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The influence of the storage temperature on the stability of lipid microparticles containing ginger oleoresin

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ABSTRACT

Ginger oleoresin (GO) can be encapsulated within a protective lipid matrix in order to facilitate handling, provide protection against the external environment or promote the stability of GO compounds. The aim of this study was to verify the ability of solid lipid microparticles (SLMs) containing GO (10–20% w/w) to maintain or improve the stability of ginger compounds, by monitoring SLMs' characteristics during storage at different temperatures (25 and 40 °C). The lipids matrix of SLMs were composed by stearic acid (90, 80, 75, 65% w/w) and oleic acid (15% w/w), The crystalline structure of the particles after 84 days of storage did not present any polymorphic alterations, while presenting spherical form upon scanning by electron microscopy. SLMs containing oleic acid showed degradation of 6-gingerol when stored at 40 °C. Major volatile compounds had better stability in particles containing oleic acid. Kinetics of volatiles release resulted in a diffusion mechanism. SLMs showed better stability of GO compounds during storage at 25 °C than un-encapsulated GO and could, therefore, improve its distribution in foods due to its conversion to powder.

1. Introduction

Ginger (*Zingiber officinale* Roscoe) is a rhizome and one of the most commonly used species of the family Zingiberaceae. It is grown in some tropical regions, such as India, China, Nigeria, Australia and Jamaica. It is used throughout the world as a spice, conferring specific flavor and odor, besides having several potential pharmacological effects, including cardiovascular protection, antioxidant potential, anti-inflammatory and anti-glycemic activities among others. The pungent compounds (gingerols and shogaols) and volatile constituents (sesquiterpenes and monoterpenes) contribute to show new perspectives on health improvement (Butt & Sultan, 2011; Said, Arya, Pradhan, Singh, & Rai, 2015; Srinivasan, 2017).

The use of spice oleoresins in the food industry has increased significantly, especially for facilitating the flavor standardization, in addition to its absence of microbiological contamination compared to the fresh spice. They are considered a GRAS (Generally Recognized As Safe) food and, because this ingredient is present in a concentrated form, storage space is reduced and only a small amount is required in formulations (Bailey-Shaw et al., 2008; Balakrishnan, 2005; Murthy, Gautam, & Naik, 2015).

Ginger oleoresin is a viscous product containing both volatile and non-volatile compounds. It is composed, in the majority, by pungent compounds, volatile oil and lipids, while other compounds are present in lower concentrations. Volatiles in the ginger essential oil can be added to the oleoresin to provide odor and taste characteristics similar to those of the fresh product (Said et al., 2015; Zachariah, 2008).

The ginger pungency is mainly due to the non-volatile compounds. The major pungent compounds of ginger oleoresin are gingerols and shogaols, which are responsible for its characteristic taste. The 6-gingerol, the most abundant compound in ginger oleoresin, can be converted into 6-shogaol, a dehydrated compound, upon heating or storage and to zingerone via condensation. The increase in concentration of these compounds can lead to a loss of ginger oleoresin quality (Bailey-Shaw et al., 2008; Gopi, Varma, & Jude, 2016; Huang, Chung, Wang, Law, & Chen, 2011). The predominant volatile compounds in ginger oleoresin are the sesquiterpenes α-zingiberene, β-sesquiphellandrene and ar-curcumene. These compounds, under inadequate storage, such as excessive light and heat, convert to ar-curcumene and, with their accumulation, a consequent loss of quality of the volatile oil occurs (Vernin & Parkanyl, 2005; Zachariah, 2008).

Flavor encapsulation is a common way to improve the performance

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and stability of compounds. In general, encapsulation provides protection for flavors by reducing losses and increasing the overall quality, by preventing their degradation or slowing their volatilization. Additionally, encapsulation provides a means for controlled release, as well as conversion of a liquid or viscous flavor into a solid powder. The use of spray chilling techniques for the formation of solid lipid microparticles (SLMs) has been studied in recent years in the pharmaceutical and veterinary areas (Martins, Siqueira, & Freitas, 2012; Meunier, Cardot, Manzanilla, Wysshaar, & Alric, 2007; Passerini et al., 2010), but there are few studies of SLMs in food applications compared to the spray drying technique. The formation of particles by the spray chilling technique consists of using lipid carriers, such as fatty acids, triacylglycerols and waxes, or a mixture of these, which must be solid at room temperature, to obtain hard consistency particles, thus ensuring good physical resistance, dispersibility, ease of handling and storage (Zuidam, Shimoni, 2010; Okuro, de Matos Junior, Favaro-Trindade, 2013; Oh, Guo, Heng, & Chan, 2014). Stearic acid can be used in the spray chilling process to act as a solid matrix, due to its high melting point, to guarantee the formation of solid particles. Nutritionally speaking, consuming it has a minimal effect on LDL cholesterol and no effect on HDL cholesterol since it can be converted more quickly to oleic acid than other saturated fat acids (O'Brien, 2009; Oh et al., 2014). The incorporation of unsaturated lipid in SLMs guarantee a less ordered solid lipid matrix consequently maintains the active in the lipid matrix. However, the incorporation of unsaturated lipid in SLMs can induce to oxidation and consequently affect the active compound resulting in degradation (Müller, Radtke, & Wissing, 2002; Sartori, Consoli, Hubinger, & Menegalli, 2015). Thus, the aims of this work were to produce SLMs of different compositions containing ginger oleoresin by spray chilling technique and to evaluate the stability of ginger volatile and pungent compounds at different storage temperatures (25 and 40 °C). SLMs characterizations, such as crystalline structure, mean diameter and morphology, were evaluated during storage in order to observe the behavior of particles.

2. Material and methods

2.1. Material

Commercial ginger oleoresin (30% of ginger essential oil) was kindly donated by NATUREX (São Paulo, Brazil). The solid lipid sample of stearic acid (Sigma-Aldrich) was used as the solid lipid matrix, and oleic acid (VETEC, Rio de Janeiro, Brazil) as liquid lipid. All other reagents used were of analytical grade.

2.2. Methods

2.2.1. Compatibility between lipids and the ginger oleoresin blend

The compatibility was determined using nuclear magnetic resonance (NMR) spectrometry (Bruker Minispec PC120) and a high precision dry bath (0–70 °C) (TCON 2000 - Duratech, USA), according to the AOCS method Cd 16b-93. The compatibility, or miscibility, of the lipids and oleoresin blend was determined by the analysis of the isothermal solid diagrams. This analysis was carried out in the Laboratory of Oils and Fats located at the School of Food Engineering, UNICAMP.

2.2.2. Production of SLMs

Each lipid component and ginger oleoresin (GO) were weighed according to their respective proportions, as shown in Table 1. The lipids were heated up to 85 °C by a temperature controlled water bath (Tecnal, TE-184, Piracicaba, Brazil). Then, they were added to GO and were kept under magnetic stirring to obtained a homogenized mixture (0.050 kg). SLMs were obtained using a Büchi-B290 spray dryer set to the spray chiller mode (Büchi, Flawil, Switzerland). The mixture was fed into a heated double fluid atomizer with nozzle diameter of 2.0 mm using a peristaltic pump, at a mass flow rate of 0.7 kg/h. SLMs were formed within a cooled chamber where inlet air temperature was set at 7 °C.

Table 1
SLMs formulations.

Components	Samples (%, w/w)			
	I	II	III	IV
Ginger oleoresin (GO)	10	10	20	20
Stearic acid (SA)	90	75	80	65
Oleic acid (OA)	–	15	–	15

2.2.3. Storage conditions for the stability study

After the production of the microparticles, the powders and the un-encapsulated ginger oleoresin were stored in sealed airtight plastic containers under two different temperatures: 25 °C (ambient temperature) and 40 °C (extreme condition) for 84 days. For each day of analysis, one container of each formulation was used, without later returning it to storage.

2.2.4. Characterization of microparticles during storage

2.2.4.1. Crystalline structure. The crystalline structure of SLMs was determined by X-ray powder diffraction technique. A Philips X-ray diffractometer (Analytical, X Ray X'Pert-MPD, Almelo, Netherlands) was deployed, with X-rays of $\lambda = 1.54056$ Å originating from a Cu Kα source. The diffraction was measured in the 2θ range from 5° to 30°, in a rate of 0.02°/s. Days of analysis: 0 and 84.

2.2.4.2. Surface morphology. The SLM surface was observed in a scanning electron microscope (SEM) (LEO Electron Microscopy 440i, Oxford-Cambridge, England), with an accelerating voltage of 10 kV and a 50 pA beam current. Microparticles were covered with a thin layer of gold in a Sputter Coater Emitech (model k450, Kent, United Kingdom). Micrographs were obtained with magnification of 500× and 5000×. Days of analysis: 0 and 84.

2.2.4.3. Mean volumetric diameter. The mean volumetric diameter ($D_{4,3}$) (Eq. (1)) of the SLMs was determined by laser diffraction technique using laser diffraction in a Mastersizer 2000 (Malvern Instruments Ltd, Malvern, UK) with air flow dispersion, using a dry accessory (Scirocco 2000, Malvern Instruments Ltd, Malvern, UK). Days of analysis: 0 and 84.

$$D_{4,3} = \frac{\sum n_i d_i^4}{\sum n_i d_i^3} \quad (1)$$

2.2.4.4. Stability of pungent compounds. The pungent compounds retention (%) during the storage stability was calculated on day 0, in relation to the proportions of 6-gingerol, 6-shogaol and zingerone, for the microparticles and the un-encapsulated GO. The analysis was repeated on days 0, 14, 28, 56 and 84.

Retention of the main GO pungent compounds (6-gingerol, 6-shogaol and zingerone) was measured by HPLC (HPLC DIONEX, model LC UltiMate 3000, USA), using the ISO 13685:1997 method (International Organization for Standardization, 1997).

2.2.4.5. Retention and stability of volatile compounds. During the storage stability of SLMs, the volatile compounds retention was calculated based on the ratio of the sums of the peak areas of ginger oleoresin compounds in the microparticles and the peak areas of the un-encapsulated GO compounds, obtained in GC-FID (HP7990, Agilent Technologies, USA). The volatiles were analyzed with an HP-5 MS capillary column (30 m × 0.25 mm × 0.25 m - J&W Scientific, USA), with helium as carrier gas, at a flow rate of 1 mL/min, as described in Oriani et al. (2016).

The degradation of α-zingiberene and β-sesquiphellandrene to ar-curcumene was verified using the peak areas for each compound.

To measure the ginger oleoresin quality, the following ratio was calculated: the sum of peak areas of volatiles, α-zingiberene and β-sesquiphellandrene, in relation to the sum of the peak area of ar-curcumene. Low ratio values indicate oleoresin quality loss.

2.2.4.5.1. Kinetics models for the volatile release during storage. Zero Order and First-Order (Vazquez-Landaverde, Qian, & Torres, 2007), Higuchi (Wang, Ding, Tao, & Chen, 2007), Hixson-Crowell (Partheniadis, Karakasidou, Vergkizi, & Nikolakakis, 2017) and Weibull/Avrami's equation (Soottitantawat et al., 2004) release kinetics models (Eqs. (2)–(6)) were used to determine the suitable model ($R^2 \approx 1$) that represents the volatile release during storage at different temperatures.

Zero Order equation:

$$Q = kt \tag{2}$$

First Order equation:

$$Q = 1 - \exp^{(-kt)} \tag{3}$$

Higuchi equation:

$$Q = k\sqrt{t} \tag{4}$$

Hixson-Crowell equation:

$$\sqrt[3]{Q} = 1 - kt \tag{5}$$

Weibull equation/Avrami's equation:

$$Q = 1 - \exp^{(-kt^b)} \tag{6}$$

where Q is the amount (%) of volatile released at the time t, k is the release rate constant and b is the release mechanism.

2.2.5. Statistical analysis

Results were subjected to analysis of variance (ANOVA) and a Tukey test with a significance level of 5%. The Minitab software trial edition (Minitab 16.1.0, Minitab Inc., State College, PA, USA) was used to compare the differences between the mean values.

3. Results and discussion

3.1. Compatibility between lipids and ginger oleoresin blend

The combination of lipids of different chemical compositions can result in different phase behaviors. Thus, to verify the compatibility among different lipids, it is necessary to study the phase behavior through phase diagrams, e.g., isothermal solid diagrams. These diagrams show the solid fat content (SFC) at different temperatures vs. blend compositions and, when the blends are compatible, the isothermal solid diagrams are linear (for ideal behavior) (Meng et al., 2011). However, as shown in Fig. 1, the graphs showed curvatures in both systems (stearic acid and ginger oleoresin; stearic acid + oleic acid and ginger oleoresin) and, therefore, these mixtures are qualified as non-ideal. The difference between curvatures and linearity may be attributed to dissolution of solid fat into liquid fat (Braipson-Danthine & Deroanne, 2006).

Braipson-Danthine and Deroanne (2006) proposed the use of second-order polynomial-type relations of SFC vs. blend graphs due their curvature, according to the equation $SFC = a(x)^2 + b(x) + c$, in which x is the concentration of fatty acid in the system; a, b, and c are dependent on the fatty acid, on the temperature, on the thermal history and also on the type of interaction between lipids and oleoresin. A high a/b ratio value is observed for strong incompatibility among fats. The value of a, for an ideal behavior, is zero (Braipson-Danthine & Deroanne, 2006). Thus, in this work, we can observe in Fig. 1 that resolving the a/b ratio in the polynomial equation (data not shown), at all temperatures, resulted in a low value, of practically zero, since, for the parameter a, all assays had a value of almost zero, proving that the blends are near the compatibility.

Comparing the stearic acid + GO blends to the stearic acid + oleic acid + GO blends, the parameter a showed a lower value for the blends containing oleic acid, a possible indication that these samples are more compatible than samples with stearic acid and GO only. This study showed that the mixture of fatty acid and ginger oleoresin is compatible, since it is next to the ideal behavior.

3.2. Characterization of SLMs during stability at different temperatures

3.2.1. Crystalline structure, surface morphology and mean volumetric diameter

X-ray diffraction is used for the study of the crystalline structure, in order to identify crystal polymorphs. Polymorphism is defined as the ability of a chemical compound to rearrange itself through intermolecular interaction, inducing the formation of specific crystalline structures (Ensikat, Boese, Mader, Barthlott, & Koch, 2006; O'Brien, 2009; Sato & Ueno, 2011). The possible change in polymorphic forms during storage is an important characteristic of SLMs. A stable polymorphic form can guarantee stability to the active compound in the lipid matrix, while the opposite behavior may cause its expulsion during crystal reorganization (Müller et al., 2002). Diffractograms presented in Fig. 2 show the crystals peaks of SLMs during storage. The major peaks in the diffraction angle for all samples, on day zero, were of $2\theta = 21.5^\circ$ and 24.1°, that are associated with d-spacing of 4.1 Å and 3.7 Å, respectively. These values represent an orthorhombic crystalline structure (Ensikat et al., 2006; O'Brien, 2009). The orthorhombic form corresponds to a geometric structure that is associated to facility of incorporation of the active due to numerous lattice defects (Jenning & Gohla, 2001; Zheng, Falkeborg, Zheng, Yang, & Xu, 2013).

After 84 days of storage under both temperatures, the variation of the diffraction angle was insignificant for samples with oleic acid and, therefore, no variation in d-spacing was observed. However, in d-spacing of 3.7 Å, storage at 40 °C for the sample containing 90% (w/w) stearic acid caused a small shift of the peak to the left, which could indicate some crystalline perturbation.

Visually, all samples were a yellow-colored powder with a fine aspect. However, samples with 20% ginger oleoresin showed an intense yellow color. The morphology of SLMs during storage maintained the characteristics acquired through spray chilling, resulting in dense spherical surfaces of variable diameters with no cracks, with an aggregation of smaller particles, ensuring lower gas permeability and, consequently, greater active compound protection (Fig. 3). The left side of Fig. 3 shows the representative particles scanned at a magnification of 500×; on the right, a closer look at individual particles at 5000× is shown. Formulations with oleic acid and 20% (w/w) ginger oleoresin resulted in smaller particles adhered to the surface of those with larger sizes, on day zero. Agglomeration may occur due to incomplete solidification of microparticles when they reach the cooling chamber (Consoli, Grimaldi, Sartori, Menegalli, & Hubinger, 2016). The surface images of SLMs (Fig. 3) in the end of storage at 25 and 40 °C to formulations containing just stearic acid showed less smooth surfaces comparing the same formulation at day zero. According to Shi, Liang, and Hartel (2005), crystal formation in lipid matrix is due to high melting point lipids. Thus, the high concentration of stearic acid on lipid matrix can be associated to the presence of crystals on microparticles surface at end of storage. The formulations with oleic acid resulted in particles with wavy surfaces at day zero, and were not observed modification on the surface in the end of storage.

The temperature and storage time can influence the crystallinity of the lipids. As was observed via X-ray diffraction, formulations with stearic acid only presented a small shift of the peak to the left at 40 °C, associated to a crystalline structure perturbation. The production of particles with spherical shape facilitates the flow of the powder and its application. Particle agglomeration may also contribute to powder

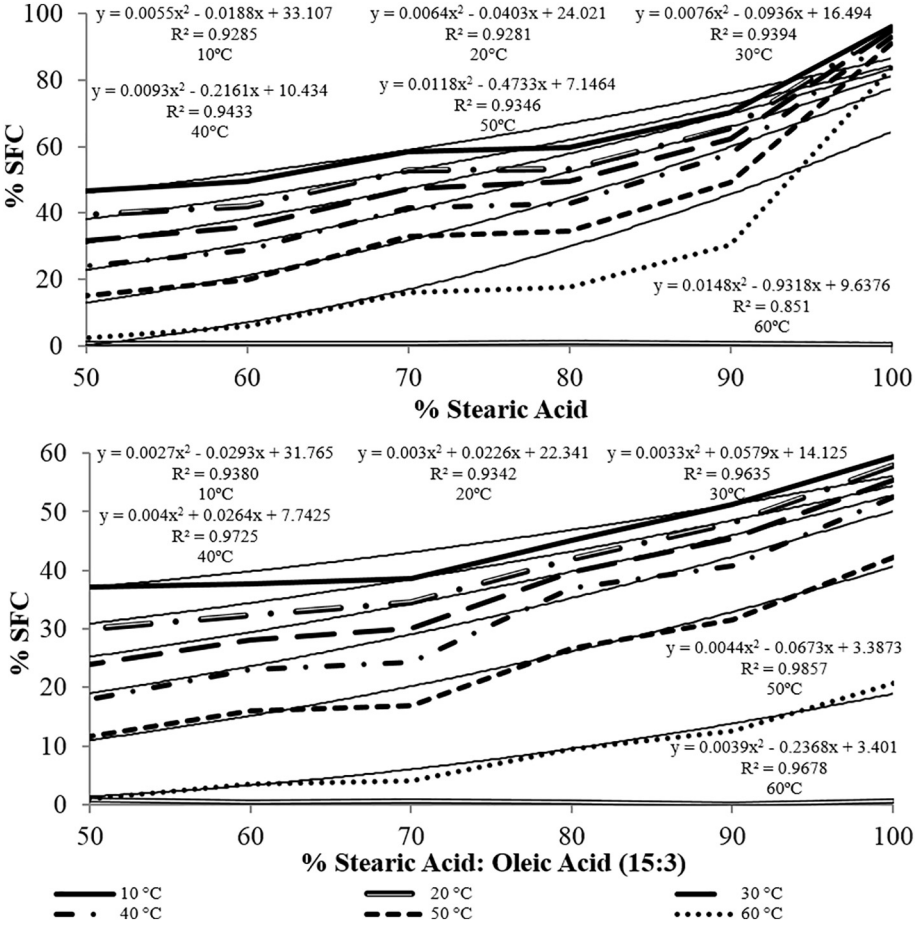

Fig. 1. Isothermal solid diagrams to verify the compatibility of lipids and ginger oleoresin blend. —: polynomial fit for each temperature. **SFC**: solid fat content.

application due to the reduction of dust formation (Pelissari et al., 2016).

The mean volumetric diameters ($D_{4,3}$) of SLMs on day zero ranged from 24 μm to 38 μm (Fig. 3). The addition of oleic acid and oleoresin in higher concentrations to the formulations contributed to an increase in the mean volumetric diameter. Higher concentrations of unsaturated lipids were shown to be related to higher mean volumetric diameter, due to less compact crystal structures. During lipid matrix crystallization to particle formation the higher concentration of saturated lipid in matrix composition is associated with more compact crystal

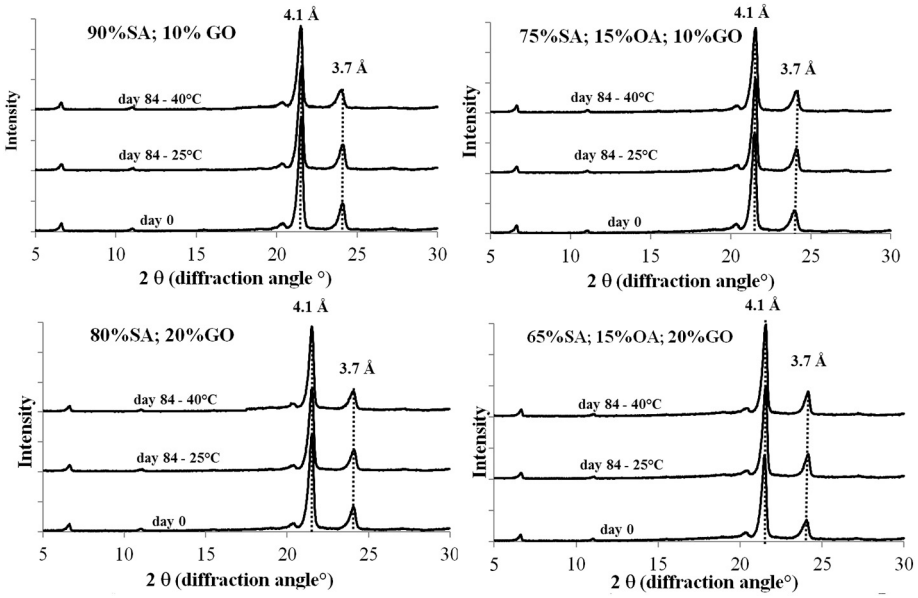

Fig. 2. X-ray diffraction of SLMs on days 0 and 84, upon storage at 25 °C and 40 °C. Dotted lines indicate the crystal spacing corresponding to the crystalline structure on day 0.

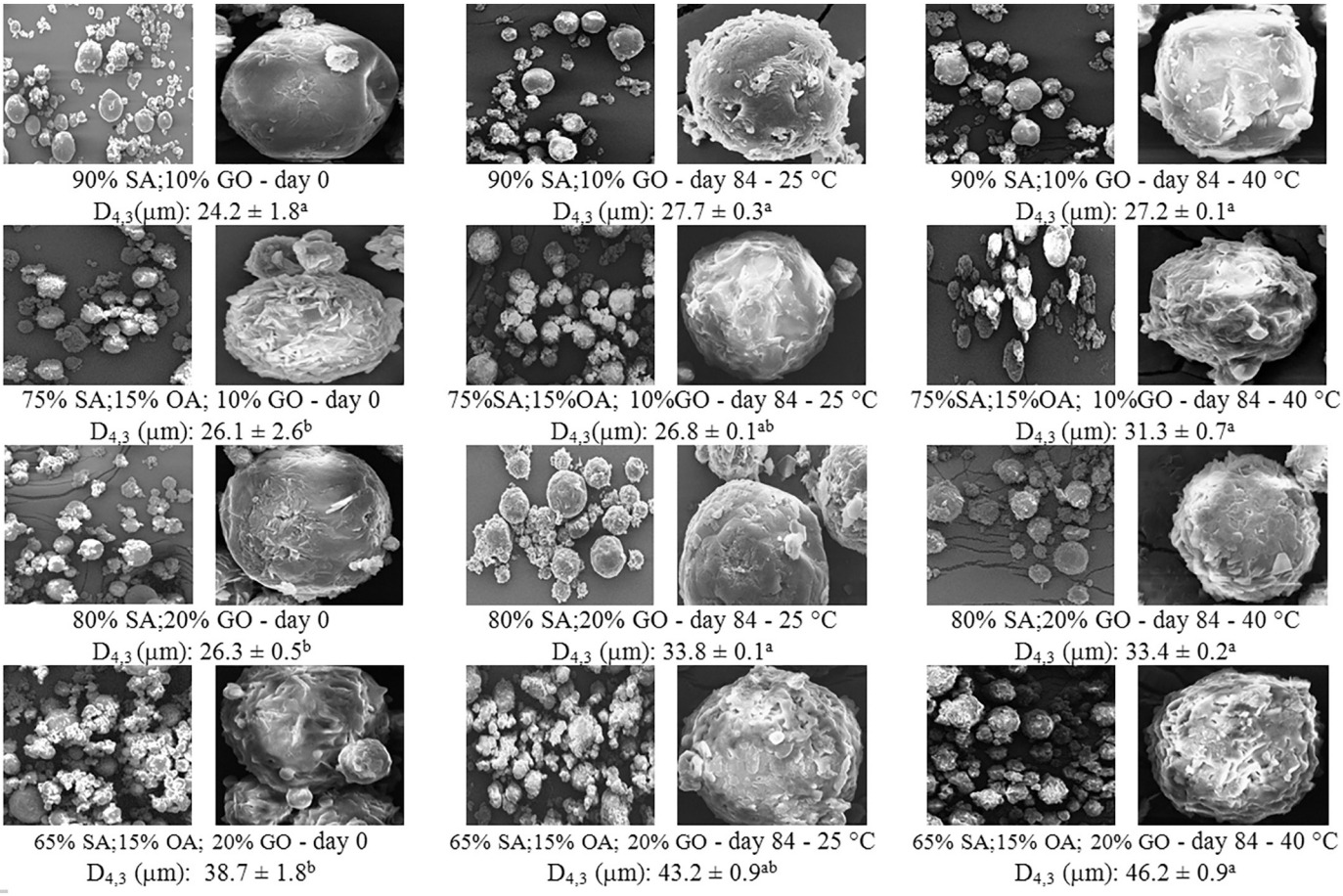

Fig. 3. Scanning electron microscopy at magnifications of 500× and 5000×. Mean volumetric diameter ($D_{4,3}$) obtained during storage at different temperatures. SA: stearic acid. OA: oleic acid. GO: ginger oleoresin. [a,b] Different lowercase letters in each line represent a statistically significant difference ($p \leq .05$) by Tukey test.

structure, due to linearity of molecules, consequently particle containing higher saturated lipid can result in lower size, however the incorporation of unsaturated lipid can lead to less compact crystal structure due to non-linearity of molecules structure, thus the particle size can result in bigger size comparing particles containing higher saturated lipid (Ribeiro, Arellano, & Grosso, 2012; Alvim, Souza, Koury, Jurt, & Dantas, 2013; Oriani et al., 2016). During the storage at any given temperature, the volumetric diameters increased compared to day zero, probably a result of agglomeration or crystalline structure melting.

3.3. Stability of 6-gingerol, 6-shogaol and zingerone

All samples of SLMs and of un-encapsulated ginger oleoresin only, on day zero, presented pungent compounds composition of approximately 115 mg for 6-gingerol, 35 mg for 6-shogaol and 25 mg for zingerone, in relation to 1 g of oleoresin, according to Fig. 4. In fresh ginger, the shogaols and zingerone content is insignificant. Both are formed when ginger is heated up to high temperatures, which results in degradation of gingerol compounds (An et al., 2016; Bailey-Shaw et al., 2008). The results obtained in this work are close to previous results obtained for ginger oleoresin, which presented higher 6-gingerol content than for any other compounds. Thus, for the initial study of SLMs stability it was ensured that the spray chilling process did not induce ginger oleoresin quality loss (Oriani et al., 2016; Varakumar, Umesh, & Singhal, 2017).

During storage at 25 °C, the SLMs and un-encapsulated ginger oleoresin only did not show alterations in the content of pungent compounds, as displayed in Fig. 4. Un-encapsulated ginger oleoresin kept stable during storage at 40 °C. However, the higher storage temperature resulted in a modification of pungent compounds of SLMs. Particles containing oleic acid (samples II and IV) showed a lowering in the 6-gingerol concentration after the 56th-day of storage and an increase in the 6-shogaol concentration, in the same period. Samples I and III showed slight variations of 6-gingerol and 6-shogaol concentrations. Bhattarai, Tran, & Duke (2001 and 2007) showed that the degradation of gingerol to shogaol was dependent on the temperature and an environment of acidic catalyzed dehydration. Thus, the oxidation products of lipids contained in SLMs could have led to the formation of such acidic environment that, in association to the elevated temperature, further led to a gingerol degradation reaction, especially for formulations containing unsaturated fatty acids, which are susceptible to oxidation at higher temperatures. This produces rancidity in oil, with accompanying off-flavors and smells (O'Brien, 2009).

Zingerone concentrations showed no difference during storage, at any given temperature, a good result for SLMs and un-encapsulated GO only, since it is a product obtained from condensation of gingerol that can cause a GO off-flavor.

Storage at 25 °C did not present difference to pungent compounds concentrations after 84-days of storage, and the same has happened to samples I, III and to un-encapsulated oleoresin through storage at 40 °C.

3.4. Volatile retention during storage

The retention profiles of the volatile compounds in SLMs and un-encapsulated ginger oleoresin only, at 25 and 40 °C, were monitored during 84 days, as shown in Fig. 5. In all cases, the volatile retention was defined as the ratio of the residual amount of volatiles on each day

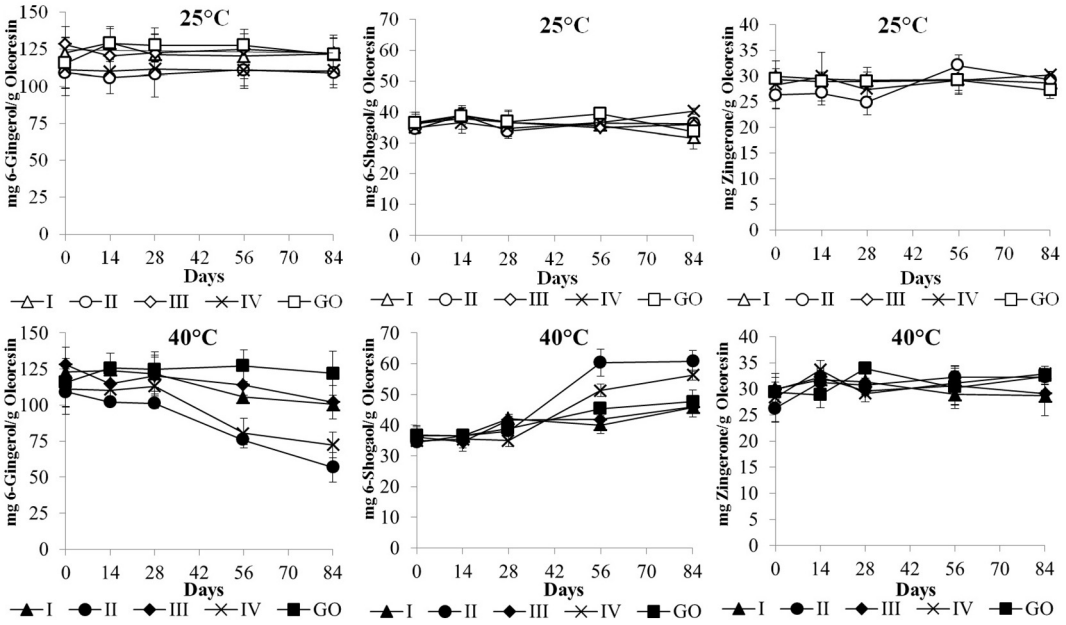

Fig. 4. Stability of pungent compounds. (GO) Un-encapsulated ginger oleoresin. Solid lipid microparticles: (I) 90% SA; 10% GO (II) 75% SA; 15% OA; 10% GO (III) 80% SA; 20% GO (IV) 65% SA; 15% AO; 20% GO. SA: stearic acid. OA: oleic acid.

in relation to their initial amount on day 0.

Specifically, the ability of sample IV to retain the aroma compound was greater than that of samples I, II, III and of un-encapsulated GO. After 84 days at 25 °C, the volatile retention was approximately of 30% and 51%, for II and IV, respectively, and of 11% and 19%, for I and III, respectively. At 40 °C, retention decreased to 19 and 30% for II and IV respectively. The storage temperature had a pronounced effect on the volatile retention. Storage at 40 °C promotes rapid volatilization of un-encapsulated GO and, after the 28th day, this resulted in its lower retention.

Samples containing oleic acid presented the best volatile retention. The efficiency of the oleic acid in stabilizing volatile compounds at all temperatures could possibly be due to better compatibility between ginger oleoresin and oleic acid, compared to blends without the later, as shown in Fig. 1. The compatibility study of the lipid mixtures (lipid + oleoresin) showed that the mixtures containing the unsaturated lipid showed better fitting to polynomial curve, consequently better compatibility with the oleoresin. The compatibility study was confirmed with the results obtained for the volatile retention of the particles during storage, since the lipid compatibility between saturated and unsaturated lipid together with the oleoresin resulted in particles with better retention of volatiles. According to Paravisini and Guichard (2016), the retention or release behaviors of volatile compounds depend mostly on their solubility in the lipid matrix. Moreover, the presence of unsaturated fatty acids leads to higher solubility of volatile compounds. However, the incorporation of a high amount of solid lipids reduces such solubility, thus increasing their release. As demonstrated in storage at 40 °C on day 7, particles with stearic acid only (I and III) resulted in a release of about 65–80%. According to Wissing, Kayser, and Müller (2004) for the active compounds on the outer surface of the matrix, or even at a short distance from it, the release is fast, like a burst effect.

3.4.1. *Kinetics models for the volatile release during stability*

Volatile release modeling studies were performed on SLMs and un-encapsulated GO as a means to observe the release mechanisms of the

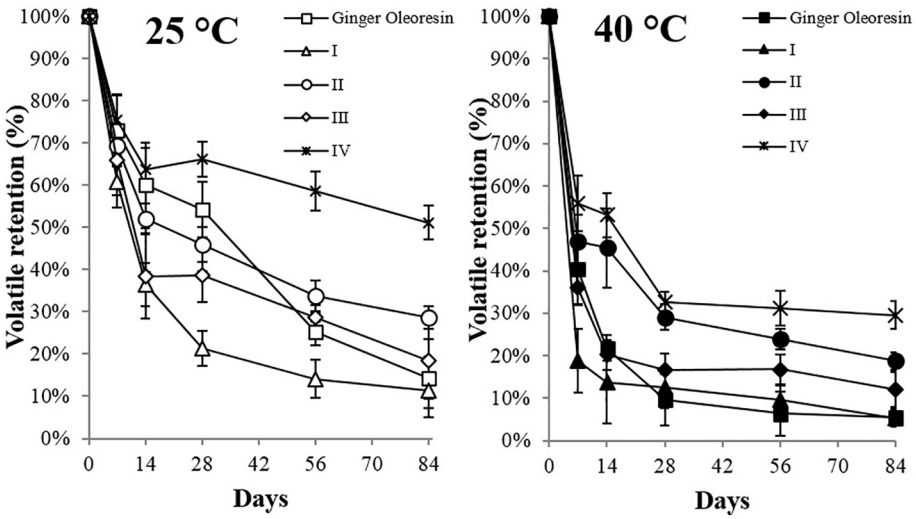

Fig. 5. Volatile retention during storage at 25 and 40 °C. (Ginger Oleoresin) Un-encapsulated ginger oleoresin. Solid lipid microparticles: (I) 90% SA; 10% GO (II) 75% SA; 15% OA; 10% GO (III) 80% SA; 20% GO (IV) 65% SA; 15% AO; 20% GO. SA: stearic acid. OA: oleic acid.

Table 2
Best-fitting models for volatile release. Release-kinetics correlation coefficients (R^2) for derived models.

	Zero order (R^2)	First order (R^2)	Higuchi (R^2)	Hixson-Crowell (R^2)	Weibull[a] (R^2)
GO (25 °C)	0.889	0.986	0.983	0.970	0.959
GO (40 °C)	0.554	0.795	0.843	0.744	0.967
I (25 °C)	0.629	0.849	0.873	0.780	0.939
I (40 °C)	0.331	0.633	0.602	0.501	0.908
II (25 °C)	0.705	0.835	0.852	0.808	0.961
II (40 °C)	0.567	0.788	0.825	0.716	0.940
III (25 °C)	0.650	0.840	0.870	0.780	0.872
III (40 °C)	0.398	0.605	0.682	0.527	0.878
IV (25 °C)	0.655	0.745	0.861	0.716	0.890
IV (40 °C)	0.524	0.652	0.789	0.610	0.817

(GO) Un-encapsulated ginger oleoresin. Solid lipid microparticles: (I) 90%SA; 10%GO (II) 75%SA; 15%OA; 10%GO (III) 80%SA; 20%GO (IV) 65%SA; 15%AO; 20%GO. SA: stearic acid. OA: oleic acid.
[a] Avrami's equation.

volatiles. Table 2 shows the release-kinetics correlation coefficients (R^2) of samples in accordance to each mathematical model evaluated.

Controlled release of uniform particles is mainly described by zero and first order kinetics, although variable morphologies, shell materials, particle sizes and release environments may differ from zero or first order (Ho, Joyce, & Bhandari, 2011; Shahidi & Han, 1993). Un-encapsulated ginger oleoresin storage at 25 °C presented First-Order as the best release model, associating the dependence of the release rate of the active to its concentration. Avrami's/Weibull equation was used to show the release mechanism, which is associated with parameter b (Table 3), in accordance to Soottitantawat et al. (2004): $b = 1$ represents the first order release mechanism; $b < 1$ means that the molecular diffusion became rate limiting; and $b > 1$ means a quick release with an induction period.

Avrami's equation was the best fit for GO-volatile release from SLMs, at different temperature conditions, and had a $b < 1$ for all assays, corresponding to the diffusion-limited system (Ho et al., 2011). This kinetic model differs in accordance to the rate-limiting factor for each particle and in accordance to the k constant we observed the influence of lipid matrix to the volatile release. For each sample, an increase in the storage temperature meant an increase in the release rate constant (k – Table 3). Thus, SLMs at higher temperatures had a quicker release compared to the same samples at 25 °C. Samples containing oleic acid (II and IV) resulted in a lower k value at 40 °C, likely a consequence of volatile solubility in oleic acid that favored its slow release. The k-value may serve as a significant index that GO volatiles release in SLMs is dependent on the matrix composition and storage temperature.

Table 3
Weibull shape b parameter values indicating the release mechanism and the release rate constant (k value) of Weibull/Avrami's equation.

	b values	k (1/day)
OG (25 °C)	0.96	0.03
OG (40 °C)	0.31	0.41
I (25 °C)	0.58	0.19
I (40 °C)	0.19	1.13
II (25 °C)	0.47	0.16
II (40 °C)	0.34	0.37
III (25 °C)	0.48	0.19
III (40 °C)	0.26	0.69
IV (25 °C)	0.30	0.16
IV (40 °C)	0.28	0.36

3.5. Stability of the main volatile compounds

The process of extraction of ginger oleoresin does not result in ginger volatile compounds and, thus, the essential oil is obtained separately and is posteriorly added to the oleoresin to obtain a product similar to fresh ginger. The ginger essential oil, which is a mixture of monoterpene and sesquiterpene compounds, contains the volatiles responsible for the characteristic flavor of ginger: α-zingiberene is its major component, with 35%, followed by β-sesquiphellandrene (15%) and ar-curcumene (14%) (Bellik et al., 2013; Huang, Wang, Chu, & Qin, 2012). The increases of ar-curcumene and decreases of α-zingiberene and β-sesquiphellandrene are responsible for the GO quality loss. Storage at high temperatures can result in α-zingiberene degradation and ar-curcumene formation (Balakrishnan, 2005). Table 4 presents the behavior of the main volatile compounds of ginger and the ratio of GO compounds during storage, used to evaluate the ginger quality.

On day zero, all volatile compounds were present in the ideal proportion. Thus, they were shown as 100%, as seen in Table 4. Every sample, on both the 7th and 14th days, at 25 °C, showed a similar percentage for all volatile compounds, indicating that no degradation occurred, even though a volatile release happened, since the proportion of each compound diminished when comparing day 7 to day 14. For samples I, III and un-encapsulated GO only, on the 28th day, at 25 °C, the high percentage of ar-curcumene and low of α-zingiberene indicated that α-zingiberene converted to ar-curcumene, showing that probably the matrix composition, of stearic acid only, was not able to maintain or protect the volatile compounds, thus resulting in their degradation, similar to un-encapsulated GO. At the 40 °C storage condition, from the 7th day on, for samples III, IV and for un-encapsulated GO, there was a higher proportion of ar-curcumene in comparison to the other two compounds, thus indicating the degradation of α-zingiberene.

The sample II (at 25 °C), containing oleic acid and 10% GO, had the best results for stability of volatile compounds, because from day 0 until the end of storage all compounds kept the same proportion, that is, they did not present statistical differences, meaning there was no degradation of α-zingiberene. Addition of oleic acid to the particles containing a maximum of 10% GO guaranteed an affinity between the matrix and the volatile compounds. This allowed a better undergoing through storage, not allowing the degradation of their compounds. On the other hand, the lipid matrix with no addition of oleic acid guaranteed 30% of volatile retention (as shown in Section 3.4).

The presence of unsaturated lipid showed to be the best way to maintaining ginger volatile stability as it was verified in the formulation containing 10% ginger oleoresin and 75% stearic acid +15%oleic acid, at 25 °C. This is an indication that oxidation reaction has not influenced on volatile compounds stability at 25 °C, because unsaturated lipid induces to oxidation reaction and verifying formulation containing just saturated lipid (90% and 80% stearic acid) we observed that this formulations resulted in ginger volatile compounds degradation, thus the volatile compounds have been affected due to matrix composition.

The ratios of main volatile compounds were used for observation of their behaviors during storage. Samples that presented little variations of ratio between days 0 and 84 showed good ginger volatile quality. The obtained ratios also showed that high temperatures were inadequate to maintain the volatile quality in SLMs and GO only through storage. They had a low value (< 2) in all samples at the end of storage; compared to their initial value, this result is a consequence of increases in ar-curcumene. Sample II presented the lowest variation of the ratio at 25 °C: from 3.7 to 3.0 (Table 4). The matrix composition containing saturated and unsaturated lipids are able to maintain the quality of ginger volatiles better than un-encapsulated ginger oleoresin, whose ratio went from 4.5 at day 0 to 1.1 at the end of storage.

Table 4
Retention of major compounds (ar-curcumene, α-zingiberene and β-sesquiphellandrene) in SLMs and their ratio as an indication of GO quality during storage.

Days	25 °C				40 °C			
	ar-curcumene (%)	α-Zingiberene (%)	β-sesquiphellandrene (%)	Ratio (α + β)/ar	ar-curcumene (%)	α- Zingiberene (%)	β-sesquiphellandrene (%)	Ratio (α + β)/ar
		Ginger oleoresin						
0	100	100	100	4.5	100	100	100	4.5
7	78 ± 5^{a}	71 ± 2^{a}	73 ± 3^{a}	4.2	46 ± 3^{a}	36 ± 2^{b}	45 ± 2^{a}	3.8
14	64 ± 4^{a}	58 ± 4^{a}	62 ± 6^{a}	4.2	34 ± 3^{a}	15 ± 1^{c}	27 ± 3^{b}	2.5
28	59 ± 3^{a}	50 ± 3^{b}	60 ± 4^{a}	4.1	27 ± 2^{a}	3 ± 1^{c}	11 ± 3^{b}	1.0
56	49 ± 2^{a}	15 ± 1^{c}	30 ± 3^{b}	1.8	20 ± 1^{a}	2 ± 1^{c}	7 ± 1^{b}	0.7
84	37 ± 4^{a}	6 ± 1^{c}	17 ± 2^{b}	1.1	17 ± 1^{a}	1 ± 1^{c}	6 ± 2^{b}	0.8
		I - 90% SA; 10% GO						
0	100	100	100	4.5	100	100	100	4.5
7	63 ± 2^{a}	58 ± 4^{a}	66 ± 3^{a}	4.3	22 ± 3^{a}	17 ± 3^{a}	21 ± 4^{a}	3.6
14	39 ± 4^{a}	34 ± 5^{a}	41 ± 6^{a}	4.1	20 ± 2^{a}	11 ± 2^{b}	14 ± 1^{b}	2.6
28	42 ± 3^{a}	16 ± 2^{b}	20 ± 3^{b}	2.5	21 ± 1^{a}	9 ± 1^{c}	15 ± 3^{b}	2.3
56	22 ± 4^{a}	11 ± 2^{b}	16 ± 3^{ab}	1.8	21 ± 4^{a}	6 ± 2^{c}	11 ± 4^{b}	1.5
84	27 ± 4^{a}	7 ± 2^{c}	12 ± 2^{b}	1.3	13 ± 1^{a}	3 ± 1^{c}	6 ± 1^{b}	1.2
		II - 75% SA; 15% OA; 10% GO						
0	100	100	100	3.6	100	100	100	3.6
7	68 ± 3^{a}	69 ± 2^{a}	72 ± 4^{a}	3.7	50 ± 2^{a}	45 ± 3^{a}	50 ± 3^{a}	3.3
14	52 ± 6^{a}	51 ± 4^{a}	54 ± 5^{a}	3.5	49 ± 5^{a}	43 ± 3^{a}	49 ± 4^{a}	3.2
28	47 ± 4^{a}	45 ± 4^{a}	47 ± 4^{a}	3.4	47 ± 5^{a}	20 ± 3^{c}	32 ± 4^{b}	1.8
56	38 ± 3^{a}	32 ± 4^{a}	34 ± 2^{a}	3.1	44 ± 5^{a}	15 ± 4^{c}	27 ± 3^{b}	1.5
84	32 ± 6^{a}	27 ± 4^{a}	30 ± 4^{a}	3.0	41 ± 5^{a}	9 ± 3^{c}	21 ± 4^{b}	1.1
		III - 80% SA; 20% GO						
0	100	100	100	4.4	100	100	100	4.4
7	80 ± 7^{a}	59 ± 9^{b}	70 ± 6^{ab}	3.5	44 ± 3^{a}	32 ± 3^{b}	39 ± 4^{ab}	3.4
14	39 ± 1^{a}	38 ± 2^{a}	40 ± 2^{a}	4.3	33 ± 3^{a}	12 ± 1^{c}	29 ± 4^{b}	2.3
28	44 ± 5^{a}	35 ± 1^{b}	42 ± 3^{a}	3.7	38 ± 5^{a}	8 ± 1^{c}	19 ± 3^{b}	1.3
56	45 ± 5^{a}	22 ± 3^{c}	31 ± 2^{b}	2.4	36 ± 3^{a}	9 ± 2^{c}	19 ± 3^{b}	1.5
84	46 ± 7^{a}	9 ± 2^{c}	20 ± 3^{b}	1.2	35 ± 3^{a}	10 ± 1^{c}	19 ± 2^{b}	1.6
		IV - 65% SA; 15% OA; 20% GO						
0	100	100	100	3.7	100	100	100	3.7
7	83 ± 7^{a}	71 ± 4^{a}	78 ± 5^{a}	3.3	65 ± 4^{a}	51 ± 5^{b}	58 ± 7^{ab}	3.0
14	68 ± 5^{a}	63 ± 6^{a}	61 ± 3^{a}	3.5	65 ± 3^{a}	46 ± 3^{b}	59 ± 4^{ab}	2.8
28	71 ± 3^{a}	64 ± 4^{b}	68 ± 4^{ab}	3.4	54 ± 6^{a}	23 ± 3^{c}	35 ± 4^{b}	1.9
56	69 ± 5^{a}	54 ± 4^{b}	61 ± 6^{b}	3.0	61 ± 4^{a}	18 ± 3^{c}	34 ± 5^{b}	1.4
84	67 ± 7^{a}	44 ± 5^{b}	53 ± 7^{ab}	2.6	68 ± 2^{a}	13 ± 4^{c}	32 ± 3^{b}	1.1

GO: ginger oleoresin. SA: stearic acid. OA: oleic acid.

4. Conclusion

Storage of SLMs at 40 °C showed that the presence of oleic acid can interfere with the degradation of 6-gingerol. However, at ambient temperature, all SLMs guarantee great ginger oleoresin performance. Samples with oleic acid ensured a better stability of the volatile compounds α-zingiberene and β-sesquiphellandene. In general, this work presented good results for SLMs, showing that they can be a substitute for un-encapsulated ginger oleoresin in food applications, guaranteeing its better distribution due to their conversion to powder, therefore maintaining the quality of ginger pungent and volatile compounds at ambient temperature.

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