Composition and Thermal Behavior of Oils from Native Seeds and Fruits of Argentina and Uruguay

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Abstract: The purpose of this work was to study the thermal characterization of oils extracted from native seeds and fruits of the Argentina, Uruguayan region. This is important because it’s necessary to find new applications for food industry. Uruguayan wild cardoon seed, Argentinian wild papaya seeds, Argentinian avocado pulp, Argentinian cherimoya seeds, Argentinian grapeseeds and four commercial brands of chia oils were studied. The thermal behaviors of the oils were analyzed on a differential scanning calorimetry (DSC), TA Instrument, Q20 model equipped with an intercooler. These oils’ thermal profiles presented differences, which are related to the compositions of fatty acids and triacylglycerols. The thermogram for the chia oil, with a high content of linolenic acid, presented a very important peak at about -40 °C; whereas, the papaya oil with an oleic acid content of 74%, showed a peak at about -3 °C. When comparing the thermal behaviors of these oils to commercial brand oils, it was found that the chia oil is similar to the flaxseed oil, the papaya similar to the olive oil and the avocado similar to the rice bran oil. The avocado oil, in particular, presents high solid content at cold store or winter temperatures, which would make its use in those conditions difficult (for example, a cosmetic cream or gourmet oil). In conclusion, the thermal behavior of one oil sample as determined by DSC provides valuable information with regards to the possible use of new oils of American origin as replacement of usual commercial others.

Key words: South American oils, thermal behavior, DSC.

1. Introduction

Chia (Salvia hispanica L.) is an annual, summer, herbaceous plant from the Labiatae family. It is native to Central and Southern Mexico and Guatemala; it has been used and grown since 3,500 BC. This plant produces numerous small seeds, mostly dark in color, which contain oil in the 25%-39% rank. This oil contains over 60% of acid linolenic, thus making it an important source of fatty acids of the omega-3 family [1-8].

The avocado (Persea americana Mill.) belongs to the Lauraceae family. This family includes approximately 150 species, most of which grow in American tropical regions. The fruit is high in lipid content and consumed as food. The oil extracted from the pulp is used in food, pharmaceutical and cosmetic preparations. It is very high in oleic acid: 44%-74% [9-18].

The papaya (Carica papaya L.) is original from Central America; the species belongs to the Caricaceae, a small family mostly from America and composed of six genera. The fruit is an oval shaped berry with pronounced furrows, very aromatic and its color is an intense yellow. The fruit’s black seeds have a strong flavor; sometimes these are ground and used as a black pepper substitute. The oil extracted from the seeds is very rich in oleic acid: 63%-79% [19-21].

The cherimoya (Annona cherimola Mill.) belongs to the Annonaceae family. Native to South America, it has been cultivated in the Peruvian Andes since the time of the Mochica culture. It was first introduced to Southern Spain before 1751, from where it was
probably taken to Italy and Portugal. In the Mediterranean region, the cherimoya has adapted well in Israel, Egypt, Greece and Algeria. The fruit is green, large and fleshy, with a characteristically reticulated surface. The fruit’s seeds are blackish, flattened, 1-1.5 cm in length. No reference to the oil extracted from these seeds has been found in the literature consulted.

The cardoon (Cynara cardunculus) is a member of the Asteraceae family, same as the artichoke (Cynara scolymus), of which it is sometimes considered a sub-specie. This plant is original from Europe, but does well in the fields of Chile, Argentina and Uruguay. It was accidentally introduced in South America in the mid 18th century, and possibly mixed in with wheat seeds to be planted. It is a perennial plant, vivacious, very invasive, with tuberous roots. The flowers are big and violet in color. The content of oil extracted varies between 18.5% and 25.3%. The range of oleic acid content is highly variable: from 23.1% to 83.6% [22]. Other fatty acids that constitute the cardoon oil are linoleic and stearic acids, ranging from 40.0% to 61.5% and 18.0% to 45.0%, respectively [22].

Grapeseed oil (Vitis vinifera) is a by-product of the wine and grape juice industry; it is sold as edible in several countries. This oil also has several uses in both the cosmetic and therapeutic industries. It is very rich in linoleic acid: 58%-78% [21, 23-28].

Knowing the thermal behaviors of the fatty materials, which is the variation in the content of solids at different temperatures, is key to defining some of their uses. Among the most frequent methods, the differential scanning calorimetry (DSC) has been employed for decades [29] and provides more complete information than other methods. The thermograms are useful for studying the continuous variation of the solid content with temperature (unlike the nuclear magnetic resonance, for example). There is little information in the literature on the relations between the position of the peaks in the thermograms and the predominant molecular species at each temperature. The difficulties in the correlation are great, as the triacylglycerols present different polymorphic shapes and their mixes render very complex phase diagrams due to their inter-solubility, compound formation, etc. [30].

The aim of this paper was to determine the composition of the fatty acids and thermal behaviors of the chia, cherimoya, papaya, avocado, cardoon and grapeseed oils, as there are no studies in this regard in the consulted bibliography. The oils studied are of additional interest, as they are from native plants of Argentina or Uruguay.

2. Materials and Methods

2.1 Materials

Uruguayan wild cardoon seeds (Cynara cardunculus), Argentinian wild papaya seeds (Carica papaya L.), avocado pulp (Persea americana Mill., Hass variety) from Purmamarca in the Argentinia province of Jujuy, Argentinian cherimoya (Annona cherimola Mill.) seeds from Palma Sola, also in Jujuy, and grapeseeds (Vitis vinifera) from a variety native to Jujuy were studied.

Four commercial brands of chia (Salvia hispanica L.) oils, labeled A, B, C and D, where A corresponds to the brand Veracruz, B corresponds to Sturla, C corresponds to America and D is unknown brand (Salta), were studied. Also studied were a commercial brand of extra virgin olive oil and refined commercial brands of regular sunflower, soybean, high oleic sunflower, rapeseed, rice bran and flaxseed oils.

2.2 Methods

2.2.1 Extraction of the Oils

Prior to the extraction, the seeds were dehydrated in a heater at 110 °C, grinded in a grinder and placed in paper filters. The oil was extracted using the Soxhlet method [31], using 60º-80º petroleum ether (quality for analysis). For the avocado oil, the extraction was performed on the pulp dehydrated by lyophilization.
2.2.2 Fatty Acid Composition

The fatty acid composition of all of the mentioned oils was analyzed (in the form of methyl esters) in a Shimadzu 2010 plus chromatographer equipped with a Supelco SP 2330 capillary column and a FID 340. The injection was performed at 250 °C in split modality. The pressure was set at 60 Kpa and the split relation was 80:1.

2.2.3 Thermal Behavior

The thermal behaviors of the oils were analyzed on DSC, TA Instruments brand, Q20 model equipped with an intercooler. An approximate of 15 mg of each sample was weighed in an aluminum capsule. This was placed in a freezer for 48 h. Afterward, the sample was analyzed on a DSC according to the following temperature program: the temperature was initially kept at -60 °C for 30 min and then elevated at a rate of 5 °C/min until reaching 60 °C.

2.2.4 Oxidative Stability

An Omnion brand oxidative stability instrument, model OSI-8, in which the temperature was set at 110 °C and pressure at 5.5 psi, was used to determine the oxidative stability of chia C, flaxseed and extra virgin olive oils. The standard AOCS Cd-12b-92 [32] protocol was followed. Five grams of sample per tube were weighed and 50 mL of deionized water were placed in the conductivity cells.

3. Results and Discussion

The composition in principal fatty acids of the oils extracted is presented in Table 1. For comparison, the composition of commercial oils was added.

3.1 Chia Oils of Different Origins

In spite of having different origins, the four chia oil samples show a very similar composition in fatty acids (Table 1).

Fig. 1a shows the thermograms of chia oils. The vortex of the largest peak takes place at around -40 °C; the vortex of the second largest peak is at around -5 °C. The four samples show very similar thermal behavior, which is to expected given the similarities in the fatty acid composition. As a consequence, the study will be performed only with chia C oil.

Fig. 1b shows the comparison of the thermal behavior of the chia C oil to flaxseed oil. Thermogram of chia oil is different from the flaxseed oil, even when the shape of the principal peak is similar (with a shoulder on the right); these are located in different temperature ranges. These differences might respond to the difference in fatty acid composition (Table 1), which would mean a different triacylglycerol composition.

<table>
<thead>
<tr>
<th>Oil</th>
<th>Fatty acid composition</th>
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<tbody>
<tr>
<td></td>
<td>16:0</td>
</tr>
<tr>
<td>Cherimoya</td>
<td>16.7</td>
</tr>
<tr>
<td>Papaya</td>
<td>12.9</td>
</tr>
<tr>
<td>Avocado</td>
<td>21.4</td>
</tr>
<tr>
<td>Grapeseed</td>
<td>6.2</td>
</tr>
<tr>
<td>Cardoon</td>
<td>11.4</td>
</tr>
<tr>
<td>Olive</td>
<td>11.1</td>
</tr>
<tr>
<td>Flaxseed</td>
<td>5.7</td>
</tr>
<tr>
<td>Rapeseed</td>
<td>3.8</td>
</tr>
<tr>
<td>Ricebran</td>
<td>18.9</td>
</tr>
<tr>
<td>Sunflower</td>
<td>5.4</td>
</tr>
<tr>
<td>High oleic sunflower</td>
<td>3.3</td>
</tr>
<tr>
<td>Soybean</td>
<td>10.4</td>
</tr>
<tr>
<td>Chia A</td>
<td>6.9</td>
</tr>
<tr>
<td>Chia B</td>
<td>6.3</td>
</tr>
<tr>
<td>Chia C</td>
<td>6.3</td>
</tr>
<tr>
<td>Chia D</td>
<td>7.0</td>
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</table>
To compare the thermal behavior of chia C oil with that of the flaxseed, the solid content for each oil sample was determined at previously established temperatures. Flaxseed shows a greater content of solids than the chia C oil at any temperature below -15 °C (Fig. 1c). Chia C oil has a greater content of linolenic acid than flaxseed oil, which would lead to a greater proportion of more polyunsaturated triacylglycerols (like 18:2/18:3/18:3 and 18:3/18:3/18:3) of lower melting points.

Even though both oils show different thermal behaviors at low temperatures, their solid content is similar starting at -15 °C (Fig. 1c). When used at relatively low temperature, these oils behaved in the same way.

As a consequence, chia oil may be stored in a refrigerator, as it is not expected to partially crystallize (like other oils, such as rice bran or olive oil). This ensures better storage conditions (even when commercialized in capsules), since the oxidative stability of both is low due to its high unsaturation. The induction times obtained through the OSI method [32] were 0.8 h for chia oil and 2.0 h for flaxseed oil. As a reference, the OSI induction time of extra virgin olive oil was 40.3 h.

### 3.2 Avocado Pulp, Grapeseed, Cardoon, Cherimoya and Papaya Seed Oils

Fig. 2a shows the thermograms of cardoon seeds oil superimposed on sunflower oil and in Fig. 2b superimposed on grapeseed oil. The cardoon seeds oil is richer in linoleic acid and poorer in oleic acid than sunflower oil (Table 1). This should lead to a greater content of more unsaturated triacylglycerols, which should cause the main peak of the thermogram to lean towards the lower temperatures and to have a more pronounced shoulder.

Content of polyunsaturated fatty acids (linoleic and linolenic) of rapeseed oil is greater compared to that of the cardoon oil, which does not contain significative quantities of linolenic acid (18:3). This accounts for the thermogram of the grapeseed oil to lean slightly towards lower temperatures, displaying a peak in a range of temperatures inferior to that of the cardoon oil.

Fig. 2c compares the variation of the solid content
of the cardoon, sunflower and grapeseed oils. All three oils show similar behavior, although the solids content of the sunflower oil is slightly lower than that of the cardoon, at any temperature. Therefore, from the thermal behavior point of view, one oil may substitute any of the other two.

Fig. 3a shows the thermograms for the cherimoya, papaya and avocado oils, all of which are native to tropical areas of America. The thermal behavior is very different for each oil sample, which is explained by their very different fatty acid composition (Table 1), as a consequence of their different triacylglycerols composition. Fig. 3b shows the solid content of the three oils at different temperatures. In order to explain the thermal behavior based on their composition, each thermogram will be studied separately.

3.2.1 Cherimoya Seed Oil

The thermogram for the cherimoya seed oil is similar to that of the rapeseed oil (Fig. 4a), in spite of having different fatty acid composition (Table 1); cherimoya oil contains more palmitic and linoleic acids and less oleic and linolenic acids. Due to its greater content of linolenic acid and smaller content of oleic acid, a greater proportion of more polyunsaturated triacylglycerols is expected, which would explain the slight movement of the peak towards lower temperatures. The presence of a shoulder to the right of the main peak could be explained by its greater content of saturated fatty acids leading to a greater content of the triacylglycerols that contain them. This results in a greater solid content at temperatures above -25 °C (Fig. 4b). However, in temperatures above those, both oils present the same thermal behavior, with no turbidity under those cold conditions.

3.2.2 Papaya Seed Oil

The papaya seed oil’s fatty acid composition (Fig. 5a) and thermal behavior (Fig. 5b) are similar to those of the high oleic sunflower oil. Both oils would not show turbidity when cold stored.

3.2.3 Avocado Pulp Oil

It is very interesting to see that the thermogram for the avocado oil shows two important peaks, which are
Fig. 3  Thermograms and variation of the solid content for the cherimoya, papaya and avocado oils.

Fig. 4  Thermograms and variation of the solid content of three oils for the cherimoya and rapeseed oils.

Fig. 5  Thermograms and variation of the solid content for the papaya and high oleic sunflower oils.
are relatively separated. This would indicate the presence of two groups of triacylglycerides with relatively different melting characteristics. The thermogram for the rice bran oil also presents two peaks. Fig. 6 shows both thermograms superimposed.

Hierro et al. [33] studied the triacylglycerol composition of the avocado oil. Yanty et al. [34] studied the varietal effect on the triacylglycerol composition and the thermal behavior of the avocado oil. The heating thermograms presented an important peak between -20 °C and -10 °C and a smaller one at higher temperatures. This thermal behavior is similar to the one determined in this paper. Yanty et al. [34] also studied the triacylglycerol composition and thermal behavior of the avocado butter compared to other oils and lard. Based on the above mentioned bibliography, Table 2 was made to group the triacylglycerols, approximately, based on whether their melting points were above or below 0 °C. The triacylglycerols composition of the rice bran oil [35] was also included, as its thermogram also showed two peaks. The content of the OOO triacylglycerols (O = oleic) was omitted, as it would fall between the previously mentioned peaks of the thermogram. The values in this table explain, approximately, the presence of two peaks of similar size in the

![Fig. 6 Thermograms and variation of the solid content for rice bran and avocado pulp oils.](image)

**Table 2  Triacylglycerol composition for the oils of two varieties of avocado and one rice bran oil.**

<table>
<thead>
<tr>
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<tbody>
<tr>
<td>POP</td>
<td>5.0</td>
<td>12.4</td>
<td>2.9</td>
</tr>
<tr>
<td>POO</td>
<td>31.0</td>
<td>22.8</td>
<td>12.5</td>
</tr>
<tr>
<td>PLP</td>
<td>1.0</td>
<td>4.0</td>
<td>4.9</td>
</tr>
<tr>
<td>Partial sum</td>
<td>37.0</td>
<td>39.2</td>
<td>20.3</td>
</tr>
<tr>
<td>POL</td>
<td>7.0</td>
<td>19.3</td>
<td>20.4</td>
</tr>
<tr>
<td>SOL</td>
<td>10.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PLL</td>
<td>4.2</td>
<td></td>
<td>10.3</td>
</tr>
<tr>
<td>OOL</td>
<td>12.0</td>
<td>9.0</td>
<td>17.9</td>
</tr>
<tr>
<td>OLL</td>
<td>2.0</td>
<td>3.2</td>
<td>15.3</td>
</tr>
<tr>
<td>LLL</td>
<td>0.9</td>
<td></td>
<td>3.4</td>
</tr>
<tr>
<td>POLn + OOLn</td>
<td>2.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Partial sum</td>
<td>33.0</td>
<td>36.6</td>
<td>67.3</td>
</tr>
</tbody>
</table>

P = palmitic; S = stearic; O = oleic; L = linoleic; Ln = linolenic.
thermogram of the avocado oil and a small peak as well as a bigger one in the thermogram of the rice bran oil.

Fig. 6b shows the variation of the solid content in avocado and rice bran oils in relation to their temperature. The solid content of the rice bran oil, at any temperature, is lower than that of the avocado oil, which is explained by the higher content of unsaturated triacylglycerols (PLL, OOL, OLL and LLL; where P = palmitic, L = linoleic and O = oleic) of the rice bran oil. The avocado oil presents a higher solid content at cold store or winter temperatures than that of the rice bran oil, which would make its use difficult when stored in those conditions.

4. Conclusions

Commercial chia oils did not present any discernible variation in neither their fatty acid composition nor their thermal behavior. This oil, due to its high content of 18:3 fatty acid, belonging to the omega-3 family, presents important nutritional advantages; but also due to a very low oxidative stability, it needs to be protected from oxidation by adding antioxidants and/or being refrigerated and/or encapsulated. The oils almost null solid content at cold store temperatures make its storage in those conditions possible.

The analyzes of other oils extracted by cardoon, grapeseed, papaya, cherimoya and avocado present different thermal behaviors. When compared to commercial oils of similar composition (virgin olive oil, regular sunflower oil, high oleic sunflower oil, rice bran oil, rapeseed oil and soybean oil), some similarities and differences were observed in the thermal behavior which are related to their compositions. The avocado oil, in particular, presents high solid content at cold store or winter temperatures, which would make its use difficult in those conditions (for example, a cosmetic cream or gourmet oil).

In conclusion, the thermal behavior of one oil sample as determined by DSC provides valuable information with regards to the possible use of new oils of American origin as replacement of usual commercial others.

References


