CHEMICAL AND THERMOANALYTICAL CHARACTERIZATION OF THE PINK PEPPER (*Schinus terebinthifolius* Raddi) SEEDS ESSENTIAL OIL

CARACTERIZAÇÃO QUÍMICA E TERMOANALÍTICA DO ÓLEO ESSENCIAL DE SEMENTES DE AROEIRA VERMELHA (*Schinus terebinthifolius* Raddi)

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Abstract: The essential oil (EO) of pink pepper has important biological properties that can enhance its application in the pharmaceutical, cosmetic and food industries. The objective of this study was to characterize the EO of pink pepper seeds in terms of their chemical composition and thermophysical properties. Certified pink pepper seeds obtained commercially were used. The EO was extracted by hydrodistillation and chemically characterized in a gas chromatograph coupled to mass spectrometer (GC/MS). The thermoanalytical characterization was performed on a simultaneous high resolution equipment, and the Thermogravimetric Analysis (TG) and Differential Scanning Calorimetry (DSC) were used to determine the physical-chemical and kinetic properties of the OE in the room temperature range up to 250 °C in the 20 °C.min⁻¹ ratio under nitrogen atmosphere. The Arrhenius kinetic model was applied to determine the activation energy of the EO. A total of 51 chemical compounds were detected in the pink pepper EO, of which 42 compounds were identified (54.7% of monoterpene compounds and 45.3% sesquiterpenes). The major components were β-pinene (26.80%), germacrene D (11.25%), sabinene (11.13%) and terpinen-4-ol (8.59%). The thermogravimetric analysis indicated a single stage of thermo-degradation of the pink pepper EO between 74.8 °C and 184.7 °C, being an endothermic peak in the physical transition of vaporization. The variation of enthalpy and activation energy of EO were found with values of Δ𝑯 = - (39.8 ± 9.5) KJ.Kg⁻¹ and 𝐸𝒂 = - (2.546 ± 0.033) KJ.mol⁻¹, respectively. The data presented in the thermogravimetric analysis of pink pepper seeds EO allowed observing important thermal parameters for the definition of industrial processes that can use it as raw material, so that its biological activities can remain stable under controlled temperature conditions and below the range degradation.

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Resumo: O óleo essencial (OE) da aroeira vermelha possui importantes propriedades biológicas que podem potencializar sua aplicação na indústria farmacêutica, cosmética e alimentícia. O objetivo deste estudo foi caracterizar o OE de sementes de aroeira vermelha quanto à sua composição química e suas propriedades termofísicas. Foram utilizadas sementes certificadas de aroeira vermelha, obtidas comercialmente. O OE foi extraído por hidrodestilação e caracterizado quimicamente em cromatógrafo gasoso acoplado a espectrômetro de massa (CG/EM). A caracterização termonalítica foi realizada em um equipamento simultâneo de alta resolução, sendo que a Análise Termogravimétrica (TG) e Calorimetria Exploratória Diferencial (DSC) foram empregadas para determinar as propriedades físico-química e cinética do OE no intervalo de temperatura ambiente até 250 ºC na razão de 20 ºC.min⁻¹ sob atmosfera de nitrogênio. O modelo cinético de Arrhenius foi aplicado para determinar a energia de ativação do OE. Foram detectados um total 51 compostos químicos no OE de aroeira vermelha, dos quais 42 compostos foram identificados (54,7% dos compostos monoterpênicos e 45,3% sesquiterpênicos). Os componentes majoritários foram β-pineno (26,80%), germacreno D (11,25%), sabínone (11,13%) e terpinen-4-ol (8,59%). A análise termogravimétrica indicou um único estágio de termodegradação do OE de aroeira vermelha entre 74,8 ºC e 184,7 ºC, sendo um pico endotérmico na transição física de vaporização. A variação da entalpia e a energia de ativação do OE foram encontradas com valores de ΔH = -(39,8 ± 9,5) KJ.Kg⁻¹ e Eₐ = -(2,546 ± 0,033) KJ.mol⁻¹, respectivamente. Os dados apresentados na análise termogravimétrica do OE de sementes de aroeira vermelha permitiram observar parâmetros térmicos importantes para a definção de processos industriais que possam o utilizar como matéria-prima, para que suas atividades biológicas possam permanecerem estáveis em condições de temperatura controlada e abaixo da faixa térmica de degradação.

Palavras-chave: Óleo essencial da aroeira vermelha. Análise termogravimétrica. Calorimetria exploratória diferencial. Energia de ativação. Composição química.
1 INTRODUCTION

The pink pepper (*Schinus terebinthifolius* Raddi) is a plant of the Anacardiacea family found on the Brazilian coast that extends from the Northeast to the South Region of the country. It’s also known as aroeira-mansa, aroeira-pimentaira, aroeira-da-praiia, aroeira-do-brejo, aroeira-do-sertão among other regional denominations. Native in Argentina, Chile, Uruguay, Bolivia, Paraguay and Peru. It’s fruits resemble a pink pepper, used as a spice in regional culinary dishes. It’s ripe fruits are red, slightly sweet and mildly spicy (LIMA et al., 2006).

The pink pepper tree has the following morphological characteristics: between 5 to 10 m in height and the diameter of the trunk in the range between 30 to 60 cm, surrounded by thicker bark. Due to the abundance of red fruits, produced for up to two annual seasons. It’s a tree recommended for reforestation on reservoir margins and recovery of degraded reserves (LIMA et al., 2004).

The biological activities of pink pepper are known mainly for their astringent, anti-diarrheal, anti-inflammatory, analgesic, diuretic and febrifugal actions (PAIVA; ALOUFA, 2009). The first biological applications of the plant were described in the first edition of Revista Farmacopeia Brasileira, published in 1926 (BRANDÃO et al., 2008). The parts of the plant used for having medicinal properties are barks, fruits and leaves. For essential oil (EO) extracted from the pink pepper, antimicrobial and antioxidant activities have been proven (EL-MASSRY et al., 2008; JOHANN et al., 2010).

In the metabolism of plants, chemical compounds essential for their development are produced, from mineral nutrients, photosynthesis, water and carbon dioxide. This metabolism can be divided into two groups: primary metabolism, responsible for cell development, in which oils, nucleic acids, carbohydrates and proteins are produced; and secondary metabolism, in which complex chemical structures of low molecular weight are produced, which compose the extracted EOs (BENNAOUM et al., 2017).
The EOs can be extracted from different parts of plants, such as flowers, leaves, fruits, seeds, stems, roots, bark or resins and can be used as raw materials in different industrial segments (KHAYYAT; ROSELIN, 2018).

Barbosa et al. (2007) considered the pink pepper EO non-toxic to animals and humans and Martinelli et al. (2017) highlighted that the EO extracted from seeds has important biological properties that can enhance its application in the pharmaceutical, cosmetic and food industries.

However, for the industrial application of pink pepper EO, it’s important to know its chemical composition and its thermal stability, due to the highly volatile nature of its compounds.

Thus, this work aimed to characterize the pink pepper seeds EO in terms of their chemical composition and thermophysical properties.

2 DEVELOPMENT

The extraction of EOs is usually make by hydrodistillation. Santana et al. (2012) obtained the EO of pink pepper leaves by the method of hydrodistillation using the Clevenger apparatus, in order to study the chemical composition and perform cytotoxicity tests.

Some factors must be considered when obtaining EOs, such as the time of exposure of the material and the temperature used during the distillation process, as they can directly influence its chemical composition and the concentrations of certain compounds, generating an increase in the concentration of less volatile compounds (camphene, α-fenchene, D-germacrene, δ-cadinene, hedicariol, α-gurjunene, α-eudesmol and β-eudesmol) and volatiles (sesquiterpenes). On the other hand, there may be a reduction in the concentration of the most volatile compounds (monoterpines) (OLIVEIRA et al., 2014).
The EOs are composed of multiple substances and highly volatile, resembling a single component system. Therefore, thermoanalytical techniques promote qualitative and quantitative characterization regarding the decomposition temperature ranges, physical endothermic events (associated with EO vaporization) or exothermic events (associated with oxidation), degree of purity, boiling temperature, among other physical events physicochemicals, determination of the variation of the reaction enthalpy and activation energy. Such information is of great importance in science and industry, with regard to the application of EOs.

Due to possible variations in the chemical composition of EOs during storage, their physical and chemical properties can also be altered. The evaporation kinetics and vaporization pressure of EOs can be analyzed using Thermogravimetric Analysis (TG) and Differential Scanning Calorimetry (DSC) (HAZRA et al., 2004).

The TG technique is very efficient for studying mass loss due to heating. In the characterization of the thermal degradation of the EOs, this technique is indicated for pointing the initial temperature of the extrapolated decomposition, temperature of greater decomposition reaction and the final temperature of the decomposition. The mass variation of a substance is subjected to controlled temperature programming. Thus, the study of the thermal stability of EOs is a determining factor in their quality and applicability (WENDLANT, 1986).

For many years, several researches have been carried out in the hope of finding detailed knowledge about the changes that heating can cause in the mass of substances, in order to determine the temperature range at which a compound starts to decompose, dehydrate or oxidize (IANOSHIRO, 2004). The fundamental principle of TG analysis is the continuous weighing of the sample during heating.

Currently, thermogravimetry equipment consists of an analytical balance predestined to continuously measure the mass of the sample deposited in a crucible, during heating and cooling, with a variation rate of °C.min⁻¹, in an inert gas system to provide a controlled atmosphere, a computer to program the...
temperature and a thermocouple (RODANTE; MARROSU, 1990). The crucible is deposited on a platform suspended by a platinum metallic wire connected to the thermobalance. The data are generated with the time, temperature and mass of the sample and are automatically recorded. The results are presented in the form of TG thermograms.

The dynamic DSC is a technique used to measure the variation of the energy supplied to a substance and a reference material as function of temperature, while the sample and the reference material are simultaneously subjected to controlled temperature programming. In this technique, the effects of heat associated with first-order phase fusion (fusion, vaporization, sublimation, crystallization, oxide-reduction, among others) and second order (glass transition and Curie temperature) are examined during endothermic and exothermic events (VOGEL, 2011). In general, phase transitions, dehydrations, reductions and certain decomposition reactions produce endothermic effects, whereas crystallizations, oxidations, some decomposition reactions generate exothermic effects. In first order transitions there is a variation in reaction enthalpy ($\Delta H$) and second order transitions are associated with changes in entropy ($\Delta S$). There is no variation in enthalpy in second-order reactions. In DSC thermograms an endothermic peak is recorded in the upward direction of ($\Delta H$), while an exothermic peak is indicated in the downward direction.

The treatment for interpreting TG thermogram data is usually performed using the Thermogravimetric Derivative (DTG) curves. The derivative ($\frac{dm}{dT}$) results in a function of temperature, $f(T)$. By this method, curves in the form of peaks are obtained (WENDLANDT, 1986) that correspond to the stages of thermal degradation. Thus, the TG technique is efficient to provide information regarding the decomposition of EOs as function of temperatures, $T_{on\_set}$ (initial temperature of the extrapolated decomposition), $T_{dec}$ (temperature of the greatest decomposition reaction) and $T_{off\_set}$ (temperature decomposition). The vaporization endothermic event and its energetic power in the EO can be observed through the DSC (PORTELA et al., 2014).
2.1 MATERIAL AND METHODS

2.1.1 Material

The pink pepper EO was obtained by hydrodistillation from certified seeds sold by https://www.sementesarbocenter.com.br/. The Clevenger distillation apparatus was used. The pink pepper seeds were crushed to reduce the size of the particles (approximate diameter of 0.5 cm). Subsequently, they were placed with a mass of approximately 50 g in a paper cartridge and 250 ml of distilled water were added in a round bottom flask. The extraction period was three hours. The EO was then separated and placed in an amber bottle under refrigeration.

2.1.2 Chemical characterization

The chemical characterization of the pink pepper seeds EO was performed in a gas chromatograph coupled to mass spectrometer – GC/MS (Shimadzu, model GCMS-plus-QP2010), in which a capillary column DB-5 with 30 meters x 0.25 mm x 0.25 mm was used. The method described by Beraldo et al. (2013) with adaptations. The injector and interface temperature was 250 ºC. The detector was operated in Electron Impact (EI) mode at 70 eV and helium was used as the carrier gas. The chromatographic conditions for pink pepper EO used were the initial temperature of 40 ºC (2 min) at rate of 3 ºC.min⁻¹, heating up250 ºC and maintaining that temperature for 10 minutes. 1:10 split injection and the injected volume of 1 µL of sample. A mixture of linear alkanes (C10 to C39) was injected into the chromatograph under the same conditions used as a standard for calculating the retention index with linear temperature programming. The identification was carried out by comparing the retention index with libraries (ADAMS, 2017, NISTBOOK, 2019).
2.1.3 Thermoanalytical characterization

The parameters of the heating rate, the atmosphere, the gain or loss of mass, the temperature and the heat flow were defined for investigation and identification of the existing events for pink pepper EO, according to the peak profiles, the temperature range and thermal stability of the sample.

The thermoanalytical characterization was performed in a simultaneous high resolution equipment (STA 6000 Simultaneous Thermal Analyzer PerkinElmer Frontier), in the temperature range from 25 to 250 °C. The tests were submitted to heating rate 20 °C.min⁻¹. Approximately 300 µL of sample was placed in an open platinum-rhodium crucible under a dynamic atmosphere of N₂ (30 mL.min⁻¹), with a heating rate of 20 °C.min⁻¹, in the temperature range from 25 to 250 °C. Through TG it’s was possible to observe information regarding the variations in mass as function of time and/or temperature under dynamic atmosphere. The experiments were performed using a thermobalance of high sensitivity, reproducibility and response to variations in mass. The equipment was previously calibrated with indium \((T_{\text{fusion}} = 156.6 \, ^\circ\text{C})\) and with zinc \((T_{\text{fusion}} = 420.0 \, ^\circ\text{C})\).

2.1.3.1 Thermogravimetric derivative

The DTG calculation was based on the first order drift of the TG thermogram. Through this treatment, Equation (1), the decomposition profile was obtained, finding the temperatures of \(T_{\text{on.set}}\), \(T_{\text{dec}}\) e \(T_{\text{off.set}}\).

\[
f (T) = \frac{dm(T)}{dT} \tag{1}
\]
Where $m(T)$ is the thermally degraded mass of the sample as a function of temperature ($T$).

### 2.1.3.2 Differential Scanning Calorimetry (DSC)

The DSC calculation was performed based on the area (A) of the peak of the DSC thermogram obtained in the thermoanalytical characterization of the pink pepper EO. The area was considered directly proportional to the enthalpy variation – Equation (2) (IANOSHIRO, 2004).

$$A = \Delta H \frac{m}{k} \quad (2)$$

Where $k$ is the calibration coefficient of the equipment associated with the geometry and thermal conductivity of the sample holder, usually determined by calibrating the system with compounds that have known transition or reaction heats.

### 2.1.3.3 Arrenhius method

The Arrhenius kinetic model (KOK; VARFOLOMEEV; NURVALIEV, 2017) was applied to determine the activation energy of the pink pepper EO sample. The kinetics of a thermal event of chemical nature with the release of gaseous compounds can be calculated by means of the Arrenhius reaction speed law - Equation (3).

$$- \frac{1}{100} \frac{dm\%}{dt} = K(T) \frac{m\%}{100} \quad (3)$$
Where $m_{\%}$ represents the mass read in TG, $\frac{dm_{\%}}{dt}$ is the first derivative of mass as a function of time and $K(T)$ designates the reaction speed constant, modeled by Equation (4).

$$K(T) = A_f e^{\frac{E_A}{RT}} \quad (4)$$

In which $E_A$ is the reaction activation energy, $A_f$ is the pre-exponential factor and $R$ is equal to 8.314J.mol$^{-1}$.K$^{-1}$, the universal gas constant. Combining Equations (3) and (4), Equation (5) is obtained.

$$-\frac{1}{100} \frac{dm_{\%}}{dt} = A_f e^{\frac{E_A}{RT}} \frac{m_{\%}}{100} \quad (5)$$

Linearizing Equation (5), the equation (6) is obtained.

$$\ln \left( -\frac{1}{100} \frac{dm_{\%}}{dt} \right) = \ln A_f - \frac{E_A}{RT} \quad (6)$$

Linear adjustment $\ln \left( -\frac{1}{100} \frac{dm_{\%}}{dt} \right)$ versus $\frac{-1}{RT}$ results in a linear coefficient line $A_f$ and the slope of the line corresponds to the activation energy.

### 2.2 RESULTS E DISCUSSION

#### 2.2.1 Chemical characterization

The chemical composition of pink pepper EO, determined by GC/MS, is listed in Table 1.
**Table 1** – Chemical composition of the pink pepper seeds essential oil.

| Compound        | Retention Index | Area (%) |
|-----------------|-----------------|----------|
| α-pinene        | 949             | 2.63     |
| savineno        | 956             | 11.13    |
| canphone        | 965             | 0.29     |
| thuja-2,4 (10) -diene | 968 | 0.24     |
| β-pinene        | 985             | 26.80    |
| mycrene         | 992             | 2.23     |
| α-felandreno    | 1004            | 0.47     |
| 3-δ-carene      | 1009            | 0.55     |
| α-terpinene     | 1014            | 1.65     |
| o-cimene        | 1022            | 3.84     |
| β-felandrene    | 1027            | 4.21     |
| γ-terpinene     | 1055            | 2.71     |
| trans-sabinene hydrate | 1064 | 0.27     |
| terpineno       | 1087            | 1.11     |
| cis-para-ment-2-en-1-ol | 1120 | 0.54     |
| trans-pinocarveol | 1137 | 0.86     |
| trans-verbenol  | 1143            | 0.27     |
| cis-p-mentha-2,8-dien-1-ol | 1146 | 0.31     |
| terpinen-4-ol   | 1179            | 8.59     |
| α-terpineol     | 1191            | 0.54     |
| mirenol         | 1196            | 0.46     |
| verbenone       | 1209            | 0.30     |
| no identified   | 1251            | 0.10     |
| no identified   | 1268            | 0.25     |
| isobornyl acetate | 1284 | 0.19     |
| no identified   | 1286            | 0.25     |
| no identified   | 1319            | 0.25     |
| δ-elemene       | 1336            | 0.19     |
| α-cubebeño      | 1348            | 0.36     |
| α-ylangene      | 1373            | 1.44     |
| syphirene       | 1388            | 0.20     |
| E-caryophyllene | 1416            | 1.80     |
| 6,9-guaiadiene  | 1426            | 0.17     |
| aromadendrene   | 1435            | 0.21     |
| humulene        | 1450            | 0.48     |
| allo-aromadendrene | 1457 | 0.47     |
| germacrene D    | 1481            | 11.25    |
| γ-amorffene     | 1488            | 0.10     |
| bicyclogermacon | 1494            | 2.70     |
| α.-muurolene    | 1498            | 0.54     |
| cuparene        | 1502            | 0.46     |
δ-amorphene 1511 0.72
α-cuprenene 1521 2.09
no identified 1551 0.37
no identified 1562 0.13
spatulenol 1574 1.68
karyophelene oxide 1578 0.34
no identified 1636 2.02
no identified 1637 0.62
α-cadinol 1651 0.37
Total 99.75

| Compound listed according to the elution order of column DB-5; b Retention Index (IR) calculated using a homologous series of n-alkanes (C10-C39) in a capillary column (DB-5); c Area (%): is the percentage of the area occupied by the compound within the chromatogram. Identification based on comparing data libraries NIST (2020) and ADAMS (2017). |
|---------------------------------------------------------------|

A total of 51 compounds were detected and 42 compounds were identified, with 54.7% of monoterpenes and 45.3% sesquiterpenes. The major components were β-pinene (26.80%), germacrene D (11.25%), sabinene (11.13%) and terpinen-4-ol (8.59%).

Although Cole (2008) found a predominance of monoterpenes (85%) in the pink pepper fruits EO, consisting mainly of δ-3-careno (30.37%), limonene (17.44%), α-felandreno (12.60 %), α-pinene (12.59%), mircene (5.82%), and sesquiterpenes (5.34%), among others, the results found in this study for the chemical composition of the pink pepper seeds EO are similar to data from other scientific researches. Salem et al. (2018) reported that the main chemical compounds for the pink pepper fruits EO were α-pinene (36.9%), α-felandreno (32.8%), limonene (11.9%) and α-terpineol (6.0%). Dannenberg et al. (2019) also investigated the chemical composition of pink pepper EO using ripe fruits and detected 18 compounds, with β-cubebeene (12%), limonene (9%) and α-pinene (8%) being the major compounds.

The physical-chemical stability and biological properties of EOs are strongly related to their chemical composition. The variation of the compounds present in the EO depends on many factors, such as variety, part of the plant, climatic conditions, drying conditions (if applied), extraction methods and the analysis method for chemical characterization (RIBEIRO-SANTOS et al., 2017).
2.2.2 Thermoanalytical characterization

The TG/DTG thermograms represent the behavior of the thermo-degradation of the pink pepper EO (Figure 1). While the TG curve showed the result of the thermo-degradation of the substance, the DTG curve showed the behavior of thermal stability. From the result it was found that this OE was thermally stable until 74.8 °C (\(T_{\text{on, set}}\)), the decomposition stage ceased at 184.7 °C (\(T_{\text{off, set}}\)) and the temperature of the highest EO decomposition kinetics was equivalent to 136.0 °C. There was a single stage of decomposition remaining approximately 5% by mass of residue at the end of the test. By comparing the boiling points according to the Chemspider database (CHEMSPIDER, 2020), it’s possible to confirm that the two main major compounds (monoterpenes), representing 37.93% of the mass of the pink pepper EO, have lower evaporation points (β-pinene: 166 °C and sabinene: 164 °C) than the following two major compounds (sesquiterpenes), with a representative mass of 19.84% (germacrene D: 279 °C and terpinen-4-ol: 212 °C).

Figure 1 – Thermograms (TG / DTG) of the pink pepper seeds essential oil.
The stability of a substance can be defined as its ability to resist vaporization. The dynamic DSC thermogram (Figure 2) showed an endothermic transition, with the peak temperature at 136.0 °C, coinciding with the fastest decomposition temperature, referring to the vaporization of volatile compounds. The variation in enthalpy at the constant pressure found (ΔH) was equal to - (39.8 ± 9.5) KJ.Kg⁻¹. The negative sign means heat absorption by EO from the medium.

**Figure 2** – Non-isothermal DSC thermogram of the pink pepper seeds essential oil.

The activation energy (Eₐ) can be considered as an energy barrier that measures the amount of energy needed for molecular disruptions to occur in physical-chemical reactions. It was calculated from the endothermic peak of the TG thermogram using the kinetic method. Observing the Arrhenius plot (In of the heating ratio versus T⁻¹) in Figure 3, the frequency factor (A) provides the measure of frequency in the reaction. The kinetic parameters found for the pink pepper EO was Eₐ = - (2.546 ± 0.033) KJ.mol⁻¹ and the frequency factor was A = (7.931 ± 0.008) . min⁻¹.
In other published studies, some research reports were found on the thermoanalytical characterization of EOs. Chaar et al. (2004) reported that the *Pimenta dioica* L. EO showed a decomposition stage between 198 and 255 °C for tested samples, whose predominant compounds were linalool and eugenol. The vaporization temperature determined by DSC corresponded to approximately 250 °C and the enthalpy variation was approximately \( \Delta H = -25.0 \pm 2.0 \) KJ.Kg\(^{-1}\). Cremasco and Nazareno (2011) characterized the long pepper (*Piper hispidinerviun*) EO and they pointed that the thermogravimetric analysis was extremely useful for the models and descriptions of separation of major components of the EO. However, the authors emphasized that the knowledge of reliable thermodynamic quantities is fundamental, since from these parameters the most appropriate separation technique is selected. In tests carried with long pepper EO in a dry nitrogen atmosphere, the vaporization temperature was 181.9 °C. The average values of molar energy and molar reaction heat of vaporization corresponded, respectively, to \( \Delta E_{vap} = 42.11 \) KJ.mol\(^{-1}\) and \( \Delta H_{vap} = 43.73 \) KJ.mol\(^{-1}\).

**Figure 3** – Arrhenius plot of the pink pepper seeds essential oil.
In northern Brazil, the kinetic parameters of EO extracted from the plant *Siparuna guianensis* Aublet, a species native to the Brazilian Cerrado, were studied by Portella et al. (2014), who performed the DSC/TG analysis with FTIR coupled with 4 cm\(^{-1}\) resolution, in a gas cell with 36 scans per measure, in which each spectrum scan was performed every 30 seconds and the spectra were recorded in the range of 600 to 3800 cm\(^{-1}\). The activation energy \((E_a)\) of the reaction was calculated from the data obtained in the DSC/TG analysis, in which the equation was defined in relation to the sample mass in mg% of the vapor produced by EO, monitored by the TG. The factor that shaped the kinetics of the thermal event was defined using the Arrhenius equation. The results found in this research observed the thermal performance of partial oxidation at 148.3 °C possibly due to oxygenated composition. And the progressive volatilization or therodegradation of the EO peaking at 194.7 °C. The activation energy \((E_a)\) found in the oxidative process corresponded to 43.1 KJ.mol\(^{-1}\) with a pre-exponential factor of 150 s\(^{-1}\). The adjustment for the calculation of the activation energy was found in the range of 115 to 167 °C. It was observed in the experiment that the oxidation effect promoted an increase in mass. Only after completion of the exothermic oxidation reaction, the EO sample return to mass decomposition, reaching 97% of thermal degradation at 400 °C.

Comparing the results found in this study of the pink pepper EO with the works already reported, some observations could be verified. Under conditions of inert atmospheres, that is, analyzing purely the physical-chemical effects of EOs, both the pink pepper EO in this study and the *Pimenta dioica* EO (CHaar et al., 2004) and *Piper hispidinerviun* EO (CREMASCO; NAZARENO, 2011) thermo-degraded into a single stage of decomposition. However, the differential thermal degradation intervals occurred by four main reasons: chemical composition, seasonality or environmental conditions in which the plants were grown and parts of the plants used for the extraction of EOs and the method of
extraction. In the case of the *Siparuna guianensis* EO (PORTELLA et al., 2014) there was an oxidation stage followed a decomposition stage.

The results of this study indicated that the major components (β-pinene, germacrene D, sabinene, and terpinen-4-ol) of the pink pepper seeds EO increased its volatilization potential, leaving it with less thermal stability and resistance to temperature increase.

Another relevant factor that can influence the thermal stability of EOs are the environmental conditions. The pink pepper EO was extracted from the plant grown in Rubiácea, State of São Paulo, a Brazilian city with predominantly tropical climate. The climatic conditions in Rubiácea are different from the climatic conditions of Northeast Brazil, for example, and may influence the metabolisms of the species. Differences in the composition of EOs extracted from plants grown in different regions and using different parts of the plant, such as fruits or seeds, can influence the kinetic degradation of EOs.

As the results of the DSC/TG analyzes of the pink pepper EO showed a thermal stability temperature of 74.8 °C, it was found that a high variation in the enthalpy and activation energy wasn’t necessary in the decomposition and vaporization processes of this EO. The variation of the enthalpy represents the thermal energy necessary for the first order phase transition associated with vaporization to occur, while the activation energy initiates the agitation of the molecules and atoms of the substances in the physical-chemical reactions. Therefore, due to the low temperature resistance of the pink pepper EO, the quantitative value obtained for activation energy to initiate molecular and atomic collisions is justified, in comparison to the other EOs mentioned in this discussion.

### 3 CONCLUSION

The EO extracted from pink pepper seeds in this study showed a diversity of chemical substances in its composition, divided into two large groups,
sesquiterpenes and monoterpenes. However, among the four major compounds that EO, monoterpenes were percentage higher than sesquiterpenes.

The important relationship between the chemical composition of the pink pepper seeds EO and its thermal stability was contacted, so that this OE didn’t require a high variation in enthalpy and activation energy for the beginning of its thermal degradation.

The data presented in the thermogravimetric analysis of pink pepper seeds EO allowed observing important parameters for the definition of industrial processes that can use it as raw material, so that its biological activities can remain stable under controlled temperature conditions and below the thermal range degradation.

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