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Abstract

Global trends in food in recent years indicate a marked interest of consumers towards certain foods, which, in addition to the nutritional value, provide benefits to the physiological functions of the human body. Sesame seeds (variety DV-9) was used for the formulation of cocoa-based spread products with partial addition of sesame oil and sesame oil cake. Physical characterization and chemical composition of raw materials and formulation were performed. The formulations presented rheological behaved like non-Newtonian fluids. F4 as thixotropic fluid and F2; F3; F5 as Bingham plastics. All formulations also presented superior nutritional properties compared to similar commercial products. The use of sesame seeds is beneficial and achievable.

Keywords: Sesame seeds, cocoa beans, spread cream, oil sesame, sesame oil cake



Introduction

Traditionally, spreadable cocoa cream (SCC) is a product made with the use of hydrogenated vegetable shortening, vegetable oils, mainly Palm. In its composition, an SCC has more than 40 percent of solid fat, because it is the continuous phase in which dissolve powder cocoa, sugar, milk and any other solid ingredients used in the formulation. SCC is a product a pseudoplastic fluid, ready to use and eat, with a spread-ability across ample (room and cooling temperature), creamy taste, smooth homogeneous structure with no fat-phase separation, and excellent oxidative stability. SCC has a generous consumer target (children, adults) because the main ingredient of the formulation is sugar. It is consumed alone or with the use of conveyors: cookies, slices of bread, cakes, among others. Some similar commercial products, in nutritional labels, indicate that with 15 grams, a contribution of 7-8 g of sugar, 5-6 g of fat, and 0.6 to 1 g of protein obtained. Usually, the fat composition of commercial products is high in saturated fatty acids (SFAs). However, SFAs suffer from a negative image in health.

In the production of SCC, it is crucial to control the water content of the raw materials. This component could affect the final product. Generally, the production time is 18-24 hours. Mainly alkaline cocoa powder (8 and 12% fat) used. A higher proportion of cocoa butter damages the typical rheological properties of the spreads. Cocoa butter has different polymorphisms that are of interest in chocolate. If cocoa butter has contact with considerable amounts of water, it generates negative interactions that avoiding the formation of stable emulsions, reducing the plasticizing effect that necessary to a product of this type. Today, there are various natural and synthetic plasticizers tested in the formulation of cocoa spread products, to generate the desired plasticizing effect, achieving the technological effect of production; however, it neglects the deterioration of the nutritional quality of the product. Oilseed raw materials such as sesame are useful for diversifying spreadable formulations. Sesame seed contains fats, proteins, carbohydrates, dietary fiber, and some minerals (Elleuch et al., 2007). Sesame oil cake, which is rich in protein, essential amino acids, minerals, and fiber contents, it is useful to improve the nutritional value of this product. Sesame oil has a high proportion of PUFA'S (linoleic acid ~ 50% and oleic acid ~ 37%) (Mohdaly et al., 2011; Gharby, 2017). content a high proportion of unsaponifiable matter, α -tocopherols, sesamol, and sesamina (Tokusoglu et al., 2013). However, the sesame cortex has concentrations of oxalic and phytic acid, which are considered anti-nutritional factors.

Based on these considerations, the aim of this work was to study sesame oil and sesame oil cake in the formulation of a spreadable cocoa cream, to obtain a functional food with reduced saturated fat, reduced sugar, and more protein content that a commercial product.

Materials and methods

Materials

Sesame Seeds, variety DV-9 (without botanical characterization) donated by Guesa Comercializadora (Turén, Portuguesa, Venezuela), was applied the first cleaning with potable water (3 times). Then a thermal-alkaline decorticated process was applied (55°C; 0.7% NaOH; 15 min). After this time, it was homogenized (30 sec) using a kitchen assistant (Metvisa®). To finally remove the hulls from the sesame seeds, a 40-mesh



stainless steel sieve was used, applying a continuous flow of water under pressure. Once the sesame seed was decorticated, it dried (55 °C x 2-3 hours) in a tray dehydrator (Mitchel dryers 6451/59). Immediately dry, cold pressing carried out in a hydraulic press (Fisher Scientific Co, Carver Laboratory Press Model B) using an approximate pressure of 1.1x105 Pa / m2. The oil (virgin extra) obtained was filtered and centrifuged to eliminate possible impurities, packed in glass bottles, and kept at 25-27 °C temperature to avoid degradation. The sesame cake obtained was reduced in size (40-50 mesh) to obtain defatted sesame flour, which was packed in plastic bags and stored under refrigeration. Sugar, defatted cocoa powder, skimmed milk powder, soy lecithin (was used as emulsifiers), and hydrogenated vegetable shortening, were purchased in a local market.

Methods

Spreadable cocoa cream preparation

After a set of preliminary experiments, five (5) final formulations obtained, leaving within these a control formulation (F1). The raw materials used in the spreadable cocoa cream production were a cocoa-cream mass, refined in a wet mill (Santha, spectra 11) of 2-roll mill in pilot-scale conditions. Constant speeds (1250 rpm) used, and the total time for processing was 22 h. The composition of the formulations spreadable cocoa cream included: hydrogenated vegetable shortening, only sesame oil, sugar, cocoa powder, skimmed milk powder, lecithin.

Physical tests

The viscosity was measured at 44 °C using Brookfield Viscometer, model LV-II (Brook Field Engineering Laboratories Company, Stoughton, Ma, USA) spindle number 4 at speed 12 rpm, for 6 minutes (Covenin 577:2007). The Bostwick consistometer evaluated at 44 °C for each of the formulas reported as the distance traveled L (cm) in 30 s (Barrette et al., 1998; Hayes et al., 1998).

Color parameters were measured using a HunterLab® ColorFlex Spectrophotometer $45^{\circ}/0^{\circ}$ Standards serial number CX-1719 (HunterLab, Inc., Reston, VA). Only values of the SCE (Specular Component Excluded) considered as these claimed to be more correlated with observations of the human eye. The Spectrophotometer calibrated with the white standard plate (X: 79.45, Y:84.20, Z:88.12, L*:93.54, a*-0.81 y b*:1.58). Results were expressed in terms of L* (lightness component), a* (green to red component), and b* (blue to yellow component). Other essential color parameters were calculated using L*, a* and b* (Method OIV-MA-AS2-11, 2006): Hue angle (hab = arctan(b*/a*)) reflected the tone and expressed in degrees on a 360° scale. Chroma (C*ab = (a*2 + b*2) 1/2) defines the chromatics, being a measure of color intensity or saturation and ranges from 0 (completely unsaturated) to 100 or more (pure color). Overall colorimetric difference between two samples ($\Delta E*ab = [(\Delta L*)2 + (\Delta a*)2 + (\Delta b*)2] 1/2$) reflects the color change of each sample in the presence of an added compound, compared to the untreated extract, where, each of the formulations established as a control to determine the differences that could exist between them.



Chemical and physiochemical analysis

The chemical composition was determined according to AOAC standard methods: moisture method 925.10, lipid method 920.39, ash method 923.03, nitrogen method 920.87, and Carbohydrates by difference. pH and titrable acidity by method 934.02 and water activity method 978.18 (AOAC 2000). Fatty acids methyl ester (FAME) was prepared according to the method by ISO 5909 (ISO 12966-2:2017). The clear supernatant subsequently injected into a Gas Chromatograph (GC) Perkin Elmer model Clarus 500, with flame ionization detector (FID), with an autosampler injector. Column: Supelco 2560 (100m, 0.25mm, d.i. 0.2 μ m) and working conditions A.O.A.C 996.06 (2000) modified: Gas arc: Hydrogen at 30 psi. Flow rate: 1.1 mL/min, Detector temperature: 250 ° C, Injector temperature: 225°C, 1 μ L of the sample. Heating ramp: 100 °C 4 min, increase up to 240°C at 3°C /min, and 240°C for 10 min. The identification was made through the use of a standard reference standard of Supelco 189-1 methyl esters. The area percent of each fatty acid was calculated (Tutorial Totalchrom Version 6.2 software) by dividing its peak area by the total peak area of the fatty acids identified (COVENIN 2281, 2002).

Statistical analysis

Data obtained were analyzed using a one-way analysis of variance (ANOVA) test. The Tukey's honest significant difference test (HSD) method was chosen for the post-hoc tests for each dataset. The Tukey Honestly Significant Difference (HSD) function of SPSS (2012) (Version 13.0, SPSS Inc., Chicago, IL, USA) was used to compare the means of all data. All statistics were based on a confidence level of 95%, and p < 0.05 was considered statistically significant.

Results and discussion

The yield for hydrothermal decorticated of sesame seed was 86.90 ± 1.79 was obtained (for 100 g of dehusked seed). The percentage of bark was 5.12 ± 0.47 (per 100 g of seed). There was a total loss in the process of 8%. The decorticated was efficient, even though the techniques used were laboratory and pilot level. The low concentration of caustic soda and the use of pressurized water streams were efficient in obtaining 100% decorticated and whole seeds. At the industrial level, the processes are more rigorous and employ more precise abrasive equipment.

For the extra virgin oil, the yield was 35.16 ± 1.63 (per 100 grams of sesame seed decorticated), so that $63.18 \pm 0.45\%$ was the fraction sesame oil cake, this cake rich in protein. Elkhaleefa and Shigidi, (2015) report an extraction rate of 37 to 40% using organic solvents and long treatment times. Other (Sabah El Khier et al., 2008; Ünal and Yalçın, 2008; Hassan, 2012; Ogbonna and Ukaan, 2013) have report yields above 50%. However, in all the mentioned, with the use of organic solvents. Ribeiro et al. (2016), has reported (using hydraulic pressure) similar results to these, the methodology was efficient, even in the case of laboratory equipment. The sesame oil cake was reduced in size (hammer mill) to 40 mesh and used in the formulation of the spreadable cocoa cream.



Physical properties of spreadable cocoa cream formulation

Relative viscosity

As shown in Figure 1, the relative viscosity indicates that there is not a directly proportional relationship between the amount of sesame oil cake used and the viscosity reflected. It could be because the proportions of sesame oil cake used in each formulation were different. Detailed below: F2 (16.8%), F3 (24.2%), F4 (32%) and F5 (21.2%), F1 (not added). In general, the relative viscosity of the formulations exhibited behaviors similar to the control, that is, the initial viscosities were higher, and as time progressed, they decreased, until stabilized except for F2, which increases the viscosity from minute 3. F5 was the formulation that presented the highest viscosity. F4 had the lowest viscosity. The determination was made at 44 ° C, but it is interrelated with the characteristics observed at room temperature, where F2; F3 and F5 behave similar to F1 (control), that is, they do not flow with gravity; however, F4 remains in a liquid state. All formulations showed characteristic rheological behaviors of non-Newtonian fluids. F2, F3, and F5 as Bingham plastics (independent of time) while F4 thixotropic type (time-dependent).

Consistency

The Bostwick consistency (Figure 2) for each of the formulas shown in Figure 2 indicate F5 proved to be the most consistent, followed by F2, F3, F1, while F4 was the most fluid (traveled 8 cm at t= 30 s). These results correspond to those reported above for relative viscosity. Although it is not the expected order (F2>F5>F1>F3>F4), these may be due to some effect relative to the solids that make up the complex matrix of each formulation.

CIELAB color parameters

The L* parameter (Table 1), diminished for all formulations concerning the control (F1), was considered a similar trend for the a* and b* parameters. All the formulations evaluated contained the same percentage of defatted cocoa powder. The results showed that there were statistically significant differences between the formulations, which indicate that there was a significant effect between the proportions of the ingredients used for each formulation. There are predominantly red colorations, which are primarily assigned to cocoa powder, raw material always affected by changes in pH; in the case of the formulations of this study, pH ranged from 7.00 to 7.45. The color analysis showed that there are trends towards yellow colorations, attributable to the proportions of sesame oil used (except the control), as well as the interaction that can affect between the oil, butter, and sesame solids (except the control). The parameters above discussed allowed us to obtain the value of the brown index (BI), obtaining that control formulation has the lowest color intensity. F4 was the one that obtained higher intensity of brown.

Hue angle (Hab) showed that the F4, have the lowest values, so it was the most reddish color formulation. The scale for red colors goes from 45° to 90° value; the results are congruent since F4, presented the lowest luminosity. Finally, F4 was the one with the lowest for chroma value (C*ab), which indicates that this is the one with the less luminous (opaque) color in comparison with the rest of the formulations. In general terms, BI; H_{ab} and C*_{ab} behaved as follows: F4> F3> F2> F5> control.



Generally, an observer can discriminate two colors if $\Delta E^*ab > 1$, but because of various interferences, color discrimination is usually worse (Xu et al., 2015). Differences in color are considered very distinct if $\Delta E^*ab > 3$, distinct if $1.5 < \Delta E^*ab < 3$ and small difference if $\Delta E^*ab < 1.5$ (Tiwari et al., 2008). When establishing the color differences between the formulations of spreadable cocoa-sesame cream elaborated, it found that there are significant differences regardless of the formulation used as a control; however, the greatest differences observed (Table 2) when F1 (control) used. When F2, is as a control, it obtained that the differences in color are less perceptible to the eye for F3 and F5, in the same way; when F3 is the control, it revealed that there is no difference with F2 and F4. Established F4 as a control, we could see that F3 behaves similarly to that described above. Finally, using F5 as a control, we obtained a positive relationship with F2 (difference equal to 1.52), which coincides when F2 used. The results discussed above are closely related to the proportions of the ingredients used in the formulations proposed in this study, these indicate that there are positive effects between the concentrations of sesame oil and sesame oil cake respect to the physical properties of spreadable creams. The critical visual recognition value for ΔE^* is 5; however, an untrained consumer it may not catch this difference so quickly.

Chemical composition

The chemical composition of spreadable cocoa cream presented in Table 3 shows significant differences (P 0.05) obtained among samples about all characteristics evaluated, indicating that the addition of sesame oil and sesame oil cake affect the chemical and compositional of these products. Moisture content was statistically different (P 0.05), below 1% for all formulations. The product manufactured is stable in terms of its physicochemical and rheological characteristics over time. In a product such as the one produced, there is no intentional addition of water. Raw materials incorporate moisture that is removed during the prolonged time the product's elaboration (22 hours for this formulations). The time of process contributes to product refining, volatilization of organic acids, and evaporation of water present in the complex matrix of the spread. However, F5 showed the lowest lipid contribution, which indicates that the proportions of ingredients used to generate a good interaction, obtaining a product with values below 40%. This product, according to the world legislations, cannot be considered as "light." Minimum reduction of 25% in a given nutrient or calories, compared to conventional food, but it is interesting to determine its contribution in fatty acids, to know the nutritional effect that would have the incorporation of sesame. Likewise, it observed that the contribution of crude protein presented statistically significant differences for each formulation, highlighting F3, with a content of more than 10g / 100g of product. This information is indispensable because commercially, there are very few products (of this type) with similar contributions. However, for more accurate comparisons, the amino acid content of the sesame oil cake should be determined. The values discussed above directly affect the carbohydrate content and, in turn, allowed to obtain a caloric contribution that decreases (F1> F2> F3> F4> F5) according to the specific order of the formulations. Similar or different values exist in the literature compared to those obtained for this work. Still, it necessary to look at the nutritional and economic benefit that a change in the original spread's formulations can cause consumers.



The data presented in Table 4 present the fatty acid composition of the cocoa spreads. The statistical analysis of the data revealed that the use of sesame significantly increased the unsaturated fatty acids compared to the control (except for F2). In contrast, monounsaturated fatty acids decreased significantly as a result of the replacer, mentioned earlier (equally, except for F2). PUFA's, were not detected in the evaluated formulations. Salinas and Bolívar (2012), report for commercial brands (MC) of chocolate analogs (spreads) obtained 1.5% in ω -9 and 42% in ω -6, and for MC J ω -9 it was 1.31% and ω -6 in 46.40%. These results are lower than the results found in the formulas developed for both omega 6 and omega 9 fatty acids. SERNAC (2015), reported monounsaturated fatty acids from 9.5% to 12.5% and polyunsaturated from 1% to 1.5%, for different commercial chocolate. The three most characteristic cocoa fatty acids (C16: 0 palmitic, C18: 0 stearic and C18: 1 oleic) are present in all formulations.

Conclusion

It is feasible to develop spreads based on cocoa with the utilization of sesame oil and sesame oil cake (and less use of hydrogenated fat). Greater incorporation of oil, it is necessary to add coadjutants agents that limit phase separation of the matrix. There is evidence that, in general, there are positive effects by incorporating sesame in the form of flour and oils on the nutritional properties of formulated spreads.

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Figure 1. Apparent viscosity of spreadable cocoa cream, measured at 44 $^{\circ}\mathrm{C}$ using Brookfield Viscometer



Figure 2. Bostwick consistometer of spreadable cocoa cream traveled (cm) at time 30 seconds



Table 1. CIELAB color parameters of spreadable cocoa cream, Lightness (L*); Green/red parameter (a*); Blue/yellow parameter (b*); index of brown (IB); Chroma (C*_{ab}); and Hue angle (h_{ab}).

	F1 (control)	F2	F3	F 4	F5
L*	30.80 ± 0.06^a	$18.81\pm0.05^{\rm c}$	16.97 ± 0.02^{d}	16.16 ± 0.04^{e}	20.04 ± 0.06^{b}
a*	17.05 ± 0.00^{a}	14.52 ± 0.01^{c}	14.74 ± 0.04^{b}	14.60 ± 0.05^{bc}	14.15 ± 0.03^{d}
b*	28.69 ± 0.19^{a}	23.20 ± 0.07^{b}	22.78 ± 0.13^{bc}	22.26 ± 0.16^c	23.34 ± 014^{b}
IB	69.20 ± 0.06^{e}	81.19 ± 0.05^{c}	83.03 ± 0.02^{b}	83.84 ± 0.04^a	79.96 ± 0.06^{d}
Chroma	33.38 ± 0.16^a	27.37 ± 0.06^{b}	27.13 ± 0.09^{bc}	26.62 ± 0.14^{c}	27.29 ± 0.13^{b}
Hue angle	59.28 ± 0.16^a	57.96 ± 0.06^{b}	57.10 ± 0.20^{c}	56.74 ± 0.22^{c}	58.77 ± 0.11^{a}

Results are means of 3 determinations \pm SE. The letters after values reveal the statistical significance of the differentiation, and two letters represent the entire interval in alphabetical order (e.g., ae means a, b, c, d, e). Different letters denote significant differences between values (Tukey HSD test, p < 0.05).

Table 2. Overall colorimetric differences (ΔE^*ab) between spreadable cocoa cream and each of the formulations used as control

	F1 (control)	F2	F3	F4	F5
ΔE^1	$0.00\pm0.00^{\text{e}}$	14.43 ± 0.05^{c}	$15.22\pm0.06^{\text{b}}$	16.18 ± 0.05^{a}	12.37 ± 0.06^{d}
ΔE^2	143.85 ± 1.39^a	0.00 ± 0.00^{d}	3.37 ± 0.06^{c}	7.02 ± 0.21^{b}	1.52 ± 0.16^{cd}
ΔE^3	191.27 ± 1.60^{a}	3.38 ± 0.17^{c}	$0.00\pm0.00^{\rm c}$	0.66 ± 0.06^{c}	9.41 ± 0.39^{b}
ΔE^4	214.44 ± 1.69^a	7.03 ± 0.25^{c}	$0.66\pm0.03^{\text{d}}$	0.00 ± 0.00^{d}	15.06 ± 0.49^b
ΔE^5	115.86 ± 1.24^a	$1.52\pm0.11^{\text{d}}$	9.40 ± 0.11^{c}	15.06 ± 0.31^{b}	0.00 ± 0.00^{d}

Results are means of 3 determinations \pm SE. The letters after values reveal the statistical significance of the differentiation, and two letters represent the entire interval in alphabetical order (e.g., ae means a, b, c, d, e). Different letters denote significant differences between values (Tukey HSD test, p < 0.05).

Table 3. Means of chemical and compositional analysis for the spreadable cocoa cream

	F1 (control)	F2	F3	F4	F5
Moisture	0.30±0.09 ^a	$0.47 \pm 0.04^{\circ}$	0.30±0.02 ^a	$0.40{\pm}0.08^{b}$	0.69 ± 0.89^{d}
Ash	$1.72{\pm}0.49^{a}$	2.76±0.11 ^e	2.60 ± 0.16^{d}	2.36±0.31°	2.02 ± 0.53^{b}
Protein	7.51±0.35 ^a	$9.54{\pm}0.46^{d}$	10.31 ± 0.15^{e}	9.47±0.52c ^e	9.41 ± 0.32^{b}
Lipid	43.52±0.58°	44.13 ± 0.14^{d}	41.68 ± 0.07^{b}	41.61±0.19 ^b	38.35±0.04 ^a
Carbohydrate*	46.95 ± 0.00^{d}	43.10±0.00 ^a	45.16 ± 0.00^{b}	46.04±0.00 ^c	49.89±0.00 ^e
Energy**	609.54	607.74	596.99	596.54	582.33

* Determinate by difference

** Expressed in Kcal/100g of spreadable cocoa cream

Results are means of 6 determinations \pm SE. The letters after values reveal the statistical significance of the differentiation, and two letters represent the entire interval in alphabetical order (e.g., ae means a, b, c, d, e). Different letters denote significant differences between values (Tukey HSD test, p < 0.05).



	F1 (control)	F2	F3	F4	F5
Palmitic	35.59 ± 1.07^{d}	40.70 ± 0.52^{e}	30.63 ± 1.17^{b}	20.94 ± 1.40^{a}	31.03 ± 1.73^{c}
Stearic	6.94 ± 0.75^{e}	5.66 ± 0.04^{a}	6.38 ± 0.11^{c}	6.32 ± 0.67^{b}	6.65 ± 0.23^{d}
Oleic (ω -6)	39.58 ± 1.73^{a}	41.04 ± 0.30^{b}	44.66 ± 0.87^{c}	48.50 ± 0.58^{e}	45.22 ± 1.84^{d}
Linoleic (ω-9)	$17.89 \pm 1.41^{\circ}$	13.06 ± 0.93^a	$18.33\pm0.22^{\text{d}}$	24.26 ± 0.21^{e}	17.09 ± 0.33^{b}
SFA	42.53 ± 0.01^{d}	46.36 ± 0.01^{e}	37.01 ± 0.01^{b}	27.25 ± 0.01^{a}	37.69 ± 0.01^{c}
UFA	57.47 ± 0.01^{b}	54.10 ± 0.01^{a}	$62.99\pm0.01^{\text{d}}$	72.76 ± 0.01^{e}	$62.32 \pm 0.01^{\circ}$

Table 4. Fatty acid composition of spreadable cocoa cream

SFA: Saturated Fatty Acids UFA: Unsaturated Fatty Acids

Results are means of 3 determinations \pm SE. The letters after values reveal the statistical significance of the differentiation, and two letters represent the entire interval in alphabetical order (e.g., ae means a, b, c, d, e). Different letters denote significant differences between values (Tukey HSD test, p < 0.05).