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# Chemical and physico-chemical characterization of seeds of melon cultivars: Valenciano and Pele de Sapo, cultivated in the Amazon

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The aim of this work was to perform chemical and physical-chemical analyzes of the oil of the cultivars Valenciano Amarelo melon (VA) and *Pele de Sapo* melon (PS) (*Cucumis melo* L.) produced in Boa Vista, Roraima, Brazil, by GC -FID, IR, <sup>1</sup>H NMR and the thermogravimetric behavior TG/DTG as well as yield of that obtained oil. Thus, the oil yield of *Valenciano* melon seeds was 28.47% and that of *Pele de Sapo* melon was 26.41%. The chemical composition of the oils of the two cultivars presented major fatty acids, such as palmitic acid, linoleic acid (57.5-59.4%) and oleic acid (22.8-23.3%). The physico-chemical characterization of these oils showed for *Valenciano* melon and *Pele de Sapo* melon, respectively, 125.02 and 120.96 g l<sub>2</sub> 100 g<sup>-1</sup> for the iodine value and 187.80 and 185.65 mg KOH g<sup>-1</sup> for saponification index. The behavior of the thermal degradation by TG/DTG of the melon seeds oils VA and PS occurred between 341.08 and 522.03°C, and 334.83 and 524.29°C, respectively.

Key words: Oleic acid, cucurbitaceas, biotechnology, essential fatty acids.

# INTRODUCTION

Melon is one of the olerícolas belonging to the family Cucurbitaceae, genus *Cucumis*. It is an herbaceous and

creeping plant of African origin (Bisognin, 2002), cultivated mainly in India and in tropical countries, with

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Author(s) agree that this article remain permanently open access under the terms of the <u>Creative Commons Attribution</u> <u>License 4.0 International License</u> varieties and cultivars (Mansouri et al., 2015), introduced in Brazil by the Europeans in the decade of the 60s (Frizzone et al., 2005).

Melon cultivation is carried out in regions with a very dry and bright climate good drainage soil and temperature ranging from 25 to 35 °C. The temperature and luminosity favor the sweetest and tasty fruits, as it helps the sugar production. The variations of melon grown in Brazil, have pleasant organoleptic characteristics, highlighting the pleasant aroma (Senar, 2007).

Melon cultivars found in Brazil are Honey Dew, Pelede-sapo, Orange Flesh, Cantaloupe, Gália, Orange and an AF-522 hybrid commercially classified as a yellow melon type (Melo et al., 2000). The main melon growing regions for the year 2013 were the San Francisco Valley (Pernambuco and Bahia), Rio Grande do Norte and Ceará in a total of land area of 14,950 hectares (2,950 in the São Francisco Valley and 12,000 in the Rio Grande do Norte and Ceará) from August /2013 to March / 2014 (Nascimento, 2014). Among the melons cultivated in Brazil, the cultivars of the odorless group, represented by the Valenciano and Pele-de-sapo types, are preferred by the producers, totaling about 90% of the planted area (Nunes et al., 2005).

In the food industry, after the use of fruit pulps the seeds of these fruits are discarded in the environment. This is due to the lack of alternatives to the use of these vegetable residues, being used as organic fertilizers or animal feed, without adequate treatment (Miguel et al., 2008). These seeds could be used as an alternative source of socioeconomic value and by generating employment and income through vegetable (Kobori and Jorge, 2005; Uchoa et al., 2008).

In this work, the chemical composition and physicochemical properties of fatty acids extracted from the seeds of two varieties of melon (Valenciano and Pelede-sapo) cultivated in the State of Roraima in Brazil were studied in order to be used as a biotechnological source for the production of other derivative products.

#### MATERIALS AND METHODS

#### Material and extraction of oil

Samples of the two melon cultivars were collected at the producer's fair in Boa Vista-Roraima (Brazil) in March 2015, in total 10 melons of each species with good appearance and in a ripe state suitable for consumption and taken to the Laboratory of Environmental Chemistry of the Graduate Program in Chemistry of the Federal University of Roraima the seeds were separated, washed with distilled water and dried in an air circulating oven at 50 °C for 48 hours until constant weight. After drying the seeds were ground and sieved in a 30-40 mesh sieve. The extraction of oil, was done in a Soxhlet extractor using cellulose cartridges covered with hydrophilic cotton and anhydrous sodium sulfate to control excessive humidity (Jorge and Luzia, 2012).

The solvent was hexane, the contact time between the solvent and the sample was 3 hours. The solvent was removed using a rotary evaporator to give melon seeds oil as the final product. The reagents and solvents were in analytical purity in all procedures performed. The oils were stored in amber flasks in an atmosphere of gaseous nitrogen in order to protect the oil and conserve its properties. These were refrigerated until further analysis.

#### Profile of fatty acids by CG-FID

Free fatty acids were measured by Gas Chromatography using HP7820A (Agilent) system equipped with flame ionization detector. An Innowax column (HP) 15 m × 0.25 mm × 0.20 µm was used and the following temperature gradient: 100 °C min and 0.7 °C min-1 up to 240 °C; injector (1/30 split) to 250 and 260 °C detector. Hydrogen was used as carrier gas (3 mL min-1) and injection volume was 1 µL. The data acquisition program used was EZChrom Elite Compact (Agilent). The peaks were identified using FAME Mix C14-C22, CRM18917 Supelco fatty acid methyl esters standard (Christie, 1989).

#### Physicochemical properties of the oil by <sup>1</sup>H-RMN

In order to determine the physico-chemical properties of melon oil, the values of <sup>1</sup>H-RMN spectra, previously studied by Carneiro (2005) and Reda and Carneiro (2006) were utilized.

Thermal analyses (TG/DTG) were conducted on Shimadzu 60 DTG equipment using approximately 10 mg heated sample in an alumina crucible. The tests were performed with a heating rate of 10°C min<sup>-1</sup>, from room temperature to 900°C, under nitrogen gas atmosphere (flow 50 mL.min<sup>-1</sup>).

### **RESULTS AND DISCUSSION**

#### **Extraction yield**

Table 1 shows the yields of the two varieties of melon studied in this work compared to the literature. The data are expressed as the mean value of the three readings with the standard deviation.

The density of the Valenciano melon seed oils was about 0.90 and 0.86 mg ml<sup>-1</sup>, respectively. The values found in the seeds oil of the melon cultivars studied was in the range proposed by the literature, as shown by the yields of the oil of the Yelow Melon (Malacrida et al., 2007) and extraction of the Japanese Melon (Melo et al., 2007).

Among the cultivars studied, the Valenciano melon seeds had higher yields compared to the *Pele de Sapo* melon species. The oils obtained were yellowish with a sweet odor.

#### Determination of fatty acids in seeds using CG-FID

In Table 2, the fatty acid profile for the seeds of the two melon varieties compared to the literature is presented. The oils of the seeds of the cultivars Valenciano Melon and *Pele de Sapo* Melon, respectively, show an average composition of 81.00 and 83.00% for unsaturated fatty acids and 19.00 and 17.00% for saturated fatty acids.

Sample	Valenciano melon	Pele de Sapo melon	Melão Amarelo (Malacrida et al., 2007)	Melão Japonês (Melo et al., 2007)
Yield (%)	28.47 ± 0.10	26.41 ± 0.09	$25,2 \pm 0,6$	29

Table 1. Oil yields for Valenciano and Pele Sapo melons.

Table 2. Composition of fatty acids in the oils of the seeds of two melon cultivars by gas chromatography in comparison to the literature.

Fatty acid	Valenciano melon (%)	Pele de Sapo melon (%)	P.E. (%)	A (%)	ANVISA
Miristic acids (C <sub>14:0</sub> )	0.1	0.1	0.22	0.13	< 0.3
Palmitic acid (C <sub>16:0</sub> )	10.2	9.3	11.08	28.29	5.5 - 11.0
Margaric acid (C17:0)	0.1	0.1	-	-	-
Oleic acids (C <sub>18:1</sub> )	22.8	23.3	19.32	49.74	12.0 - 28.0
Linoleic acids (C <sub>18:2</sub> )	57.5	59.4	40.19	7.57	58.0 - 78.0
Linolenic acids (C <sub>18:3</sub> )	0.7	0.3	0.61	1.49	< 1.0
Araquidic acids (C <sub>20:0</sub> )	0.3	0.2	-	-	< 1.0
Behenic acids (C <sub>22:0</sub> )	0.3	-	-	-	-
Other	8.0	13.1	0.42	1.49	-
Satured	19.00	17.00	15.67	39.09	-
Unsatured	81.00	83.00	84.3	60.91	-

The values obtained by the CG-FID for the composition of saturated fatty acids of the seeds oils of the cultivars *Valenciano* Melon and *Pele de Sapo* Melon shown in Table 2, present a very close composition with *Passiflora edullis* (Silva, 2011) and quite different from Andiroba (Farias, 2013).

Among the unsaturated fatty acids, the oils of the seeds of the cultivars Valenciano Melon, Pele de Sapo Melon and *Passiflora edullis* (Silva, 2011), the  $\omega$ -9 acid presented very close values, whereas in Andiroba seed oil (Farias, 2013), the value found was higher than the others. The  $\omega$ -6 oil of the seeds of the cultivars Melão Valenciano Amarelo and Melão Pele de Sapo presented values similar to those of the oil of the passion fruit *Passiflora edullis* (Silva, 2011), whereas in Andiroba seed oil (Farias, 2013), the value found was lower than the others.

A high content of linoleic acid was observed in melon seed oils which may characterize this oil as having nutritional properties and beneficial physiological effects in the prevention of diseases such as cancer and coronary heart disease (Azhari et al., 2014). The  $\omega$ -3 oil of the seeds of the Melon Valenciano Amarelo and *Passiflora edullis* (Silva, 2011) seeds were similar. For the oil of the seeds of the cultivar Melão Pele de Sapo, the value obtained was lower than the former two, while for the Andiroba seed oil (Farias, 2013) the value found is superior to all.

As for the saturated fatty acid composition, palmitic acid presented the highest concentration followed by myristic acid for the oils studied and those in the literature.

# Thermogravimetric analysis of melon seeds

Figures 1 and 2 present the TG / DTG curves of the melon seed oil where there is only one mass loss stage attributed to the volatilization and/or decomposition of triacylglycerides.

In the temperature range of 210 to 330°C, a low and continuous mass loss is observed. However, higher mass loss occurs at approximately 390°C, which can be attributed to the volatilization and/or decomposition of triacylglycerides (Garcia et al., 2004).

It was observed through the TG/DTG curves that the seed oils of the two melon species (Figure 1 and 2) undergo decomposition at temperatures below the stability temperatures of the oils. The oils analyzed presented an increasing order of stability as described below: Melon Pele de Sapo and Melon Valenciano Amarelo.

The analyzed oils had similar profiles with mass loss of 99.82 to 99.78%, where the process of volatilization and/or thermal decomposition occurred in a single stage, between 334 and 341°C, with a final temperature between 522 and 527°C (Table 3).

This similarity was observed in the curves profiles between the compositions of fatty acids in the oils of melon seeds which mainly present linoleic and oleic acids also known as omega-6 and omega-9 (Antolin and Meneses, 2000).

In comparison with other species such as Andiroba oil, a loss of mass of 96.16% was observed, while grape and soybean oils presented 97.02 and 94.49% of loss,

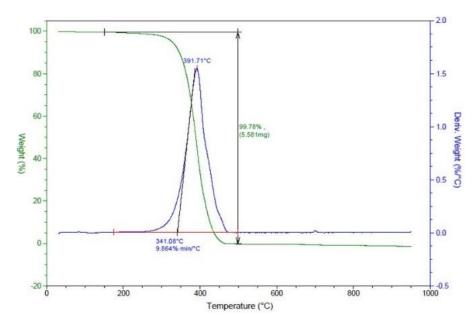


Figure 1. TG/DTG Yellow Valenciano Melon.

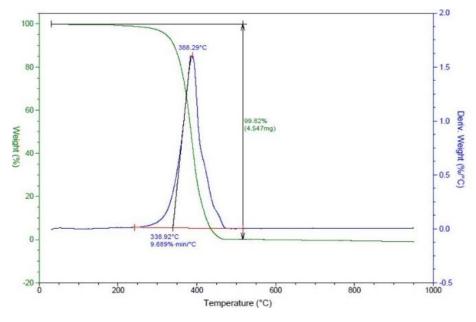


Figure 2. TG/DTG Pele-de-sapo Melon.

respectively, where the process of volatilization and/or thermal decomposition of the Andiroba oil was produced in the stages of 332.90°C with a final temperature of 641.78°C, and the Andiroba oil presented a thermal stability within the range found for the grape and soybean oils studied by Barreto (2009).

The profile of the curve of Figures 1 and 2 is due to the similarity between fatty acid compositions of the oils, which mainly present palmitic and oleic acid (Antolin and

Meneses, 2000).

Samples of melon seed oil were found to follow a pattern, where the degradation started at 310°C and ended at approximately 527°C. At 527°C, mass loss of approximately 99.9% was found.

The results obtained by TG/DTG in nitrogen atmosphere showed that the thermal behavior of the oils of melon seeds was similar, especially with respect to the beginning and end temperatures of the degradation, for all the samples. Andiroba

Pelede Sapo melon

White Niagara grape (Barreto, 2009)

Commercial soybean oil (Barreto, 2009)

Sample	T <sub>i</sub> (°C)	Т <sub>f</sub> (°С)	Weight loss (%)
Valenciano melon	341.08	522.03	99.78

334.83

332.90

345.01

324.49

524.29

522.93

522.93

527.50

99.82

96.16

97.02

94.49

Table 3. Values for the different initial and final temperatures, ell as the values of mass loss obtained the TG/DTG curves.

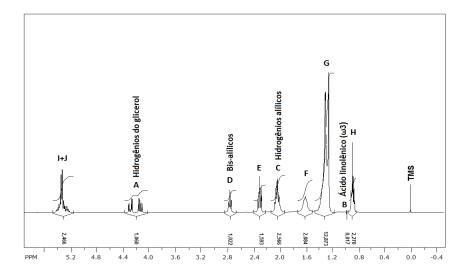
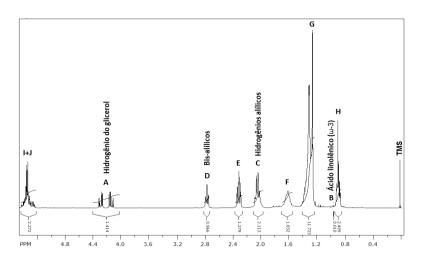


Figure 3. <sup>1</sup>H-NMR spectrum of Valenciano melon seeds.



**Figure 4.** <sup>1</sup>H-NMR spectrum of *Pele Sapo* melon seeds.

# Physicochemical properties of melon seeds by <sup>1</sup>H-NMR

The values of <sup>1</sup>H Nuclear Magnetic Resonance spectra (Figures 3 and 4) were used to obtain the acid number, iodine, and saponification of the average molecular mass of the seeds of the three melon cultivars according to the

equations previously studied by Reda and Carneiro (2006).

The iodine index indicates the degree of fatty acid instabilities present in vegetable oils; the greater the degree of saturation the more the oil becomes unfit for human consumption (Reda and Carneiro, 2006). The oil of the seeds of the two melon cultivars presented an

Physical-chemical parameter	(mg l <sub>2</sub> 100g <sup>-1</sup> ) (II)	(mg KOH g⁻¹) (IS)	(mg KOH g <sup>-1</sup> ) (IA)	(g mol <sup>-1</sup> ) (MM)	R <sub>o,A</sub>
Valenciano Melon	125.02	187.78	0.73	893.33	3.85
Pele-de-sapo Melon	120.96	185.65	0.75	902.33	3.64
Crimson Sweet(Citrullus lanatus)	101.04	193.47	0.17	869.14	0.93
Andiroba(Caraca guianensis)	48.41	161.67	1.84	1004.02	0.27

Table 4. Physical-chemical characterization of the oil of the seeds of two melon cultivars, in relation to the literature.

iodine content of 125.02 mg  $I_2$  100 g<sup>-1</sup> for the oil of the *Valenciano* Melon seeds and 120.96 mg  $I_2$  100 g<sup>-1</sup> for the oil of the *Pele de Sapo* Melon seeds.

In Table 4, the values of the oils of the seeds of the two melon cultivars were higher than that the Crimson Sweet watermelon seeds (Citrullus lanatus) studied by Holanda, (2013) and the oil of Carapa guianensis studied by Farias (2013). However, due to the low values of saturation index expected, it leads to the iodine index values being within the established values.

The saponification index is an approximate measure to establish the average molecular weight, being indicative of the presence of high and low molecular fatty acids (Solomons and Fryhle 2012; Morreto and Fett, 2008). The oil of the seeds of the two melon cultivars presented a saponification index of 187.78 mg KOH g-1 for the oil of the Valenciano melon seeds and 185.65 mg KOH g-1 for the oil of the Pele-de-sapo Melon seeds. The value found for the saponification index indicates that the oil of the Crimson Sweet watermelon seeds has a low degree of deterioration (Holanda, 2013).

The values found for the saponification index of the oils of the seeds of the two melon cultivars were lower than the oil of the Crimson Sweet watermelon seeds studied by Holanda (2013) and higher than the Caraca guianensis oil studied by Farias (2013).

The oil of the seeds of the two melon cultivars had an acid value of 0.73 mg KOH g-1 for the oil of the Valenciano Melon seeds and 0.75 mg KOH g-1 for the oil of the Pele-de-sapo Melon seeds respectively. The observed values from this study were higher acidity index than the value found in Crimson Sweet watermelon oil (Holanda, 2013) and lower than the value found in Caraca guianensis oil by Farias (2013). However, the acid values of the melon oils remain between the maximum value established by ANVISA, (2000) which is 0.6%. Since the acidity index establishes the degree of conservation of an oil, the values found indicate that the oils were well conserved for further analysis.

A value greater than or equal to 0.66 indicates that vegetable oil is suitable for human consumption. This parameter needs to be calculated to obtain the acidity index of a vegetable oil (Reda et al., 2005). The oil of the seeds of the two melon cultivars presented oleophilic/ aliphatic hydrogen ratio of 3.85 for the oil of the melon yellow seeds, 3.64 for the oil of the *Pele de Sapo* Melon

seeds.

Table 4 shows the values obtained for the oleophilic/aliphatic hydrogen Ro ratio of the oils of the seeds of the two melon cultivars, which were higher than the value found in Crimson Sweet watermelon oil (Holanda, 2013) and the value found in the oil of Caraca guianensis (Farias, 2013). The values indicate that the oils of the melon seeds are suitable for human consumption.

The average molecular mass of a triglyceride is inversely proportional to the saponification index (Moretto and Fett, 2008). The oil of the seeds of the two melon cultivars presented a mean molecular mass of 893.33 g mol-1 for the oil of the Pele-de-sapo Melon seeds and 902.33 g mol-1 for the oil of the Pele-de-sapo Melon seeds. The values found show that the lower the value found for the average molecular mass of the vegetable oils of the larger melon seeds was the saponification index.

# Conclusion

The oil Valenciano Melon seeds and Pele-de-sapo Melon seeds presented good values of 28.47% and 26.41% respectively, appearing as an alternative source for utilization of two agroindustrial rejects.

The analysis of the composition of the major fatty acids present in the oil of the Valenciano Melon and Pele-desapo Melon seeds demonstrates the presence of Palmitic, Arachidonic, Linoleic ( $\omega$ -6), Oleic ( $\omega$ -9), Linolenic ( $\omega$ -3) and Behenic.

The thermogravimetric analysis showed, through the graphs obtained by TG/DTG, the thermal behavior of the oils of the melon seeds, evaluating their stability, being this a determinant factor in the quality control, besides characterizing its viability of degradation through temperature and industrial use.

The quality parameters of the seeds oils of the two melon cultivars showed that they have a good state of conservation, since their quality parameters point to a possible use in human consumption, being able to be used in the food, pharmaceutical and cosmetic industries.

# CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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