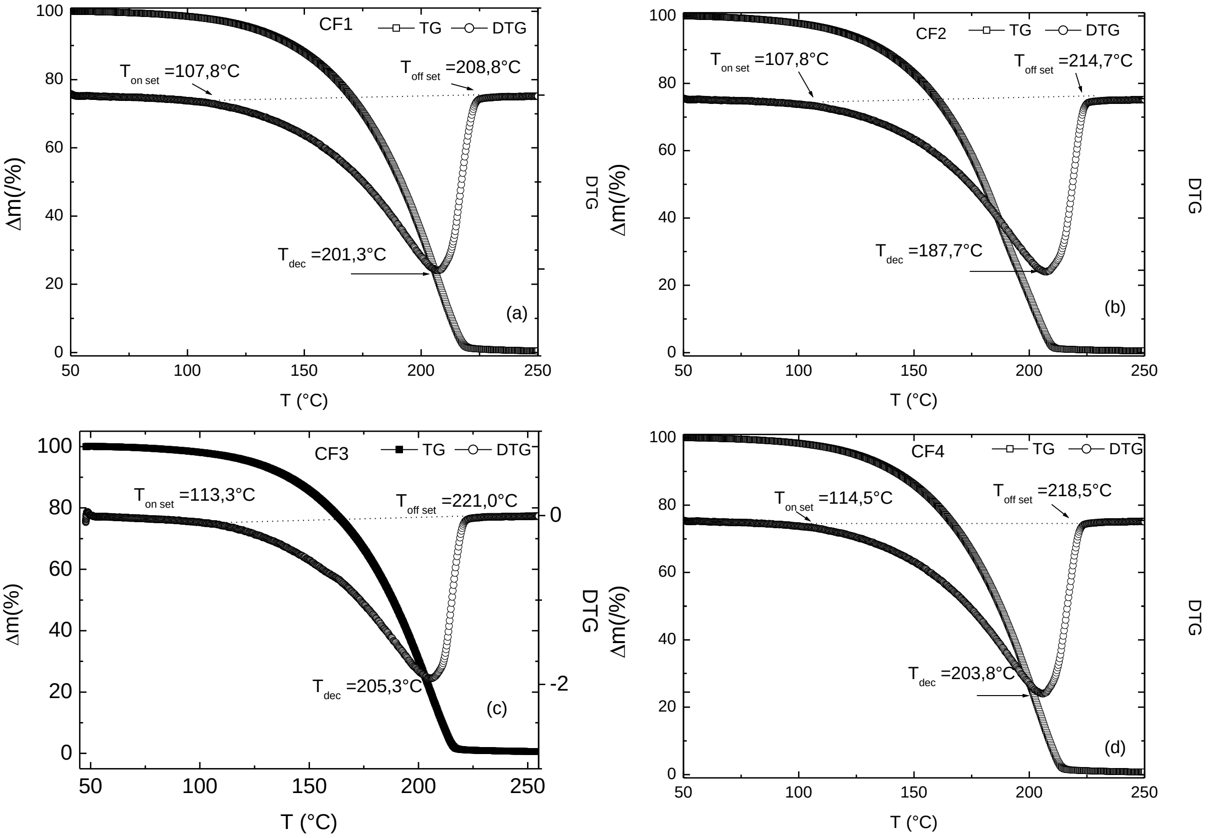


Fig. 3. Curves obtained from the thermogravimetric decomposition and its first derivative for open cinnamon oil. CA1: at 28°C; CA2: at 40°C; CA3: at 60°C; CA4: at 80°C; and CA5: at 100°C.



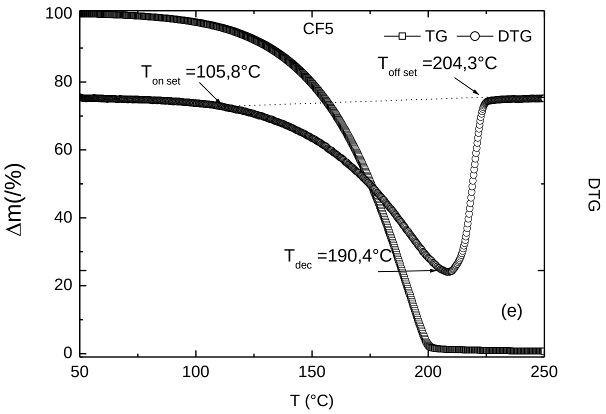


Fig. 4. Curves obtained from thermogravimetric decomposition and its first derivative for closed cinnamon oil. CF1: at 28°C; CF2: at 40°C; CF3: at 60°C; CF4: at 80°C; and CF5: at 100°C.

With the exception of the CA3 cinnamon oil, all the curves showed a single stage of mass loss during heating. The samples heated at 100°C were found to be slightly less stable than those heated at lower temperatures. Results obtneid by chromatographic suggested that Lazllo's cinnamon OEs are mainly composed of cinnamic aldehydes and eugenol. It is possible that volatile compounds vaporized quickly when the sample is heated.

Cinnamon OEs previously plated from 60°C and 80°C and stored in closed vials were more thermally stable because the temperature T_{onset} was equal to 113.3°C and 114.5°C, respectively, while for open *vials,* CA3 and CA4 thermal stability occurred from 99.7°C and 103.3°C. These results suggest that the compounds were possibly more thermally resistant when stored closed. Samples CF3 and CF4 exhibited the best thermal stability.

The inflection temperature, T_{dec}, did not significantly change during the thermal treatment of the oils. At this temperature, degradation is more faster. However, the graphs showed that every stage of mass loss before reaching T_{offset} proceeded more slowly in the OEs stored in open vials.

The influence of temperature and OEs during storage suggested that there may have been a change in the resistance to the initiation of vaporization of cinnamic substances, eugenol, thymol and carvacrol in closed oils, and the entire stage of decomposition became faster. Interactions with air may have exposed cinnamon OEs to lower thermal stability and greater decomposition. The decrease in volatile compound concentrations under these applied conditions may be associated with the antioxidant effect of the substances [30]. As no sample showed any mass gain, the thermoanalytical results suggest that the compounds only vaporized; therefore, there was no oxidation reaction with the air for any sample.

Gravimetric decomposition at set intervals during heating is attributed mainly to evaporation substances and moisture. It was noted from the results found that cinnamon OE decomposed at higher temperatures when stored in closed *vials*. This result can be explained by the fact that as cinnamon OEs became the most thermally resistant compounds, the hydrophilic interactions of the oil increased.

Curves profiles of cinnamon OE plants stored in open and closed vials are presented in Figures 5 and 6, respectively. All the results presented endothermic peaks showed to evaporation.

Characteristic peaks associated with vaporized DSCs are typically more widely and more dispersed because this phenomenon is directly related to the thermogravimetric decomposition of the samples. Point found at the center peak in the DSC profile is known as the vaporization temperature, and it approximately coincides with the T_{dec} temperature in the DTG curves.

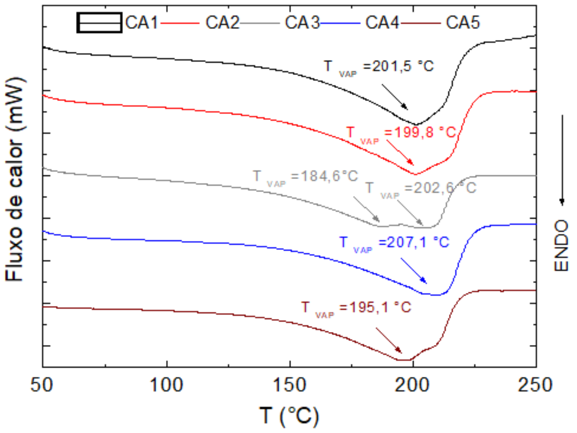


Fig. 5. DSC profile of cinnamon OE plants stored in an open *vial* at room temperature and 100 ºC.

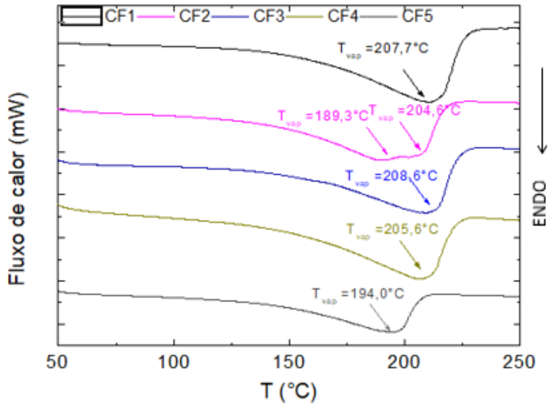


Fig. 6. DSC profile of cinnamon OE plants stored in a closed vial at room temperature 100 °C.

For the DSC profile, two vaporization peaks were detected for CA3 and CF2 possibly due to the greater sensitivity of these samples to the best flow at the examined heating rate.

Cinnamon OE plants treated from 100°C were evaporated at 195.1°C and 194.0°C when stored in open and closed vials, respectively. Compared to the other samples, which exhibited vaporization temperatures higher than those mentioned above 100 °C thermal treatment precipitated the phenomenon of sample evaporation, likely due to the majority of the OEs of the prior evaporation compounds. Treatment from 100°C made cinnamon oil less thermally resistant. For cinnamon OE CF2, subjected to a thermal bath from 40°C, the results suggest slight vaporization at 189.3°C, however, the majority of the compounds evaporated from 204.6°C.

However, the results indicated that the treated cinnamon OEs stored in a closed system for to 60°C were slightly more optimized than the open samples. No significant variation in the T_{vap} was observed among the treatments carried out at 80°C. Cinnamon OE degraded until reached a maximum temperature of 232.3°C. From T_{offset}, the mass of the oils was reduced by approximately 94.6% to 99.6% [18]. Thermoanalytical measurements were carried out on oil from the same batch without heat treatment, in which was found thermal behavior similar to these results present work was found. Physicochemical properties of cinnamon-perilla OE incorporated into edible films presented decomposition and vaporization temperatures between 150°C and 170 ℃ attributed to volatilization of cinnamic aldehydes.

The enthalpy variation involved during the phase transition between liquid and gas for the samples is presented in Table 5. This physical quantity reflects the variation in thermal energy necessary for the oil to vaporize. Negative sign is associated with the endothermic peak.

With heating, the latent heat of substances increases, consequently influencing the change in enthalpy. The change in enthalpy is described by the relationship $\Delta H = C_p \Delta T$ (5), where $C_p = mc$ (6) is the heat capacity at constant pressure or product mass m and specific heat c, and ΔT is the temperature variation.

In the phase transition, the heat involved in the transitions Q = ml (7), where L is the latent heat. When the temperature increases during heat treatment, the enthalpy variation increases, indicating that during the phase transition more energy must be absorbed to evaporate the OE. Results thus sugged that there was an increase in thermal energy for vaporization when OEs heated at treatments.

Table 5. Variation in enthalpy transition calculated by integrating the area under the peak for cinnamon essential oils.

Sample	$\Delta H\ (kJ/kg)$	Sample	$\Delta H\ (kJ/kg)$
CA1	- (110.50 ± 1.80)	CF1	- (21.88 ± 0.36)
CA2	- (264.28 ± 4.33)	CF2	- (203.27 ± 3.33)
CA3	- (458.53 ± 7.51)	CF3	- (267.71 ± 4.39)
CA4	- (533.09 ± 8.73)	CF4	- (463.61 ± 7.60)
CA5	- (640.74 ± 10.49)	CF5	- (487.71 ± 7.99)

Thermal analysis results corroborated the data from the chemical characterization tests. During the heating treatments, the stretching bonds underwent changes due to expansion caused by temperature variations. As a result, some infrared (IR) peaks exhibited shifts in their bands.

However, heated also caused the evaporation of compounds that did not have sufficiently strengthened bonds, thus conserved more thermally resistant functional groups. The functional groups of esters, hydrocarbons, benzenes and aromatics were most damaged by heating. Results suggested greater optimization of thermal and chemical stability for samples of cinnamon OEs stored in a closed system and treated up to 80°C considering T_{onset} as the main temperature that influences native conservation of the natural properties of cinnamon OE. However, results showed that for sample OF5, there was a slight reduction in the percentage of compounds and peak numbers of vibration and stretching bonds, indicating that when the oregano OE was stored in a closed bottle, having its characteristics physicochemical characteristics were preserved.

Analysis of the thermal behavior of oregano OE samples

Profiles obtained the oregano OEs showed stages of decomposition associed to gravimetric loss with heating (TG and DTG curves) and endothermic peaks in the DSC curves. Table 6 briefly presents the characteristic temperatures of the thermal behavior and the ΔH values calculated for the samples.

Table 6. Characteristic temperatures and enthalpy variations found by DTG and DSC for OAs and OFs.

Sample	T_{onset} (°C)	T_{dec}(°C)	T_{offset}(°C)	T_{vap}(°C)	$\Delta H\ (kJ/kg)$
OA1	107.4 ± 0.3	191.7 ± 0.3	211.3 ± 0.3	196.9 ± 0.3	- (68,.8 ±1.44)
OA2	103.1 ± 0.3	1961.2 ± 0.3	211.5 ± 0.3	197.3 ± 0.3	- (181.22 ±3.83)
OA3	102.1 ± 0.3	172.2 ± 0.3 e 187.6± 0.3	205.4 ± 0.3	173.6 ± 0.3 e 195.2 ± 0.3	- (423.78 ±8.95) – (201.04 ±4.25)
OA4	99.1 ± 0.3	187.9 ± 0.3	207.3 ± 0.3	193.8 ± 0.3	- (400.39 ± 8.45)
OA5	91.6 ± 0.3	190.7 ± 0.3	209.6 ± 0.3	195.6 ± 0.3	- (640.03 ±10.35)
OF1	95.2 ± 0.3	186.8 ± 0.3	206.4 ± 0.3	192.8 ± 0.3	- (44.20±0.93)
OF2	96.5 ± 0.3	191.6 ± 0.3	211.6 ± 0.3	193.2 ± 0.3	- (175.84± 3.7 1)
OF3	97.0 ± 0.3	170.1 ± 0.3 e 188.2 ± 0.3	203.1 ± 0.3	167.0 ± 0.3 e 190.8 ± 0.3	- (352.04 ±7.42) / - (221.10±4.66)
OF4	96.7 ± 0.3	184.8 ± 0.3	202.5 ± 0.3	188.4 ± 0.3	- (1200.45 ±25.33)
OF5	91.6 ± 0.3	192.1 ± 0.3	211.2 ± 0.3	195.7 ± 0.3	- (1629.57 ± 34.44)

First decomposition stage occurred at a temperature less than 108°C, in especially, results indicted out that OEs treated at up to 80°C stored in closed vials, showed thermal stability T_{onset} close to 96°C. Results suggesting that the thermal stability of oregano essential oils (OEs) tends to decrease with temperature compared to that of cinnamon essential oils (OEs) stored in closed conditions, with an approximate difference of at least thirteen degrees. However, for open OEs and OEs treated at up to 80 °C, both oils showed similar T_{onset}. The thermal stability of OEs previously heated to 100 °C slightly decreased under both storage conditions. Resistance to heat application was lower in the closed storage condition for oregano OEs compared to the open storage condition. Therefore, the DTG results confirmed the thermal stability of oregano essential oil and its resistance to degradation during heating and storage.

The TG/DTG profiles showed only a single-stage decomposition and rapid mass loss upon heating, except for the essential oils (OEs) treated at 60°C, which exhibited two stages: significant decomposition and slow evaporation, in contrast to OEs treated at other temperatures.

Oregano essential oil (OE) thermally degraded until it reached a maximum temperature of 211.6°C. At T_{offset}, the sample masses were reduced to range 93% and 100% of the initial mass. Analysis of the heat flow profiles revealed endothermic curves for all samples. Similar to DTG, the calorimetric technique was sensitive in detecting the two stages of evaporation in OEs treated at 60°C under both storage conditions.

Variation in enthalpy increased with heating. Enthalpy represents the energy involved in the physic state transition from liquid to gas. With heating of temperature rises during an endothermic reaction, atomic bonds that require more absorbed energy are broken. The stronger these bonds are, the more energy is needed to break them. Consequently, a greater amount of energy is absorbed by the samples to facilitate the evaporation of the oils.

Most reactions involving vaporization occur spontaneously. During this process, energy is absorbed by the compounds. In this study, given that the material requires significant energy absorption for the event to take place, the initial, decomposition, final, and vaporization temperatures needed to be high, as reflected in the variation in enthalpy of the examined essential oils (OEs). Therefore, we can conclude that cinnamon and oregano OEs are thermally resistant, as their constituents remain stable despite the changes likely caused by heat application.

For better understanding, a table summarizing all the temperatures related to the thermal behavior of the samples can be found in Appendix 1 (Supporting Information) of this work.

4. Conclusions

The results suggest that heating and conditioning systems can influence the concentrations of characteristic components in essential oils (OEs). Additionally, potential changes in the percentages of each compound, as well as shifts or alterations in the intensity of infrared absorption peaks, indicate modifications in the stability of organic functions and functional groups. These changes suggest that heat might catalyze irreversible degradation reactions. The most optimal thermal stabilities were observed for cinnamon OE after heat treatment at 60°C and 80°C in closed systems. Cinnamon OEs treated and stored in open systems showed slightly greater thermal resistance compared to oregano OEs. The thermal behavior of oregano OEs did not vary significantly with the storage system used. Heating requires increased energy absorption during the phase transition.

Author Contributions

Angela Maria Picolloto: Methodology, Writing, Resources; Cristiane Mengue Feniman Moritz: Writing, Conceptualization, Supervision, Project ,Administration, Angela Maria Ariati: Data Curation, Investigation, João Marcos Azevedo Gomes dos Santos: Investigation, Visualization; Lidaiane Mariah Silva dos Santos Franciscato: Resources, Methodology; Milene Ribeiro da Silva: Methodology; Paulo Rodrigo Stival Bittencourt: Formal Analysis, Methodology, Investigation; Otavio Akira Sakai: Resources, Formal Analysis, Conceptualization, Methodology, Investigation.

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