Journal of Essential Oil Research

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/tjeo20

Drying kinetics of cinnamon (*Cinnamomum zeylanicum* J. Presl) leaves: effects on individual volatile compounds and external color

Juliana Aparecida Celia, Osvaldo Resende, Marcio Carocho, Tiane Finimundy, Kenia Borges de Oliveira, Francileni Pompeu Gomes, Wellytton Darci Quequeto, Lillian Barros & Weder Nunes Ferreira Junior

To cite this article: Juliana Aparecida Celia, Osvaldo Resende, Marcio Carocho, Tiane Finimundy, Kenia Borges de Oliveira, Francileni Pompeu Gomes, Wellytton Darci Quequeto, Lillian Barros & Weder Nunes Ferreira Junior (2023) Drying kinetics of cinnamon (*Cinnamomum zeylanicum* J. Presl) leaves: effects on individual volatile compounds and external color, Journal of Essential Oil Research, 35:2, 117-127, DOI: 10.1080/10412905.2022.2160843

To link to this article: https://doi.org/10.1080/10412905.2022.2160843

JOURNAL OF ESSENTIAL OIL RESEARCH
2023, VOL. 35, NO. 2, 117–127
https://doi.org/10.1080/10412905.2022.2160843

Taylor & Francis
Taylor & Francis Group

Drying kinetics of cinnamon (*Cinnamomum zeylanicum* J. Presl) leaves: effects on individual volatile compounds and external color

Juliana Aparecida Celia[a], Osvaldo Resende[a], Marcio Carocho[b], Tiane Finimundy[b], Kenia Borges de Oliveira[a], Francileni Pompeu Gomes[a], Wellytton Darci Quequeto[a], Lillian Barros[b] and Weder Nunes Ferreira Junior[a]

[a]Federal Institute of Education, Science and Technology Goiano-Campus of Rio Verde, Rio Verde, Goiás, Brazil; [b]Centro de Investigação de Montanha (CIMO), Instituto Politécnico de Bragança, Campus de Santa Apolónia, Bragança, Portugal

ABSTRACT

The post-harvest stage of crops aims to minimize losses occuring during storage and commercialization. Drying process are some of the most used methods to minimize those losses. This work aimed at studying the drying kinetics of cinnamon (Cinnamomum zeylanicum), subject to two different drying conditions, one of which in an experimental fixed-bed dryer relying on an ambient air and speed of 0.5 m s−1, and the other with a forced air circulation oven at different temperatures (313.5, 323.15, 333.15 and 343.15 °K). The time required to reach the moisture equilibrium contents was 1.42, 3.0, 6.41, 14.0 and 21 h for drying temperatures of 343.15, 333.15, 323.15, 313.5 and 307.95 ºK, respectively. The Arrhenius equation described the diffusivity's dependence on temperature, defining the activation energy of 64.77 kJ mol−1. The essential oils of the samples were analyzed through gas chromatography, which identified 23 individual compounds being eugenol the most abundant.

ARTICLE HISTORY
Received 18 January 2022
Accepted 15 December 2022

KEYWORDS
Essential oils; cinnamon; activation energy; mathematical modeling; essential oil

1. Introduction

Cinnamon (*Cinnamomum zeylanicum*) belongs to the Lauraceae family, and its aromas are among the most used in the food, beverage and cosmetic industries worldwide. The vegetative parts of this species have therapeutic properties, including antioxidant, anti-inflammatory, anti-diabetic and antimicrobial. Anticancer properties are also attributed to them, namely due to the presence of active compounds in cinnamon, such as benzaldehyde, cuminaldehyde and terpenes, which have been reported to prevent cancer by influencing various cell signaling pathways, besides reducing cardiovascular diseases. Cinnamon is one of the most popular and oldest spices used as a traditional herb-based medicine, which has recently been gaining interest as an anticancer agent (1).

Medicinal and aromatic plants produce high amounts of bioactive compounds in their normal metabolism as secondary metabolites, being these molecules important in the adaptation of the plant to its surrounding environment, adapting to different stress conditions and fighting off predators and pests. For these reasons, some of these molecules must be volatile, to create an invisible barrier around stems, flowers and fruits, thus protecting the plant. These volatiles are simple molecules but have proven their worth by showing several biological properties (2). There are four biosynthetic classes of volatiles, the terpenoids, fatty acids catabolites, aromatics and amino acids derived volatiles (2).

For cinnamon, the most important element that determines its value is the chemical composition of its essential oil, largely composed of volatile molecules, which are responsible for the aromatic scent and flavour (3). Due to this, cinnamon is used in various products such as tea, vinegar, shampoo, liquid soaps, fragrances, perfumes and many other products that take advantage of its pleasant scent (3). The bioactivities of aromatic molecules can be used for specific purposes when added to food packages, namely, to preserve food by acting as antioxidants and antimicrobials, reducing growth, or even eliminating bacteria, fungi, and yeast. The addition of cinnamon essential oil in food packaging showed good antibacterial activity and antioxidant capacity by effectively inhibiting bacterial growth and lipid oxidation of refrigerated chicken during the storage period (4). Although these compounds have been briefly explored for these purposes, there are still many opportunities and technologies that can be improved to bring them to the front line of the food industry.

To increase the useful life of aromatic and medicinal plants after harvest, it is necessary to perform

CONTACT Marcio Carocho mcarocho@ipb.pt; Lillian Barros lillian@ipb.pt

(a) (b) (c)

Figure 1. Applied Equipment: (a) Metal Layer Dryer with Removable Trays, (b) Oven with Forced Air Circulation, (c) Data Logger.

a drying process, which should occur immediately after harvesting to minimize product loss and decomposition of active ingredients (5). Still, the drying process can destroy some volatile compounds, and thus, it is important to determine quality control measures to understand what compounds can be lost at different temperatures. Studying drying kinetics is very important to obtain the best conditions of the drying process and promote a better product quality. In addition, the fitting of a mathematical model to the drying process allows the best choices and conditions of operation for specific products. While the essential oils of cinnamon have been previously studied (6), to the authors knowledge, this manuscript is the first report of the behavior of those essential oils after different drying temperatures. Thus, the objective of this work was to study the drying kinetics of cinnamon leaves (*Cinnamomum zeylanicum*) under different drying conditions and temperatures, in an experimental fixed bed dryer with ambient air at 307.95 °K and in a forced air circulation oven at temperatures of 313.5, 323.15, 333.15 and 343.15 °K, with subsequent determination of the leaf color, the essential oil yield, as well as the essential oils profile, extracted at different drying temperatures.

2. Materials and methods

The drying was carried out at the Post-Harvest Laboratory of Plant Products of the Federal Institute of Education, Science and Technology of Goiás – Campus of Rio Verde, Goiás, Brazil. Cinnamon leaves (*Cinnamomum zeylanicum*) were collected from a mother tree in the city of Rio Verde – GO, Brazil (17º 47' 23" S – 50º 53' 57" W, altitude of 780 m). The leaves were collected at 7:00 am, placed in polyethylene plastic bags and transported to the laboratory.

2.1. Drying process

The leaves were dried in natural air using a metal layer dryer with an air speed of 0.5 m s^{-1} using removable trays with perforated a bottom (0.28 m × 0.28 m × 0.15 m), which were placed in the drying chamber, allowing the passage of air through the leaf layer.

Cinnamon leaves were wrapped in voile fabric and placed in the trays, approximately 0.025 kg. The ambient air during the drying process had an average temperature of 307.95 ± 1.30 °K and average relative humidity of 33.23 ± 7.05%, recorded by data logger (Figure 1).

Drying was carried out in an oven with forced air circulation (MA-035) with a drying air speed of 1.5 m s^{-1}, and the samples were homogenized and placed in circular, perforated stainless steel trays with a diameter of 0.28 m and height of 0.10 m, each one containing 0.025 kg of sample. The drying conditions in the oven were temperatures that varied between 313.5, 323.15, 333.15 and 343.15 °K, with a relative humidity of 26.11, 12.53, 7.03 and 4.35%, respectively. The temperature and relative humidity of the ambient air were monitored using a data logger, and the relative humidity inside the oven was obtained through the basic principles of psychrometrics, with the help of the GRAPSI computer program.

2.2. Drying kinetics

Moisture contents, before and after drying, were determined through a gravimetric method recommended for forage and leaves, in an oven with forced air circulation at 376.15 ± 1 °K, for 24 hours. The initial moisture content of the leaves was 1.49 d.b. To understand the weight loss, the trays were weighed at different time intervals until a constant weight was measured.

2.2.1. Mathematical modeling

From the drying kinetics experimental data, the values of moisture content ratio were calculated according to Eq. 1.

$$RX = \frac{X^* - X^*_e}{X^*_i - X^*_e} \quad [1]$$

Where:

RX - Moisture content ratio, dimensionless;

$X*$- Moisture content, decimal d.b.;

X^*_i:- Initial moisture, decimal d.b.;

X^*_e:- Equilibrium moisture, decimal d.b.

Table 1 presents the mathematical models used to describe drying kinetics. The models were fitted by non-linear regression analysis using the Gauss-Newton method using Statistica 10.0® software.

All values were represented by mean±SD (standard deviation). The magnitude of the estimated mean error (SE), coefficient of determination (R^2) and relative mean error (P) were the basis for model selection. SE and P for each of the models were calculated according to the following expressions:

$$P = \frac{100}{N} \sum \frac{|Y - \hat{Y}|}{Y} \quad [15]$$

$$SE = \sqrt{\frac{\sum (Y - \hat{Y})^2}{DF}} \quad [16]$$

Where:

Y - Experimental value;

$\hat{Y}$ - Value estimated by the model;

N - Number of experimental observations;

DF - Degrees of freedom of the model (number of experimental observations minus the number of coefficients of the model).

In order to select a single model to describe the drying process under each condition, the models that preliminarily obtained the best fits (according to the criteria R^2, P and SE) were subjected to the selection criteria of Akaike Information (AIC) and Schwarz's Bayesian Information (BIC). (Equation 17)

$$AIC = -2\text{loglike} + 2p \quad [17]$$

Where:

P - Number of parameters; and,

Loglike - Logarithm of the likelihood function considering the estimates of the parameters.

Schwarz stated that the degree of parameterization of the model, its similarity and the lower the BIC value the better the model fits. Its expression is given by:

$$BIC = 2\text{loglike} + p \cdot \ln(n) \quad [18]$$

Where:

n - Number of observations

2.3. Effective diffusivity and activation energy

The effective diffusion coefficient for the drying of cinnamon leaves, under different conditions was calculated using Equation 12, based on the mathematical model of liquid diffusion for the analytical solution of an infinite flat plate, with an eight-term approximation:

$$RX = \frac{X^* - X^*_e}{X^*_i - X^*_e} = \frac{8}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{(2n+1)^2} \exp\left[-\frac{(2n+1)^2 . \pi^2 . D . t.}{4} \cdot \left(\frac{s}{v}\right)^2 \right] \quad [12]$$

Where:

n - Number of terms;

D - Effective diffusion coefficient, $m^2\ s^{-1}$;

t - Drying time, h.

S - Leaf surface area (m^2)

V - Leaf volume (m^3)

Table 1. Mathematical Models Used to Predict the Drying Kinetics of Agricultural Products.

Model designation	Model	Equation number
Two Terms (7)	$Rx = a^{k_o * t} + b^{-k_1 * t}$	[2]
Two-term Exponential (8)	$Rx = a^{-k*t} + (1-a)^{-k*a*t}$	[3]
Logarithmic (9)	$Rx = a^{(-k*t)+c}$	[4]
Midilli (10)	$Rx = a^{(-k*t^{n})} + b * t$	[5]
Newton (11)	$Rx = a^{-k*t}$	[6]
Page (12)	$Rx = a^{-k*}t^{n}$	[7]
Thompson (13)	$Rx = \frac{a^{\left(-a-\left(a^2+4*b*t\right)^{0.5}\right)}}{2*b}$	[8]
Verma (14)	$Rx = a^{(-k*t)} + (1-a)^{(-k_1*t)}$	[9]
Henderson and Pabis (15)	$Rx = a^{(-k*t)}$	[10]
Wang and Sing (16)	$Rx = 1 + a * t + b * t$	[11]

Where: *t* - Drying time; h; k, k_0, k_1 - Drying constants; a, b, c, *t* - Coefficients of the models.

The average volume (v) of cinnamon leaves was calculated using Equation 13. Their average thickness was obtained using a digital Pachymeter, with resolution of 0.01 mm at 3 different points of 30 leaves. The leaf surface area was calculated with the help of the computer program ImageJ.

$$V = \pi \frac{(abc)}{6} \qquad [13]$$

Where,
V - leaf volume, m^3
a - dimension of the longest leaf axis (m);
b - dimension of the intermediate leaf axis (m);
c - dimension of the shortest leaf axis (m).

The Arrhenius equation was used to evaluate the influence of temperature on the effective diffusion coefficient:

$$Df = D_0 \cdot \exp\left(\frac{E_a}{R \cdot T_{abs}}\right) \qquad [14]$$

Where,
Df - Effective diffusion coefficient, $m^2\ s^{-1}$;
D0 - Arrhenius factor for the drying process, $m^2\ s^{-1}$;
Ea - Activation energy, kJ mol^{-1};
R - Universal gas constant (8.314 kJ $kmol^{-1}$ K^{-1});
T_{abs} - Absolute temperature, K^{-1}.

2.4. Color analysis and essential oil yield

Cinnamon leaves were dried to a moisture content of 0.16 d.b. in a fixed-bed dryer at a temperature of 307.95 °K and at varying temperatures between 313.5, 323.15, 333.15 and 343.15 ºK in an oven, with subsequent color analysis. A Hunter Lab colorimeter was used, applying the CIE-L*a*b* (*Commision Internationale L'Eclairage)* system, in which the parameters of lightness (0 black to 100 white), green-redness (-a* green to +a* red) a*, and blue-yellowness (-b* blue to +b* yellow) b*, were obtained.

For the extraction of the essential oil (EO), the material was homogenized and crushed in a blender, totaling 0.03 kg of leaves under each condition. Essential oil extraction was carried out at the Natural Products Laboratory of IF Goiano, Campus of Rio Verde, using a Clevenger apparatus, with hydrodistillation by steam drag, adapted to a flask with a rounded bottom. For every 0.03 kg of dry leaves, 500 mL of distilled water was added, and the extraction lasted 3.5 h for each sample. Dichloromethane was used to extract the essential oil from the aqueous phase by means of a liquid-liquid extraction. Then, three hydrolate washes were performed with three 10 mL portions of dichloromethane. The extracted essential oil was dried with anhydrous sodium sulfate, and protected from light at room temperature for approximately 24 hours to complete evaporation of dichloromethane. Finally, the yield was calculated (%) for each temperature.

The oils were placed under refrigeration in amber glass vials (10 mL) sealed to prevent leaks and exposure to light. The mean values of the results for the 4 drying treatments for the parameters of color and oil yield were evaluated using an analysis of variation (ANOVA) with Tukey being used as a post-hoc test for homoscedastic values and Tahmane T2 for heteroscedastic values using the SPSS program version 26 (IBM, Armonk, NY, USA), all of which with a 5% significance level.

2.5. Essential oil identification and quantification

The essential oil (EO) analysis was performed on a GC-MS Perkin Elmer system with a Clarus® 580 GC and a Clarus® SQ 8 S MS module, equipped with DB-5 MS fused-silica column (30 m × 0.025 mm i.d., film thickness 0.25 µm; J&W Scientific, Inc.) (17). The carrier gas was helium gas adjusted to a linear velocity of 0.3 cm s^{-1}. The oven temperature program was as follows: 313.5 °K for 4 min, raised at 276.15 °k min^{-1} to 448.15 °k, then at 288.15 °K min^{-1} to 573,15 °K and held for 10 min. The injector temperature was set at 533.15 °K, with a transfer line at 553.15 °K and an ion source at 493.15 °K. The ionization energy was 70 eV and a scan range of 35–500 µ with a scan time of 0.3 s was used. For each essential oil, 1 µL of sample diluted in HPLC grade *n*-hexane (1:100) was injected with a split ratio of 1:3. Identification of components was assigned by matching their mass spectra with NIST17 data and by determining the linear retention index (LRI) based on the retention times obtained for a mixture of *n*-alkanes (C8–C40, Supelco) analyzed under identical conditions. Comparisons were also performed with published data and with commercial standard compounds, when possible. Quantification was performed using the relative peak area values obtained directly from the total ion current values and the results were expressed as the relative percentage (%) of total volatiles. For the GC analysis of the essential oils, the results were analysed using the same statistical protocols as detailed in the previous section (18)**.

3. Results and discussion

Regarding the cinnamon modeling, in terms of the moisture content ratio, there was an increase in drying time as the drying temperature decreased (Figure 2),

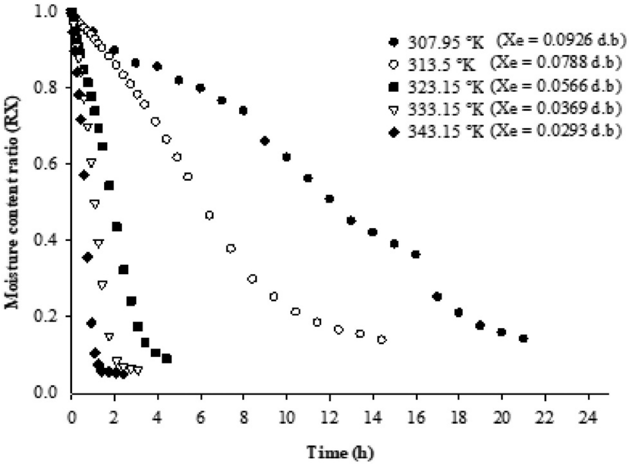

Figure 2. Drying Kinetics of Cinnamon Leaves at Temperatures of 307.95 °K (Natural Air in Fixed-Bed Dryer) and 313.5, 323.15, 333.15 and 343.15 °K (Forced Air Circulation Oven). Temperatures (307.95 °K – 34.8 °C, 313.5 °K – 40.35 °C, 323.15 °K – 50 °C, 333.15 °K – 60 °C, 343.15–70 °C).

which was in line with several findings by other researchers (19) when performing Drying kinetics of blackberry leaves, at temperatures of 307.95, 313.5, 323.15, 333.15 and 343.15 °K. (Figure 2).

The drying time for each temperature was 21, 14.41, 6.41, 2.75 minutes and 1.42 hours for the temperatures of 307.95, 313.5, 323.15, 333.15 and 343.15 °K respectively, with a final equilibrium moisture content of 0.0926, 0.0788, 0.0566, 0.0369 and 0.0293 d.b. The higher the drying temperature, the lower the equilibrium moisture content.

Table 2 presents the parameters used to help choose the best model that describes the process of drying kinetics of cinnamon leaves.

The used models estimated mean values (SE) close to zero, which represents a good model fit. Regarding the relative mean error (P), only the Logarithmic [4], Midilli [5] and Wang and Singh [11] models showed values below 10% for all drying conditions (Table 2). According to (20), this is a condition that determines a good fit for the drying conditions. At all temperatures used during the drying of cinnamon leaves, only the Verma model had a low coefficient of determination (64.77%), while the others showed coefficients of determination higher than 96.50%, which is a quite satisfactory for the drying process.

The models that stood out were subject to the Akaike Information Criterion (AIC) and Schwarz's Bayesian Information Criterion (BIC) in order to choose the best model to predict the drying curve of cinnamon leaves under different conditions (Table 3). According to Gomes et al (21), the lowest values for these criteria indicate the best fit of the model to the experimental data of drying kinetics.

Table 2. Values of the Estimated Mean Error (SE), Mean Relative Error (P) and Coefficient of Determination (R^2) for the ten Models Analyzed in the Drying of Cinnamon Leaves.

	307.95 °K (34.8 °C)			313.5 °K (40.35 °C)			323.15 °K (50 °C)			333.15 °K (60 °C)			343.15 °K (70 °C)		
Model	SE	P	R^2	SE	P	R^2	SE	P	R^2	SE	P	R^2	SE	P	R^2
2	0.042	12.28	98.120	0.014	5.37	99.820	0.035	11.86	98.820	0.014	7.36	99.850	0.069	26.39	97.030
3	0.052	20.35	96.730	0.039	17.69	98.430	0.033	12.13	98.780	0.056	29.73	97.270	0.049	9.05	99.920
4	0.028	6.11	99.070	0.014	6.09	99.800	0.012	2.30	99.850	0.014	7.79	99.840	0.009	3.29	99.930
5	0.025	6.95	99.310	0.009	3.30	99.700	0.009	2.79	99.930	0.013	5.75	99.880	0.011	3.58	99.920
6	0.050	20.35	96.730	0.039	17.69	98.430	0.032	12.13	98.780	0.039	29.73	99.960	0.059	28.74	96.500
7	0.045	13.49	97.570	0.020	7.02	99.590	0.028	8.99	99.160	0.025	11.88	99.430	0.032	12.84	99.080
8	0.052	20.36	96.730	0.039	17.69	98.430	0.033	12.14	98.780	0.056	29.73	97.260	0.063	28.74	96.500
9	0.053	19.56	96.790	0.333	83.01	64.770	0.013	3.39	99.820	0.014	7.64	99.840	0.056	9.12	97.220
10	0.052	19.94	96.760	0.0373	16.24	98.620	0.033	11.86	98.820	0.049	25.96	97.870	0.059	26.39	97.030
11	0.034	6.99	98.60	0.0090	2.67	99.920	0.019	3.77	99.580	0.010	5.33	99.910	0.009	2.70	99.920

Table 3. Values of Akaike Information Criterion (AIC) and Schwarz's Bayesian Information Criterion (BIC) for the Models Fitted to the Drying Kinetics of Cinnamon Leaves, at Temperatures of 307.95, 313.5, 323.15, 333.15 and 343.15 °K.

	307.95 °K (34.8 °C)	
Model	AIC	BIC
Logarithmic [4]	−70.8886	−68.0639
Midilli [5]	−72.2310	−68.6695
Wang and Singh [11]	−66.8940	−64.2229
313.5 °K (40.35 °C)		
Logarithmic [4]	−140.2800	−135.2476
Midilli [5]	−172.5772	−166.2868
Wang and Singh [11]	−165.9657	−162.1915
323.15 °K (50 °C)		
Logarithmic [4]	−90.8830	−87.7926
Midilli [5]	−100.7717	−96.9087
Wang and Singh [11]	76.3516	−74.0338
333.15 °K (60 °C)		
Logarithmic [4]	−68.8775	−66.6177
Midilli [5]	−78.8486	−77.1537
Wang and Singh [11]	−70.9005	−68.0757
343.15 °K 343.15 °K (70 °C)		
Logarithmic [4]	−28.1684	−26.2288
Midilli [5]	−46.4812	−44.0566
Wang and Singh [11]	−28.2311	−26.7763

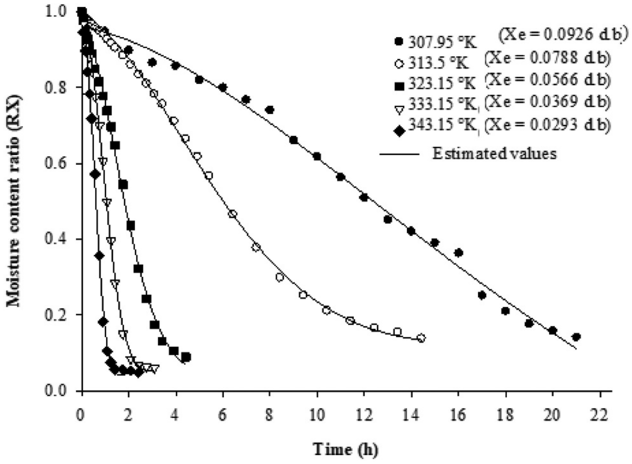

Figure 3. Data Observed Experimentally and Estimated by the Midilli Model to Describe the Drying Curves of Cinnamon Leaves for Different Temperatures. Temperatures (307.95 °K – 34.8 °C, 313.5 °K – 40.35 °C, 323.15 °K – 50 °C, 333.15 °K – 60 °C, 343.15– 70 °C).

The Midilli model had lower values of both AIC and BIC for the drying conditions evaluated (Table 3) and was therefore selected to represent the drying of cinnamon leaves. Other authors have recommended the Midilli model to estimate leaf drying kinetics due to its good fit to the experimental data, namely: Mujaffar and John (22), when performing drying West Indian lemongrass leaves (*Cymbopogan citratus*) between twenty-two empirical and semi-empirical thin layer models found the Midilli model as the most suitable for describing the behavior of drying. Martinazzo et al (23), reporting for *Cymbopogon citratus* leaves at temperatures between 303.15 and 333.15 °K. The Midilli model best fits the experimental data due the fact that plants tend to lose higher volumes of water in a first stage resulting in a sharp decrease of the curve that is positively correlated with this model, visible in Figure 3. Furthermore, it is also possible to infer the overlap of the estimated values of the model and the ones observed from the drying.

The parameter 'k' increases with the elevation of drying air temperature (Table 4), which reflects the effect of external conditions, since this parameter is a drying constant (equation [15]). Conversely, the parameters 'a', 'b', and 'n' did not show a defined trend. This behavior corroborates the results obtained by Dorneles et al (5), when studying the effect of air temperature and speed on the drying kinetics and composition of essential oil of *Piper umbellatum* leaves.

As shown in Table 4, the values of diffusivity increased with the elevation of drying temperature, corroborating the results obtained by Gomes et al (21). These showed magnitudes from 0.121 to 1.435 × 10^{-11} m^2 s^{-1} for the temperature ranging from 307.95 to 343.15 °K. These values are consistent with those reported by Madamba et al (24), in the order of 10^{-9} to 10^{-11} m^2 s^{-1}, quite similar to the ones reported herein. Martins et al (25), when determining the effective diffusion coefficient of blackberry leaves (*Morus nigra* L.), found values from 0.7038 to 6.6212 × 10^{-11} for temperatures ranging from 313.5 to 343.15 °K. The different values of diffusivity can be justified by the specific characteristics of each sample.

Table 4. Parameters of the Midilli Model and Diffusion Coefficient of the Drying of Cinnamon Leaves at Different Temperatures.

	Parameters				
Temperature °K	a	b	n	k	Def. x10^{-11} m^2s^{-1}
307.95	0.9992	0.0376	0.1027	0.103	0.121
313.5	0.9738	−0.0065	0.1297	0.129	0.212
323.15	1.0012	−0.1029	0.4541	0.454	0.719
333.15	0.9885	−0.0838	0.9068	0.907	1.229
343.15	0.9969	−0.3573	1.0478	1.048	1.435

Def. – Diffusivity.

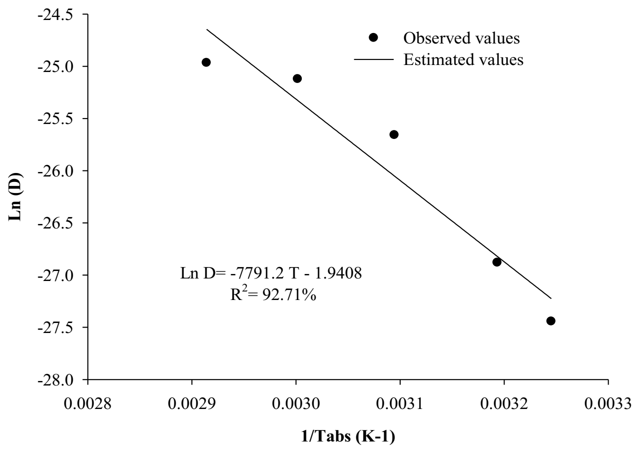

Figure 4. Arrhenius Representation for the Effective Diffusion Coefficient, as a Function of Air Temperature, During the Drying of the Cinnamon Leaves.

Figure 4 depicts the Arrhenius equation that describes the dependence of effective diffusivity on the temperature of the drying air.

The activation energy (Ea) for the water diffusion during the drying cinnamon leaves drying was 64.77 kJ mol^{-1}, and this value is close to those reported by Martins et al (25), while drying *Morus nigra* L. leaves (65.94 and 66.08 kJ mol^{-1}).

Regarding the cinnamon leaves, the fresh samples were darker, while those subject to temperatures of 307.95 and 313.5 °K tended to become paler (Table 5), as chlorophyll pigments were degraded at low temperature, causing a loss of the darker hue. In general, at the highest temperatures the leaves tended to black with the reduction of the L* coordinate, caused by the rapid degradation of chlorophyll due to high temperature, differing from the degradation at low temperature, at which the leaves tended to white.

The values of the coordinate a* increase with the increment in temperature, ranging from green (-a*) to red (+a*), indicating loss of the initial characteristic color, and exhibits tendency to reddening, evidenced by the positive values at the two highest temperatures (Table 5). Lima-Corrêa et al (26). studying the drying of basil (*Ocimum basilicum* L.) leaves, observed that the values of the coordinate a* increase with the increase in temperature. With the increase in drying temperature, green pigmentation decreases due to chlorophyll degradation caused by the high temperatures, and the color tends to red, which was observed at temperatures of 333.15 and 343.15 °K (Table 5).

For the parameter b* (-b* blue to +b* yellow), the leaves tend to yellow (+b*), both in the fresh state and when they are subjected to drying. The values of the coordinate b* increased with increasing drying temperatures, while the fresh leaf had lower magnitude, which is due to the reduction of chlorophyll contents, resulting in yellowish colors due to the presence of other pigments. This result differs from that obtained by Téllez et al (27), who studied the color of stevia (*Stevia rebaudiana*Bertoni) leaves and found reduction in the values of the coordinate 'b', after the drying process, at temperatures of 318,15 and 328,15 °K.

Cinnamon leaves subjected to the extraction of essential oils showed difference between drying temperatures. Fresh leaves had an oil content of 0.35%, while leaves subjected to drying at ambient temperature (307.95 °K) showed no oil yield, possibly due to the drying time of approximately 21 hours, which may have influenced the loss of volatile compounds. The temperature of 313.5 °K led to a content of 0.70%, while the temperature of 323.15 °K promoted higher essential oil yield, with a value of 1.23%. From the temperature of 323.15 °K, the yield of essential oil dropped. Drying air temperature values above 323.15 ° K may have caused damage to the essential oil secreting and storing structures of the dry product.

Dorneles (5), when analyzing the essential oil yield of *Piper umbellatum* L. leaves at temperatures of 313.5, 323.15, 333.15 and 343.15 °K, identified that the best yield was obtained at 313.5 °K. Wang et al (28), when studying the influence of drying temperature on the yield and chemical composition of *Cymbopogon*

Table 5. Values of the Color Coordinates L*, A* and B* and Essential Oil Yield of Cinnamon Leaves in Fresh State and at Temperatures of 307.95, 313.5, 323.15, 333.15 and 343.15 °K.

Temperatures and fresh state	L*	a*	b*	Yield %
Fresh	27.83 c	−6.08 d	11.31 b	0.35 d
307.95	49.47 a	−1.91 dc	17.04 a	-
313.5	47.28 a	−4.47 cb	17.26 a	0.70 b
323.15	38.97 b	−1.24 cb	14.83 a	1.23 a
333.15	40.30 b	1.37 ba	16.67 a	0.52 c
343.15	39.04 b	3.12 a	17.83 a	0.23 e

Equal letters in columns do not differ by Tukey test at 5% significance level. Lightness (0 black to 100 white), a* (-a* green to +a* red), b* (-b* blue to +b* yellow).

Table 6. Individual Essential Oils Detected Through GC for Each of the Drying Conditions and with No Drying Treatment, Expressed in Relative Percentage.

			Cinnamon Oil relative %$^{¥}$				
Compound	LRI*	LRI§	*In natura*	313.5 °K (40.35 °C)	323.15 °K (50 °C)	333.15 °K (60 °C)	343.15 °K (70 °C)
α-pinene	939	932	tr.	tr.	0.023±0.002	tr.	tr.
Camphene	954	946	n.d.	tr.	0.017±0.002	n.d.	n.d.
Benzaldeyde	966	952	0.02±0.01^{a}	tr.	tr.	0.017±0.001^{a}	0.018±0.001^{a}
o-cymene	1029	1022	n.d.	tr.	tr.	n.d.	0.025±0.002
β-phellandrene	1036	1031	tr.	0.014±0.001^{a}	0.027±0.002^{b}	tr.	tr.
Benzyl alcohol	1040	1031	0.059±0.002^{d}	0.013±0.001^{a}	0.05±0.001^{c}	0.036±0.001^{b}	0.0513±0.003^{c}
β-linalool	1111	1095	0.14±0.01^{b}	0.111±0.001^{a}	0.15±0.01^{b}	0.11±0.01^{a}	0.10±0.01^{a}
Hydrocinnamaldehyde	1167	1162	0.0191±0.001^{a}	tr.	0.023±0.002^{d}	0.015±0.001^{c}	0.011±0.004^{b}
Borneol	1176	1165	0.02±0.002^{c}	0.011±0.001^{a}	0.0313±0.002^{d}	0.018±0.001$^{b, c}$	0.017±0.001^{b}
α-terpineol	1199	1186	0.011±0.001^{a}	tr.	0.012±0.001^{a}	tr.	tr.
Cinnamaldehyde	1222	1227	0.031±0.002^{a}	tr.	0.018±0.001^{c}	0.013±0.001^{b}	0.0147±0.001^{b}
Hydrocinnamyl alcohol	1237	1224	tr.	n.d.	n.d.	n.d.	n.d.
trans-cinnamaldehyde	1283	1267	4.8±0.2^{d}	0.34±0.01^{a}	0.55±0.02^{b}	0.4±0.02^{a}	0.84±0.03^{c}
trans-cinnamyl alcohol	1322	1303	0.037±0.004^{b}	0.0152±0.001^{a}	0.014±0.001^{a}	tr.	n.d.
Eugenol	1368	1356	93.8±0.1^{b}	83.4±0.3^{a}	98.22±0.03^{c}	98.75±0.02^{b}	98.12±0.02^{c}
Hydrocinnamyl acetate	1377	1366	0.26±0.02^{c}	0.28±0.01^{c}	0.19±0.01^{b}	0.14±0.01^{a}	0.509±0.001^{d}
α-copaene	1381	1374	0.29±0.02^{b}	15.5±0.3^{c}	0.18±0.02$^{a, b}$	0.1932±0.003$^{a, b}$	tr.
β-caryophyllene	1422	1417	0.07±0.01^{b}	0.039±0.003^{a}	0.081±0.002^{c}	0.043±0.003^{a}	tr.
trans-cinnamyl acetate	1453	1443	0.19±0.02^{c}	0.067±0.002^{a}	0.2±0.005^{c}	0.16±0.01^{b}	0.1797±0.005^{b}
Humulene	1456	1454	tr.	tr.	0.071±0.001	tr.	n.d.
Spathulenol	1575	1577	0.011±0.001^{b}	tr.	tr.	0.01±0.001^{a}	tr.
Caryophyllene oxide	1580	1582	0.027±0.002^{c}	tr.	0.027±0.002^{c}	0.0121±0.001^{a}	0.02±0.002^{b}
Benzyl benzoate	1761	1759	0.19±0.01^{c}	0.049±0.003^{a}	0.0813±0.001^{b}	0.049±0.004^{a}	0.0577±0.002^{a}
Monoterpene hydrocarbons			0.22±0.02^{d}	0.032±0.002^{b}	0.07±0.01^{c}	0.0156±0.0003^{a}	0.042±0.003^{b}
Oxygen-containing monoterpenes			93.8±0.1^{b}	83.6±0.3^{a}	98.41±0.04^{c}	98.89±0.03^{d}	98.25±0.03^{c}
Sesquiterpene hydrocarbons			0.4±0.03^{a}	15.6±0.3^{a}	0.358±0.02^{a}	0.25±0.01^{a}	0.026±0.002^{a}
Oxygen-containing sesquiterpenes			0.011±0.001^{a}	tr.	tr.	0.01±0.001^{a}	tr.
Others			5.5±0.2^{d}	0.79±0.03^{a}	1.15±0.04^{b}	0.832±0.05^{a}	1.68±0.04^{c}

*LRI, linear retention index determined on a DB-5 MS fused silica column relative to a series of *n*-alkanes (C8–C40). § linear retention index reported in the literature (29). ¥ relative % is given as mean ±SD, *n*=3. In each row, different letters mean significant statistical differences. n.d. - not detected; tr. – trace amounts.

winterianus black cardamom (Amomum tsao-ko) essential oil, found better yield at 328,15 °K and observed marked quantitative variation in the chemical composition of the essential oil as a function of the different temperatures tested (298.15, 313.15, 343.15, 358,15 and 363,15 °K). Therefore, it can be verified that, for each type of plant, there is an ideal temperature for the best yield of essential oil. The definition of drying methodologies for each species is necessary, to ensure the levels of active substances.

The treatment subjected to temperature of 343.15 °K had lower essential oil yield, followed by the fresh leaves (Table 5). Lower yield is a consequence of damage caused the high temperature. The low oil yield of fresh leaves is explained by their high moisture content, which caused agglutination of the oil, preventing the vapor from penetrating more evenly in the plant tissues, which makes it difficult to extract the essential oil.

Table 6 shows the individual essential oils detected in each sample, obtained through GC, as well as the groups of essential oils, namely the monoterpene hydrocarbons, oxygen-containing monoterpenes, sesquiterpene hydrocarbons and the oxygen containing sesquiterpenes. 23 individual compounds were detected, being eugenol by far the most abundant essential oil. Eugenol varied between 83% for the cinnamon dried at 313.5 °K and 98% for temperatures of 323.15 and 333.15 °K, showing that these drying temperatures benefit the extractability of this volatile, known to be the most abundant compounds in clove and cinnamon (30). All other aromatic compounds were detected in values under 1% independently of the drying temperature, except for *trans*-cinnamaldehyde, found at 4% in non-dried cinnamon, showing a high degradation of this compound even at low drying temperatures of 313.5 °K. Overall, it seems that drying temperatures of 313.5 °K seemed to reduce the production of the essential oils, due to being the temperature were most of the individual compounds showed lower percentages, being higher without any drying and when drying was used at higher temperatures. Interestingly, temperatures above 323.15 °K only showed higher percentages for hydroxycinnamaldehyde (333.15 °K) and hydoxinnamyl acetate (343.15 °K), with the highest percentages of compounds being higher either without any drying or dried at 323.15 °K. These results are quite interesting and show that drying kinetics are important to understand the threshold of temperatures that can help achieve higher yields of volatiles or destroy them. In this case, it could be concluded that drying at 323.15 °K helps achieve higher yields of more individual compounds than no drying at all or drying at higher or lower temperatures. Hydroxycinammyl alcohol was the only compound that was only detected in natural, without any drying, apparently being destroyed by even the lowest drying temperature. Compounds like camphene, *trans*-cinnamyl alcohol and humulene were destroyed by the drying temperature of 343.15 °K. Considering the groups of compounds, the most abundant were the oxygen-containing monoterpenes, mainly due to the amounts of eugenol, although the highest yield was found at a drying temperature of cinnamon of 323.15 °K. Sesquiterpene hydrocarbons were the second most abundant group, especially due to the high percentage of α-copaene, detected at 15.6% in cinnamon dried at 313.5 °K. Oxygen-containing sesquiterpenes was the group detected in lower amounts with no statistically significant difference among the samples The group that joins all other volatiles was the one with the third highest percentage, averaging from 0.79 to 5.5%, in which the samples without any drying temperature showed the highest yields.

Limitations:

4. Conclusion

The higher the temperature, the shorter the time for drying cinnamon leaves. Among the models that did fit the values, Midilli was the one that showed the best results. Leaves subjected to drying temperatures above 323.15 °K showed loss of green color and tendency to yellowing, due to chlorophyll degradation. The best essential oil yield was obtained from leaves subjected to drying temperature of 323.15 °K in an oven, hence being the best condition for drying cinnamon leaves. Furthermore, this temperature was the one that showed the highest amount of individual essential oils, showing the importance of these treatments to determine the optimal conditions to obtain the highest yields of volatiles. It was found that the drying temperature applied to cinnamon leaves showed direct interference in the essential oil molecules, which can be eliminated, reduced or increased, depending on the drying temperature. This could have implications in the optimization of increasing yields of specific compounds for several industries.

Nomenclature

±	approximate
a, b, c, n	Coefficients of the models
d.b.	dry base
°	degree
D	Effective diffusion coefficient
Df	Effective diffusion coefficient
D0	Arrhenius factor for the drying process
DF	Degrees of freedom of the model
Ea	Activation energy
HPLC	High Performance Liquid Chromatography
h	Drying constants
k, k_0,k_1	Drying constants
°K	degrees kelvin
kJ/mol	kilojoule per mole
kg	kilogram
$m\ s^{-1}$	meter per second
m	meter
’	minutes
m^2	square meter
m^3	cubic meter
n	Number of terms;
N	Number of experimental observations
P	relative mean error
%	percent
RX	Moisture content ratio
R	Universal gas constant (8.314 kJ $kmol^{-1}$ K^{-1})
R^2	coefficient of determination
S	Leaf surface area
SD	standard deviation
SE	estimated mean error
”	seconds
s	south
t	Drying time
T_{abs}	Absolute temperature
V	Leaf volume
X^*	Moisture content, decimal
X^*_i	Initial moisture, decimal
X^*_e	Equilibrium moisture
w	west
Y	Experimental value
$\hat{Y}$	Value estimated by the model
π	3,141592

Disclosure statement

No potential conflict of interest was reported by the authors.

Funding

The authors are also grateful to the Foundation for Science and Technology (FCT, Portugal) for financial support through national funds FCT/MCTES to CIMO (UIDB/00690/2020). L. Barros thanks FCT, P.I., through the institutional scientific employment program-contract while M. Carocho thanks FCT for the individual scientific employment program-contract CEECIND/00831/2018. To IF Goiano, CAPES, FAPEG, FINEP and CNPq for the indispensable financial support to conduct the study.

ORCID

Marcio Carocho http://orcid.org/0000-0002-8978-4547

Wellytton Darci Quequeto http://orcid.org/0000-0002-0658-2692
Lillian Barros http://orcid.org/0000-0002-9050-5189
Weder Nunes Ferreira Junior http://orcid.org/0000-0002-2931-9352

References

1. M. Saki, S.S. Mohammadi, E.A. Montazeri, A. Siahpoosh, M. Moosavian and S.M. Latifi, In vitro antibacterial properties of *Cinnamomum zeylanicum* essential oil against clinical extensively drug-resistant bacteria. European Journal of Internal Medicine, **37**, 1–6 (2020). 10.1016/j.eujim.2020.101146
2. S. Zielińska and A. Matkowski, Phytochemistry and bioactivity of aromatic and medicinal plants from the genus Agastache (Lamiaceae). Phytochemistry Reviews : Proceedings of the Phytochemical Society of Europe, **13** (2), 391–416 (2014). 10.1007/s11101-014-9349-1
3. C.Y. Lin, T.F. Yeh, S.S. Cheng and S.T. Chang, Complementary relationship between trans-cinnamaldehyde and trans-cinnamyl acetate and their seasonal variations in Cinnamomum osmophloeum ct. cinnamaldehyde. Industrial Crops and Products, **127**, 172–178 (2019). 10.1016/j.indcrop.2018.10.074
4. L. Zhou, J. Fu, L. Bian, T. Chang and C. Zhang, International Journal of Biological Macromolecules, **212**, 211–219 (2022). 10.1016/j.ijbiomac.2022.05.137
5. L.N.S. Dorneles, A.L.D. Goneli, C.A.L. Cardoso, C. B. Silva, M.R. Hauth, G.C. Oba and V. Schoeninger. Effect of air temperature and velocity on drying kinetics and essential oil composition of Piper umbellatum L. leaves, Industrial Crops and Products, **142**, 2–8 (2019).
6. S. El Amrani, A.E.O. Lalami, Y. Ez Zoubi, K. Moukhafi, R. Bouslamti and S. Lairini, Evaluation of antibacterial and antioxidant effects of cinnamon and clove essential oils from Madagascar. Materials Today: Proceedings, **13**, 762–770 (2019). 10.1016/j.matpr.2019.04.038
7. S.M. Henderson, Progress in Developing the Thin Layer Drying Equation. Transactions American Society of Agricultural, **176**, 1167–1168 (1974). doi: 10.13031/2013.37052.
8. Y.I. Sharaf-Eldeen, J.L. Blaisdell and M.Y. Hamdy, A model for ear corn drying. Transactions of the American Society of Agricultural Engineers?, **23**(5), 1261–1265 (1984). 10.13031/2013.34757
9. T.I. Togrul and D. Pehlivan, Modeling of drying kinetics of single apricot. Journal Food Engineering, **m58**, 23–32 (2003). 10.1016/S0260-8774(02)00329-1
10. A. Midilli, H. Kucuk and Z.A. Yapar, A new model for single-layer drying. Drying Technology, **20**(7), 1503–1513 (2002). 10.1081/DRT-120005864
11. W.K. Lewis, The rate of drying of solid materials. Industrial & Engineering Chemistry Research, **13**, 427–433 (1921). 10.1021/ie50137a021
12. I. Doymaz, *The kinetics of forced convective air-drying of pumpkin slices*. Journal of food engineering, **79**, 243–248 (2007). 10.1016/j.jfoodeng.2006.01.049
13. T.L. Thompson, R.M. Peart and G.H. Foster, Mathematical simulation of corn drying?a new model. Transactions of the American Society of Agricultural Biological Engineers?, **11**, 582–586 (1968). 10.13031/2013.39473
14. L.R. Verma, R.A. Bucklin, J.B. Endan and F.T. Wratten, Effects of drying air parameters on rice drying models. Transactions of the American Society of Agricultural Biological Engineers?, **28**, 296–301 (1985). 10.13031/2013.32245
15. S.M. Henderson and S. Pabis, Grain Drying Theory I. Temperature Effects on Drying Coefficient, Journal of agricultural engineering research, **6**, 169–174, (1961).
16. C.Y. Wang and R.P. Singh, Use of variable equilibrium moisture content in modeling rice drying. Transactions of the American Society of Agricultural Biological Engineers?, **11**, 668–672 (1978).
17. S. Falcão, I. Bacém, G. Igrejas, P.J. Rodrigues, M. Vilas-Boas and J.S. Amaral, Chemical composition and antimicrobial activity of hydrodistilled oil from juniper berries. Industrial Crops and Products, **124**, 878–884 (2018). 10.1016/j.indcrop.2018.08.069
18. H. Akaike, A new look at the statistical model identification. IEEE Transactions on Automatic Control, **19**, 716–723 (1974). 10.1109/TAC.1974.1100705
19. L. Ye, H.S. El-Mesery, M.M. Ashfaq, Y. Shi, H. Zicheng and W.G.H. Alshaer, Analysis of energy and specific energy requirements in various drying process of mint leaves, Case Studies in Thermal Engineneerings, **26**, 1–13 (2021).
20. D. Mohapatra and P.S. Rao, A thin layer drying model of parboiled wheat. Journal of food engineering, **66**, 513–518 (2005). 10.1016/j.jfoodeng.2004.04.023
21. F.P. Gomes, O. Resende, E.P. Sousa, D.E.C. Oliveira and F.R.A. Neto, Drying kinetics of crushed mass of 'jambu': Effective diffusivity and activation energy. Revista Brasileira de Engenharia Agrícola e Ambiental (in Portuguese), **22**, 499–505 (2018). 10.1590/1807-1929/agriambi.v22n7p499-505
22. S. Mujaffar and S. John, Food Science and Nutrition, **6**, 1085–1099(2018). 10.1002/fsn3.642
23. A.P. Martinazzo, P.C. Corrêa, O. Resende and E. C. Melo, Análise e descrição matemática da cinética de secagem de folhas de capim-limão. Revista Brasileira de Engenharia Agrícola e Ambiental, **11**, 301–306 (2007). 10.1590/S1415-43662007000300009
24. P.S. Madamba, R.H. Driscoll and K.A. Buckle, The thin-layer drying characteristics of garlic slices. Journal of food engineering, **29**, 75–97 (1996). 10.1016/0260-8774(95)00062-3
25. E.A.S. Martins, A.L. Goneli, A.A. Gonçalves, C.P. F. Hartmann and V.C.O.B.A.G.C. Siqueira, Drying kinetics of blackberry leaves. Revista Brasileira de Engenharia Agrícola e Ambiental, **22**, 570–576 (2018). 10.1590/1807-1929/agriambi.v22n8p570-576
26. R.A.B. Lima-Corrêa, M.S. Andrade, M.F.G.F. Silva, J. T. Freire and M.C. Ferreira, Thin-layer and vibrofluidized drying of basil leaves (Ocimum basilicum L.): analysis of drying homogeneity and influence of drying conditions on the composition of essential oil and leaf colour. Journal of Applied Research on Medicinal and Aromatic Plants, **7**, 54–63 (2017). 10.1016/j.jarmap.2017.05.001
27. M.C. Téllez, I.P. Figuero, B.C. Téllez, E.C.L. Vidaña and A. L. Ortiz, Solar drying of Stevia (Rebaudiana Bertoni)

leaves using direct and indirect technologies. *Solar Energy*ar Energy, **159**, 898–907 (2018). 10.1016/j.solener.2017.11.031

28. J. Wang, Y. Li, Q. Lu, Q. Hu, P. Liu, Y. Yang, G. Li, H. Xie and H. Tang, Drying temperature affects essential oil yield and composition of black cardamom (Amomum tsao-ko). Industrial crops and products, **168**, 1–9 (2021). 10.1016/j.indcrop.2021.113580
29. A. Plata-Rueda, J.M. Campos, G.S. Rolim, L. C. Martínez, M.H. Santos, F.L. Fernandes, J.E. Serrão and J.C. Zanuncio, Terpenoid constituents of cinnamon and clove essential oils cause toxic effects and behavior repellency response on granary weevil, Sitophilus granarius. Ecotoxicology and Environmental Safety, **156**, 263–270 (2018). 10.1016/j.ecoenv.2018.03.033
30. D.F. Cortés-Rojas, C.R.F. Souza and W.P. Oliveira, Clove (Syzygium aromaticum):a precious spice. Asian pacific journal of tropical biomedicine, **4**, 90–96 (2014). 10.1016/S2221-1691(14)60215-X