

Composition, properties, stability and thermal behavior of tamarind (*Tamarindus indica*) seed oil

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SUMMARY: The composition, thermal stability and phase behavior of tamarind (*Tamarindus indica*) seed oil were analyzed to contribute to the exploration of their potential uses. The oil was extracted from the kernel of the tamarind seed with hexane, and its main physical, chemical and thermal properties were analyzed by infrared spectrometry, gas chromatography-mass spectrometry, DSC, and TGA. The results showed that the tamarind seed had a $3.76 \pm 0.20\%$ oil with a saponification index of 174.80 ± 9.87 mg KOH/g and the major fatty acids were lignoceric (20.15%), oleic (18.99%) and palmitic (11.99%). Stearic, behenic, linoleic, arachidic, and other fatty acids were also present. TGA and DSC showed that in an inert atmosphere, the triacylglycerols of tamarind seed oil (TSO) are decomposed in a single stage that starts at 224.1 °C and in an air atmosphere in three stages, initiating its decomposition at 218 °C. The TSO showed crystallization and fusion curves with a single maximum peak with T_{onset} and T_{offset} of 20.16 and -38.8 °C and -22.2 and 28.6 °C, respectively. The solid fat profile of the oil showed a semi-solid and liquid consistency in the ambient temperature range. The composition, thermal and phase behavior showed that TSO is potentially useful for alimentary, pharmacological, and cosmetological purposes.

KEYWORDS: DSC; Lignoceric acid; Tamarind seed oil; *Tamarindus indica*; TGA

RESUMEN: *Composición, propiedades, estabilidad y comportamiento térmico del aceite de semilla de tamarindo (Tamarindus indica).* La composición, estabilidad y comportamiento térmico del aceite de semilla de tamarindo (*Tamarindus indica*) fueron analizadas con el fin de contribuir al conocimiento de sus potenciales usos. El aceite fue extraído del núcleo de la semilla con hexano y analizado mediante sus principales propiedades físicas, químicas y térmicas mediante espectrometría infrarroja, cromatografía de gases, espectroscopia de masas, calorimetría (DSC) y termogravimetría (TGA). Los resultados mostraron que las semillas del tamarindo tuvieron un contenido de aceite de $3,76 \pm 0,20\%$, con un índice de saponificación de $174,80 \pm 9,87$ mg KOH/g y ácidos grasos mayoritarios: Lignocérico (20,15%), oleico (18,99%), palmítico (11,99%) y en cantidades menores los ácidos esteárico, behénico, linoleico y araquídico, entre otros. El análisis mediante TGA y DSC mostró que la temperatura inicial de descomposición del aceite fue de 224,1 °C en una sola etapa en atmósfera inerte y en atmósfera de aire fue a 218 °C en tres etapas. El aceite mostró curvas de cristalización y fusión con un solo máximo, iniciándose y finalizando estos cambios de fase a 20,16 y $-38,8$ °C, and $-22,2$ y 28,6 °C, respectivamente. Estas propiedades mostraron que el aceite de la semilla de tamarindo tiene potenciales aplicaciones en alimentos y productos farmacológicos y cosméticos.

PALABRAS CLAVE: Aceite de semilla de tamarindo; Ácido lignocérico; DSC; *Tamarindus indica*; TGA

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1. INTRODUCTION

Tamarind, (*Tamarindus indica*) known in Senegal and India since ancient times, has been considered a multi-purpose plant. Several reports have shown that in addition to the known uses for the pulp as a food, its husk, seeds, leaves, flowers, wood, and tree bark, have diverse potential uses (Rasala *et al.*, 2011; Rao *et al.*, 2015). The food, pharmaceutical, and cosmetic industries are the main receiving sectors, due to the presence of fractions and chemical components of relevant interest to them (De Caluwé *et al.*, 2010; Bhadoriya *et al.*, 2011; Rasala *et al.*, 2011).

In Mexico, the tamarind does not reach an important industrial level or a full and integral use yet, as is also the case in many of the poorest producing regions of this fruit located in Latin America, Asia or sub-Saharan Africa. This tropical plant has been introduced and naturalized in more than 50 countries around the world (Rao *et al.*, 2015).

The flowers, leaves and pulp of the fruit are edible and have important nutrients. The latter has a characteristic sweet-acidic flavor due to the combination of high contents of tartaric acid and reducing sugars. In fact, the tamarind is the largest natural source of this acid widely used in Asian gastronomy (De Caluwé *et al.*, 2010). The fruit is appreciated for its characteristic flavor, sometimes qualified as exotic, because its pulp contains more than 16 volatile components which participate in the conformation of its flavor. The sesquiterpene aromadendrene, also found in oils of eucalyptus trees, has been identified as the major volatile constituent (Rasala *et al.*, 2011).

In several countries, the tamarind pulp, aside from being consumed fresh, is used for flavoring and applied as a component of food, for example in jams, sweet sauces and hot sauces, and also as an important ingredient in juices and some soft drinks (El-Siddig *et al.*, 2006; De Caluwé *et al.*, 2010). In most of those applications the seed is discarded as a residue without any value. However, in some countries the seed has been considered a by-product of the industries that process the pulp of the fruit, on the basis that further use has been found for it, derived from some of its properties (Rao *et al.*, 2015). Studies and experimental analyses on the properties of the tamarind seed from the perspective of its potential use are relatively scarce as yet.

The tamarind seed, which includes an external cover or testa (20–30%) and the nucleus or endosperm (70–75%), contains important compounds such as antioxidants and dyes (Bhadoriya *et al.*, 2011). Its endosperm has proteins of relevant quality, carbohydrates with important functional properties to be used as thickeners and gums, and an interesting lipid fraction from the point of view of some of its properties (Kumar and Bhattacharya, 2008).

The presence in seeds of tannins and some other colorant materials in the test portion, makes its direct consumption inadequate for food (Kumar and Bhattacharya, 2008), but treatments such as soaking and cooking in water make it an edible product, mainly for animals (El-Siddig *et al.*, 2006). Currently, the largest industrialized product of tamarind seed is in powder form which is a material used in the paper, textile and jute industries (Kumar and Bhattacharya, 2008; Rao *et al.*, 2015).

Tamarind seed is the raw material for the elaboration of the polysaccharide jellose, some adhesive products, and for obtaining tannins. Jellose with gelling properties is commercially available as a food additive and is recommended to be used as a stabilizer in ice cream, mayonnaise and cheese, and as an ingredient or agent in pharmaceutical products (El-Siddig *et al.*, 2006).

Concerning the tamarind seed oil (TSO), studies have been reported about some of its properties, such as its fatty acid composition and other basic physicochemical characteristics. Several authors have reported different extraction yields of tamarind seed oil from different producing regions, some of them with relatively high values such as 16.25% (Morad *et al.*, 1978) although most in a range between 3.0–10.91% of extracted oil with hexane, ether or mixtures of chloroform/methanol (Adriamanantena, *et al.*, 1983; Ajayi *et al.*, 2006).

The fatty acid composition of tamarind seed oil has been addressed by several authors such as Pitke *et al.*, (1977), Reddy *et al.*, (1979), Morad *et al.*, (1978), Andriamanantena *et al.*, (1983), and Ajayi *et al.*, (2006). However, their results still show important discrepancies in terms of some of its fatty acid components.

The knowledge concerning the effects of heating fats and oils is basic and can be used to determine some of their physical and chemical properties which are important for the evaluation of their potential applications. The complexity and diversity of the thermal profiles and phase behavior of fats and oils are due to the variety of both the triacylglycerides (TAG) and their main fatty acid constituents, FA (Tan and Che Man, 2000; Santos *et al.*, 2004; O'Brien, 2008; Borugadda and Goud, 2014; Solís-Fuentes *et al.*, 2015). However, there are currently no studies aimed at analyzing the thermal and phase properties of the tamarind seed oil that contribute to determine, in a better way, their possible alternative uses.

As it is known, information on the thermal stability of vegetable fats and oils is essential for the identification of their potential uses, and many of the most important properties of fats and oils are related to their phase behaviour, mainly in the solid/liquid and liquid/solid transitions. This behavior is dependent on, among other variables, the composition of fatty acid and triacylglycerides, as well as the

polymorphic properties assumed in the solid phase (O'Brien, 2008; Roos, 2016).

In order to contribute to tamarind seed oil knowledge and to visualize alternatives uses within the perspective of an integral use of tamarind, the objective of this paper was to study the seed of the tamarind and characterize its extracted oil by infrared spectroscopy and fatty acid composition, as well as analyzing the thermal stability and phase behavior of the tamarind seed oil by thermogravimetry and differential scanning calorimetry.

2. MATERIALS AND METHODS

2.1. Obtaining tamarind samples

Samples of tamarind fruits (*Tamarindus indica*) chosen according to their physiological maturity, which is in terms of the color and texture of their skin and pulp, were acquired in a local market near the production area of this product, in the municipality of Paso de Ovejas (19° 17' north latitude, 96° 26' west longitude), in the central coastal region of the State of Veracruz in Mexico. The samples were evaluated in terms of the number of seeds per pod, the masses and percentages of the husk, pulp, and seed, and kernel of the seed. For the latter, two samples of five tamarind fruits each were separated and weighed in their main portions in an analytical balance and the average mass and percentage of each portion in the total of the fruit were estimated.

2.2. Physicochemical analysis of the seed nucleus

The official analysis techniques were used to determine the moisture, ash, crude fiber and crude fat (Horwitz, 1995) contained in the nuclei of the tamarind seed.

2.3. Extraction, purification, physical and chemical characterization of seed oil

The oil was extracted from the dehydrated kernels of the tamarind seed (with approximately 10% moisture) using hexane as a solvent in a Soxhlet apparatus and the resulting micelle was processed in a rotary evaporator for oil recovery. The raw TSO was purified by a modification of the Wesson method described in Solís-Fuentes *et al.*, (2015). The purified oil was deposited in glass containers and stored under refrigeration conditions (−5 °C) and protected from light, until analysis and/or further processing. The purified TSO was evaluated by a group of untrained judges, in terms of the perception of its consistency at room temperature, color, odor and taste. The oil was physicochemically analyzed to determine its refractive index, free fatty acids, acidity index, and saponification index using the official analysis techniques (Horwitz, 1995).

2.4. Infrared spectroscopy (FT-IR) of tamarind seed oil

A Perkin-Elmer Spectrum Two FT-IR spectrophotometer was used. The data were processed with the help of the Spectrum software. In the case of the liquid sample, its IR analysis did not require any previous preparation.

2.5. Analysis of the fatty acid composition of tamarind seed oil

Fatty acid methyl esters were prepared by saponification of purified tamarind seed oil and an acid-catalyzed methylation, using an alcoholic solution of 2.5% KOH and a methanol solution to 2% H₂SO₄ (Anu and Rao, 2001).

For the analysis of the fatty acids constituents of the acylglycerols of TSO, a gas chromatograph Shimadzu was used, equipped with a column of polydimethylsiloxane with 5% phenyl, ZB-5MSi, of 30 m x 0.25 mm x 0.25 μm, coupled to a Shimadzu mass spectrometer provided with a full spectrum scan detector (SCAN) of 50 to 500 -m/z. A mixture of fatty acid standards (FAME mix 37 SUPELCO) was used to support the identification of the methyl esters in the sample. The operating conditions in the chromatograph were: an initial temperature of 100 °C for 5 min, with a heating rate of 4 °C/min up to 250 °C for 15 min; the carrier gas was helium at 0.8 mL / min, the injector temperature was 250 °C and, an ionization source of electronic impact was used.

2.6. Thermal stability of TSO

The thermal stability of the TSO was analyzed by thermogravimetry in atmospheres of nitrogen and air in a TGA Q5000 IR (TA Instruments), using a sample holder of alumina. The changes in mass were monitored in a working interval of 25 to 1000 °C to obtain the TG and DTG data and graphs. The capture of the data in an ASCII code made analysis possible and the results were graphically edited in the Origin software (OriginLab, 2007).

2.7. Phase behavior of TSO

TSO samples were analyzed in a TA Instruments DSC Q2000 differential scanning calorimeter equipped with a TA Universal Analysis data analysis station. The purge gas was nitrogen at a flow of 50 mL/min. The instrument was calibrated with Indium (melting point 156.6 °C; DH_f, 28.45 J/g). Samples between 2 and 12 mg were weighed in a thermobalance (TA instruments) in aluminum SFI capsules with a precision of ±0.1 mg and then hermetically sealed. An empty and sealed capsule was used as reference. Each of the samples was heated

up to 90 °C with an isotherm of 5 min with the aim of destroying its thermal history. To analyze the thermal behavior of the oil, the following conditions were used: Crystallization profile: the sample was heated up to 90 °C for 5 min and cooled to 5 °C/min to -80 °C to record the crystallization profile, crystallization enthalpies, and the onset and offset temperatures of the phase changes.

Fusion profile: the sample was heated from -80 to 5 °C/min up to 90 °C, and the melting profile, the enthalpy and the onset and offset temperatures of the phase changes were recorded.

2.8. Solid/Liquid relationships of TSO

The amount of solids in the oil samples as a function of temperature were calculated based on the experiments in the DSC, according to the methodology outlined by Lambelet and Raemy (1983) and with the use of the computation package Origin (OriginLab, 2007). Since the contents of solid fat depend on the temperature, these values can be presented as a function of it. The values for the solid content can be expressed, by sequential integration of the melting curve, by means of equation 1. The partial areas of the thermograms were calculated and correlated with the percentage of solids considering that at -80 °C the oil samples are practically 100% solid.

$$\%Solids(T) = \frac{\int_{T_0}^T H(T) dt}{\int_{T_0}^{T_1} H(T) dt} \quad (1)$$

3. RESULTS AND DISCUSSION

3.1. The fruit of tamarind and its constituent portions

The samples of the physiologically mature tamarind fruit were pods with brown skin rind and rust colored pulp with an average mass of 16.37 g per fruit. The mass of each anatomical constituent part of the pods was on average 21.61% husk, 58.0% pulp and 20.34% seeds. The fruit had between 3 to 4 seeds for each pod unit.

3.2. Physicochemical analysis of the seed nucleus

The tamarind seeds had an average mass of 0.87 g/seed with a bright, dark color. They were constituted by an external cover or testa and a nucleus or endosperm; the latter represented, on average, 77.73 ± 3.56% of the total seed mass. Table 1 presents some of the main physical and chemical characteristics of the fruit, seeds and oil extracted from tamarind. The chemical analysis of the endosperm

TABLE 1. Physical and chemical characteristics of the fruit and oil extracted from the tamarind seed

Characteristic	Value±SD ^a
<i>Tamarind fruit</i>	
Average mass, g	16.37±4.31
Husk, %	21.61±4.90
Pulp, %	58.00±2.10
Seeds, %	20.34±2.50
Seeds, average number	3.81±1.60
<i>Tamarind seed</i>	
Moisture, %	11.61±0.33
Nucleus of the seed, %	77.73±3.56
Ash, % db	3.71±0.27
Crude fiber, % db	2.09±0.51
Crude fat, % db	3.76±0.20
<i>Tamarind seed oil</i>	
Consistency, 25 °C	Liquid
Color:	Amber
Odor:	Characteristic
Taste:	No taste
Refractive index	1.465
Saponification value, mg KOH/g	174.80±9.87
Free fatty acids, %	3.12±0.24
Acidity index, mg oleic acid/g	6.22±0.47

^a: Average values of two determinations ± standard deviation

of the tamarind showed moisture content of 11.61 ± 0.33%. The main fractions were the carbohydrates and the proteins accounting for around 90% of the dry solid. Its contents of ashes, crude fiber and crude fat were of 3.71 ± 0.27, 2.09 ± 0.509, and 3.76 ± 0.20% (d.b.), respectively.

3.3. The oil of the tamarind seed

The refined oil of the tamarind seed had a liquid consistency under environmental conditions (around 25 °C), a light amber color, a characteristic smell, and an undefined flavor.

TSO had a refractive index of 1.465, saponification and acidity indices of 174.80 ± 9.87 mg KOH/g and 6.215 ± 0.47 mg oleic acid/g, respectively; and a content of 3.12 ± 0.24% of free fatty acids. These values are close to those reported by Pitke *et al.*, (1977) and Adewuyi *et al.*, (2011). Table 1 summarizes the physical and chemical characteristics of this oil.

3.4. FTIR spectrum of tamarind seed oil

Figure 1 shows the FTIR spectra of TSO. Figure 1(a) corroborates that the hexane fraction extracted from the tamarind seed corresponds to a

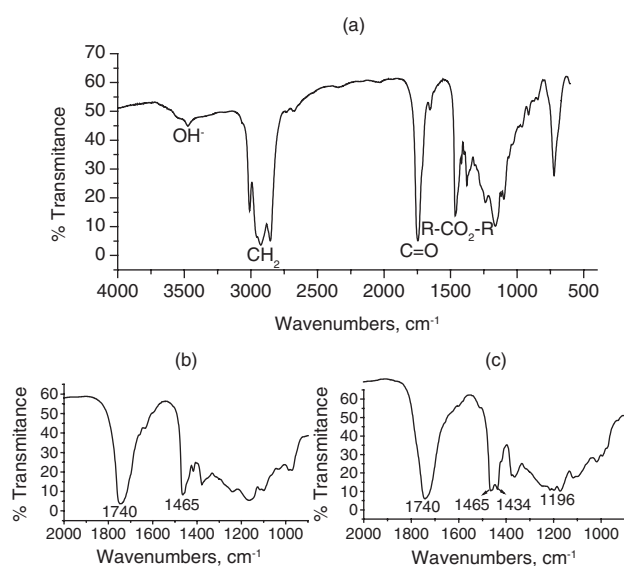


FIGURE 1. FTIR spectra of (a) refined tamarind seed oil; (b) main signals from 2000-900 cm^{-1} of purified tamarind seed oil; (c) main signals from 2000-900 cm^{-1} of methyl esters of fatty acids from tamarind seed oil.

vegetable oil. The peaks and shoulders provide information about their structure and functional groups. In the region of high frequencies (around 3465 cm^{-1}), the absorption corresponding to the hydroxyl groups, including water (residual moisture in the analyzed sample), is identified; at lower frequencies, the signals ($3025\text{--}2838 \text{ cm}^{-1}$) of the methyne and methylene groups (from the double bonds and the aliphatic chains of the triacylglycerols) and methyl groups (methyl terminal) are identified.

At the center of the spectrum near 1753 cm^{-1} there is a strong signal corresponding to the carbonyl groups due to the ester bonds of fatty acids and glycerol of the triacylglycerols of the oil, including free acid carbonyl bonds from the free fatty acids present in the sample analyzed. Finally, the region of low frequency between $1500\text{--}800 \text{ cm}^{-1}$, is considered the area where a group of signals appears due to the absorption of characteristic groups of lipid compounds, including double bonds, conjugated dienes, etc. (Shahidi and Wanasundara, 2002).

The FTIR analysis was also used together with the thin layer chromatography, as a complement to corroborate the progress and result of the methylation process of the tamarind seed oil, prior to the determination of its composition. Figures 1b and 1c present the FTIR spectra of both the tamarind seed oil and the oil after having been derivatized to their corresponding methyl esters of the fatty acids. These figures show the frequency range which goes from 1500 to 1000 cm^{-1} , and covers the region considered as characteristic of each vegetable oil ($1500\text{--}800 \text{ cm}^{-1}$). The peak at 1434 cm^{-1} corresponds to the asymmetric stretching of $-\text{OCH}_3$

and is present in the spectrum of fatty acid methyl esters of tamarind seed, but not in the oil spectrum. This peak is typical of a mixture of methyl esters of fatty acids. (Shahidi and Wanasundara, 2002; Rabelo *et al.*, 2015).

3.5. Fatty acid composition of TSO

Table 2 presents the results of the fatty acid analysis of TSO made by gas chromatography and mass spectroscopy. The composition of this oil has a higher content of saturated fatty acids, with 63.95% of the total; highlighting a high content of long-chain saturated FAs: lignoceric acid with 20.15%, palmitic (11.91%) and stearic (7.63%), followed by behenic (7.57%) and arachidic (5.33%). The saturated medium-chain fatty acids, caprylic, capric, azelaic and lauric, as well as myristic, margaric and long-chain tricosylic acid, were present in this tamarind seed oil with individual percentages lower than 2% each.

TSO fatty acids are 32.39% unsaturated, with the majority being oleic acid (18.99%), linoleic (4.94%), and palmitoleic acid (4.22%). Also, 9-cis-hexadecenoic acid (palmitoleic 1.95%) and 7-cis-hexadecenoic acid (0.45%), were present. Some other complex fatty acids were also identified: Epoxy acids, oxo acid, and hydroxylated and branched fatty acids, whose content as a whole was 7.48%. 3.65% of the total fatty acids could not be identified.

Different reports found on the fatty acid composition of tamarind seed oil differ greatly from one another, both considering the presence of different fatty acids in the oil, as well as in the percentages assigned to each of them. The results obtained in the present work are closely related, but with some differences, to those reported by Pitke *et al.*, (1977), which include palmitic (14.8%), stearic (5.9%), oleic (27.0%), linoleic (7.5%), linolenic (5.6%), arachidic (4.5%), behenic (12.2%), and lignoceric (22.3%) acids.

According to the results of this work, the TSO does not contain short-chain fatty acids ($< 6\text{C}$) and the percentages of saturated fatty acids classified according to chain length were medium-chain fatty acids (MCSFA, between 6C and 12C): 2.95%, long-chain saturated FA (LCSFA, between 14C and 20C): 30.73% and very-long-chain saturated FA (VLCSFA, $> 20\text{C}$): 28.46%. The unsaturated fatty acids in the oil were all of long-chain.

An interesting feature of the composition of the TSO is its high content of LCSFA and mainly VLCSFA. The saturated fatty acids with aliphatic-chain $> 20\text{C}$, that is arachidic, behenic, tricosylic, and lignoceric acids, were 33.79% in total.

The role of long- and very-long-chain saturated fatty acids in nutrition and human health is not fully established yet, but it is known that very-long-chain saturated fatty acids (VLSFA) play an important

TABLE 2. Fatty acid composition of tamarind seed oil

Fatty acid	Delta notation	Retention time	% Area
Caprylic	8:0	8.174	0.23
Capric	10:0	14.801	0.08
8-oxooctanoic	8-O=8:0	15.090	0.47
9-oxo nonanoic	9-O=9:0	18.583	1.18
Azelaic	8-COOH-8:0	22.246	0.55
Lauric	12:0	21.476	0.44
Tridecylic	13:0	24.588	0.22
Cis-7-Hexadecenoic	16:1-delta-7c	26.795	0.41
Myristic	14:0	27.544	1.44
Pentadecylic	15:0	30.335	0.85
Palmitoleic	16:1-delta-9c	32.410	1.95
Palmitic	16:0	33.222	11.91
cis-10-Heptadecenoic	17:1-delta-10c	34.961	0.26
Margaric	17:0	35.542	0.95
Linoleic	18:2-delta-9c, 12c	37.567	4.94
Oleic	18:1-delta-9c	37.718	18.99
Stearic	18:0	38.102	7.63
Oxiraneoctanoic, 3-octyl	9,10-O-18:0	41.549	1.78
Paulinic	20:1-delta-13c	42.036	4.22
Arachidic	20:0	42.604	5.33
6-Hexadecenoic acid, 7-methyl	7-Me-16:2-delta-6t	43.197	1.62
Octadecanoic, 9,10-dihydroxy	R9,R10-di-OH-18:0	44.604	2.43
Behenic	22:0	47.809	7.57
Tricosylic	23:0	51.049	0.74
Lignoceric	24:0	55.933	20.15
Non identified			3.65
Total saturated fatty acids			63.95
MCSFA			2.95
LCSFA			32.32
VLCSFA			28.46
Total unsaturated fatty acids			32.39

MCSFA: medium-chain saturated FA; LCSFA: long-chain saturated FA; VLCSFA: very-long-chain saturated FA

role in the structure, cellular and organic functioning of the body. The VLSFA are major components of ceramides and sphingomyelins, lipids formed by a main chain of sphingosine with an acylated FA, often saturated (Quehenberger *et al.*, 2010). Recent studies have analyzed the role of circulating levels of very-long-chain fatty acids on some metabolic and cardiovascular diseases (Fretts *et al.*, 2014; Lemaitre *et al.*, 2014, 2015). The determining causes of high levels of VLSFA can be either dietary or metabolic. VLSFA such as behenic, arachidic, and lignoceric acids are found in only some foods such as peanuts, macadamia nuts, and canola oil, and their

consumption has been associated with high levels of these FA in plasma.

Lemaitre *et al.*, (2015) found an association of higher levels of VLSFA with plasma phospholipids with a lower risk of incidence of diabetes, which may be mediated by lower levels of triglycerides and palmitic acid phospholipids in plasma. Fretts *et al.*, (2014) and Lemaitre *et al.*, (2014) determined inverse associations of VLSFA with an incident of atrial fibrillation and an incidental sudden cardiac arrest.

On the other hand, as ceramides are the base molecules of sphingolipids, they are very abundant

in the lipid bi-layer of cell membranes and their exocytosis to the intercellular space allows them to function as the cementing substance due to the amphiphilic chemical structure in the stratum corneum, one of the four different sublayers of skin epidermis (Sahle *et al.*, 2015). The fact that ceramides usually contain very-long-chain fatty acids such as lignoceric, nervonic, or cerebronic acids, has led to the consideration that, particularly lignoceric acid, has an interesting potential use in the elaboration of dermatological oils and medicines, products that have been developed up to now, mainly based on behenic acid, due to its softening and moisturizing action on the skin (Sahle *et al.*, 2015).

Lignoceric acid is found in trace amounts in almost all edible vegetable oils, with some exceptions, such as peanut oil, whose content is close to 1%. It is contained in higher amounts in sources with no commercial production. Some wild plant seeds have been reported with high content of long- and very-long-chain saturated fatty acids, in which lignoceric acid is present in high percentages (Spitzer *et al.*, 1990). Akhtar *et al.*, (1986) reported that some seeds of the Cruciferae family, such as *Erysimum perofskianum*, have lignoceric acid in their oils up to 23.2%; Hondelmann and Radatz (1982) found that *Lunaria annua* oil has 21% of this FA; and Sultana and Gulzar (2012) found that this fatty acid is present in the *Adenantha pavonina* oil at a level of 20.24%.

The tamarind seed, being a residue of the consumption and industrialization of this fruit with a wide acceptance in the world, acquires an interesting role as a potential source of oil with long- and very-long-chain fatty acids and especially as a source of lignoceric acid, identified, as noted earlier, with important functional properties which are protective of the health of the human organism in regards to the cardiovascular, endocrine and skin systems.

3.6. Thermal stability of TSO

When vegetable fat and oils are exposed to high temperatures, a process of deterioration occurs. However, these oils sometimes have natural antioxidants that tend to increase the stability of the products made with them. The stability of the oil to heat treatment is an aspect of great importance as is the degree and speed of decomposition of the constituents of the oil. It depends on many factors that include both the treatment conditions (time, temperature level, presence of oxygen, water and other constituents, etc.) and the fatty acid and acylglyceride compositions of the oil.

Figure 2 shows the TG and DTG curves of TSO in a nitrogen atmosphere and allows the decomposition process of the oil sample to be analyzed by

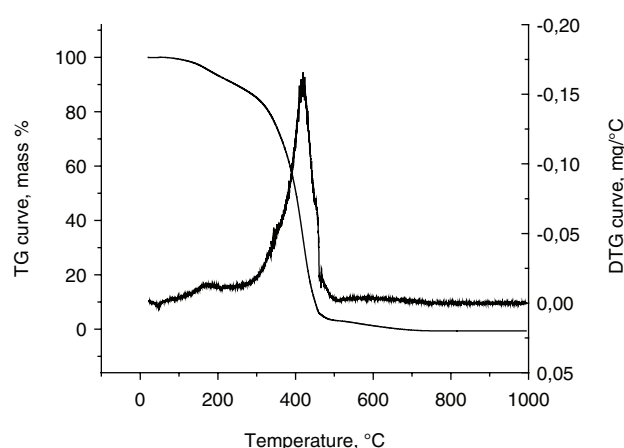


FIGURE 2. TG and DTG curves of tamarind seed oil in nitrogen atmosphere.

this thermal treatment by heating it from 25 °C to 1000 °C. The curves show a process completed in only two stages. The first one is attributed to the elimination of residual water and volatile oil materials appreciated in the characteristic aroma of the TSO, as was found in the FTIR analysis. This stage had a maximum decomposition speed of 0.014 mg/°C at 166.8 °C, and a total loss in mass of 6.94%, starting at 108.8 °C and ending at 223.16 °C.

The second stage corresponded to the decomposition of the constituent acylglycerols of the TSO, which, as has been identified by other researchers, occurs in an inert atmosphere, around an interval that was from 220 to 420 °C (Melzer *et al.*, 2013). This stage of tamarind seed oil decomposition was observed from 224.1 to 509 °C, with a maximum speed of 0.163 mg/°C at 418.42 °C, and with a mass loss along this stage of 90.48%. The global residue obtained was 2.58%.

The main data of the thermogravimetric analysis of TSO are presented in Table 3, and Figure 3 shows the TG and DTG curves of the oil sample in an air atmosphere. In this case the decomposition process includes a more complex set of reactions due to the presence of oxygen from the air and in addition to the first stage corresponding to the loss of residual moisture and volatile compounds, whose maximum peak occurs at 145.41 °C. The whole decomposition process of the neutral lipids of TSO required three additional stages, from which the first one started at 218 °C and ended at 361.25 °C, with a mass loss of 22.79%. The next stage occurred with a maximum decomposition speed of 0.079 mg/°C at 417.63, finishing at 477.91 °C. Finally, one last stage was present, which ended at 616 °C. The residual mass resulting from the thermal and oxidative decomposition of the TSO was 4.78%. This thermal behavior of decomposition of TSO is similar

TABLE 3. Main data of thermogravimetric analysis of tamarind seed oil

Stage	Nitrogen atmosphere				Air atmosphere			
	ΔT_{decom} °C	T_{peak} °C	$-\Delta_{\text{mass}}$ %	R_{decom} mg/°C	ΔT_{decom} °C	T_{peak} °C	$-\Delta_{\text{mass}}$ %	R_{decom} mg/°C
1	108.88–223.16	166.80	6.94	−0.014	93.88–217.36	145.41	6.58	−0.008
2	224.10–509.07	418.42	90.48	−0.163	218.00–361.25	322.27	22.79	−0.019
3					362.10–477.91	417.63	50.78	−0.079
4					478.50–600.16	544.02	15.07	−0.017
Total	108.88–509.07		97.42		93.88–600.16		95.22	
Residue			2.58%				4.78	

Value of temperature (T) and rate (R) in the Table represents the means of two determinations, with SD < 1.0 °C and SD < 0.001 mg/°C, respectively, from Fig. 2 and 3. ΔT_{decom} : Decomposition interval; T_{peak} : Temperature of the maximum decomposition rate; $-\Delta_{\text{mass}}$: Percentage of mass loss; R_{decom} : Decomposition rate

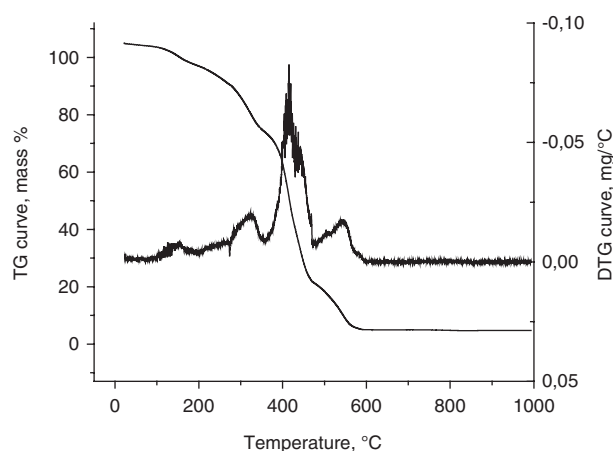


FIGURE 3. TG and DTG curves of tamarind seed oil in air atmosphere.

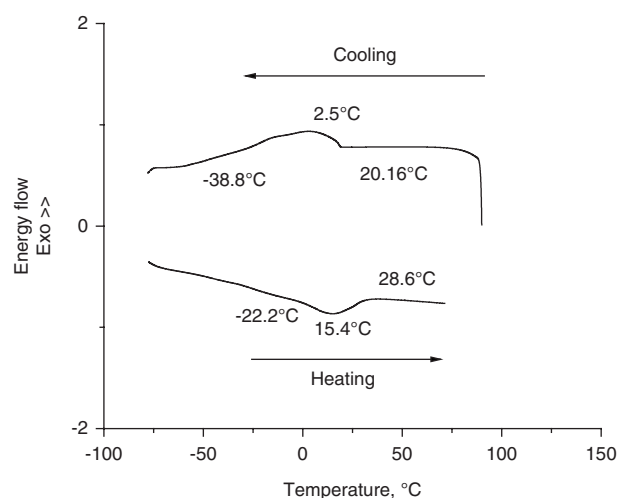


FIGURE 4. Crystallization and fusion curves of tamarind seed oil.

to that reported by Santos *et al.*, (2004) for the thermal decomposition, in air, of several vegetable oils (rapeseed, sunflower, rice, corn, olive and soybean) in which the said process was constituted by three decomposition stages at temperatures between 200 °C and 600 °C.

3.7. TSO phase behavior

The phase behavior of TSO was analyzed by DSC. Figure 4 shows the crystallization and fusion curves obtained at 5 °C/min. Both curves are very simple with a single transition peak. The oil began to crystallize by cooling at 20.16 °C and ended at −38.2 °C, with a maximum solidification close to 2.5 °C. The enthalpy of crystallization was −27.35 J/g. On the other hand, the onset and offset melting temperatures of TSO were −22.2 °C and 28.6 °C, respectively, with a maximum at 15.4 °C, and a 20.26 J/g of transition heat. The melting behavior of TSO resembles that of coconut oil and one of the liquid fractions (RFL) of sapote Mamey seed oil; the first with a melting range from −25.8 to 25.30 (Tan and Che Man, 2000) and

the second from 22.1 to 21.0 (Solís-Fuentes *et al.*, 2015). In both cases a simple melting curve with the predominance of one maximum melting peak was observed.

3.8. Solid/liquid relationships

Figure 5 shows the solid profile of TSO, which provides data regarding the levels of the S/L ratio of the oil at various temperatures. The figure includes the characteristic intervals of the refrigeration, environmental and corporal temperatures that serve to understand the liquidity and functionality of the mixtures of triacylglycerides. These mixtures are constituents of the fat fraction under these temperature conditions.

In relation to body temperature, for example, for edible fats and oils products, these data on oil phase behavior can give valuable indications about their palatability, gumminess, workability, and general behavior. The same happens with refrigeration, environmental, or higher temperatures.

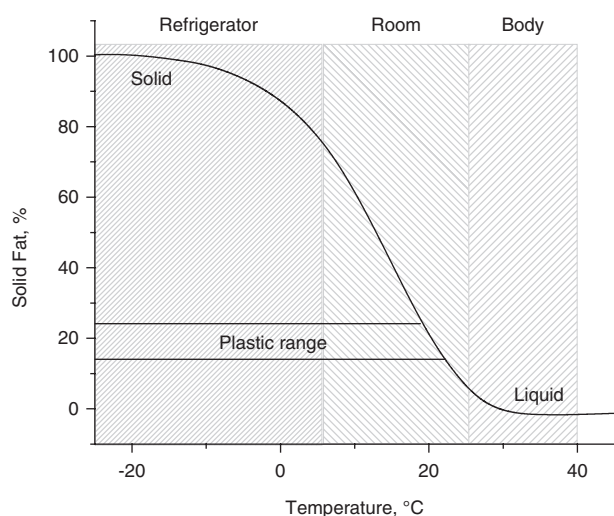


FIGURE 5. Solid/liquid relationships of tamarind seed oil in the characteristic refrigeration, environmental, and body temperature ranges.

The most important factor in the consistency of fats and oils is the proportion of the solid and liquid phases; they become firmer as the solid content increases. The solid-fat profile shows the temperature range in which the oil changes its consistency and therefore, transits from the solid phase to the liquid one (or vice versa), including the temperature region in which it has the ability to be molded, called the plastic range (between 15 and 25% of solids). There is an interval where the fat or oil has the best consistency to be worked on. The solid profile also shows the lowest temperature at which the oil is totally liquid, and if the profile of solids is flat (with a wide plastic range) or if the profile has a steep slope. In this sense, the TSO has a melting range of 50.8 °C (from -22.2 to 28.6 °C). At temperatures higher than 28.6, the oil is completely liquid, with a total absence of crystalline nuclei. Said range mainly includes the temperatures considered as environmental. Those that correspond from the refrigeration conditions to close to the body temperature. From 5 °C and lower, the percentage of solids in TSO is greater than 78%.

Within the range of temperatures that are considered environmental, around 5 to 25 °C, the percentage of solid fat in the liquid oil fluctuates from 78 to 5.15%. Thus, TSO in this environmental temperature range is perceived as a semi-solid to liquid consistency as the temperature increases. In the range of body temperatures the oil shows a gradual decrease in the solid content until it reaches zero at 28.6 °C.

As shown in Figure 5, the plastic range of the TSO is very short and occurs at a temperature 18.75 and 22.18 °C. The slope of the solid fat profile of this oil is not flat and neither is it notoriously deep. As is known, the plasticity and consistency of an

edible fat and oil depends not only on the quantity, but also on the size, shape, predominant polymorphic form and distribution of the solid material, as well as the development of crystalline nuclei capable of withstanding high temperatures to serve as initiator nuclei for the growth of crystals.

Some of the most critical factors in the behavior of products made with fats and oils refer to these two properties; for example, butter, margarine and spreads depend on the consistency of the fat portion and its ability to be spread over a slice of bread. A wide plastic range and a soft consistency are required for the fillers and margarines used for thin rolling at refrigerator temperatures. This same plasticity is necessary for the handling of shortenings in ice cream and aerated milkshakes (O'Brien, 2008). So, the consistency and plasticity of a fat product should be known for a range of temperatures.

According to Figure 5, the solid profile and consistency of TSO is closer to that presented by the frying shortenings than those of confectionary fats and plastic fats or, on the other end, liquid shortenings (O'Brien, 2008).

4. CONCLUSIONS

According to the results obtained in this work, the oil extracted from the tamarind seed has a refractive index of 1.465, and a saponification value of 174.8 mg KOH/g. The major FA of the TSO are: Lignoceric, oleic, palmitic, stearic, and behenic acids, with the presence of arachidic, linoleic, and palmitic acids, among others in smaller quantities.

The high content of saturated fatty acids of long- and very-long-chain acids is notable, and whose concentration encompasses about 60% of the total, of which lignoceric acid represented more than a third.

The TSO showed an initial decomposition temperature of its triacylglycerol components of 224.1 °C in inert atmosphere and 218 °C in air atmosphere. The analysis of the phase behavior of the oil showed that the transition to the solid phase starts at 20.16 °C and the transition to the liquid phase ends at 28.6 °C.

The S/L ratios showed that at temperatures considered environmental, the oil has a semi-solid and liquid consistency within that temperature range.

The composition, thermal stability and phase behavior presented by the tamarind seed oil make it potentially usable in applications in the food industry, Pharmacology, and cosmetology.

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