

IONIZING RADIATION EFFECTS IN AÇAÍ OIL ANALYSED BY GAS CHROMATOGRAPHY COUPLED TO MASS SPECTROMETRY TECHNIQUE

Felipe Valli¹, Carlos Eduardo Fernandes¹, Sergio Moura¹, Ana Carolina Machado¹, Helio Akira Furasawa¹, Maria Aparecida Faustino Pires¹ e Oscar Vega Bustillos¹.

¹Instituto de Pesquisas Energéticas e Nucleares (IPEN / CNEN - SP)
Av. Professor Lineu Prestes 2242
05508-000 São Paulo, SP
ovega@ipen.br

ABSTRACT

The Açai fruit is a well know Brazilian seed plant used in large scale as a source of feed stock, specially in the Brazilian North-east region. The Açai oil is use in many purposes from fuel sources to medicine. The scope of this paper is to analyzed the chemical structures modification of the açai oil after the ionizing radiation. The radiation were set in the range of 10 to 25 kGy in the extracted Açai oil. The analyses were made by gas chromatography coupled to mass spectrometry techniques. A GC/MS Shimatzu QP-5000 equipped with 30 meters DB-5 capillary column with internal diameter of 0.25 mm and 0.25 μ m film thickness was used. Helium was used as carried gas and gave a column head pressure of 12 p.s.i. (1 p.s.i. = 6894.76 Pa) and an average flux of 1ml/min. The temperature program for the GC column consisted of a 4-minutes hold at 75°C, a 15°C /min ramp to 200°C, 8 minutes isothermal. 20°C/min ramp to 250°C, 2 minutes isothermal. The extraction of the fatty acids was based on liquid-liquid method using chloroform as solvent. The chromatograms resulted shows the presences of the oleic acid and others fatty acids identify by the mass spectra library (NIST-92). The ionization radiation deplete the fatty acids presents in the Açai oil. Details on the chemical qualitative analytical is present as well in this work.

1. INTRODUCTION

Açaí (*Euterpe oleracea*) is a Brazilian native palm. It has a reddish dark color due to natural pigment antocianines which is a family of the flavonoids. Besides these compounds Açai is well know by the content of fatty acids. Comparing with a well know European olive oil, it has almost same amount of oleic acid and higher palmitic acid. This comparison is show in Table 1. The nutrition orientation for ideal oil, it suppose to have 50 % of fatty acid non-insaturated, 33 % of saturated and the rest be poli-insaturated fatty acid, this blend gives a healthy oil [1]. The Açai extracted oil has in its composition good quality acids, with 60 % mono-unsaturated and 13 % poli-unsaturated. The proteins proportion are higher than milk – 3,50 % or egg – 12,49 %, while the aminoacids are similar to egg.

The fatty acid is a carboxylic acid derived from or contained in an animal or vegetable fat or oil. All fatty acid are composed of a chain of alkyl groups containing from 4 to 22 carbon atoms usually even numbered and characterized by a terminal carbonyl group – COOH. The

generic formula for all above acetic is $\text{CH}_3(\text{CH}_2)_x\text{COOH}$. The fatty acid may be saturated or unsaturated well know as olefinic, and either solid, semisolid or liquid. They are classed among the lipids together with soap and waxes.

The saturated is a fatty acid in which the carbon atoms of the alkyl chain are connected by single bonds. The most important of these are butyric – C_4 , lauric – C_{12} and stearic – C_{18} . They have a variety of special uses. Stearic acid leads all other fatty acids in industrial use, primarily as a dispersing agent and accelerator activator in rubber products and in soaps.

The unsaturated is a fatty acid in which there are one or more double bonds between the carbon atoms in the alkyl chain. These acids are usually vegetable derived and consist of alkyl chain containing 18 or more carbon atoms with the characteristic end group – COOH . Most vegetables oils are mixtures of several fatty acids or their glycerides, the unsaturation accounts for the broad chemical utility of these substances, specially of drying oils. The most common unsaturated acids are oleic, linoleic, and linolenic all C_{18} . Sunflower oil is high in linoleic acid, peanut oil contain 21 %, olive oil is 38 % oleic acid, palmitoleic acid is abundant in fish oils. Aromatic fatty acid are now available.

Linoleic, linolenic and arachidonic acid are called essential fatty acids by biochemists because they are necessary nutrients that are not synthesized in the animal body. The fatty acids are use in special soap, lubricants, paints, candles, salad oil, synthetic detergent and cosmetics.

The Açai fruit is a well know Brazilian seed plant used in large scale as a source of feed stock, specially in the Brazilian North-east region. The Açai oil is use in many purposes from fuel sources to medicine.

2. METHODOLOGY

The Açai Oil was conditioned in bottles of PVC, and envoy for irradiation in source of Co-60, in the dose of 25 kGy. After the irradiation the sample was submitted to the extration liquid-liquid, with solvent Chloroform degree HPLC, the objective to extract the maximum of fatty acid. The dilution was carried through until reaching the concentration of $50\mu\text{g/mL}$ of Açai Oil in Chloroform.

The composition of the Açai Oil was analysing by Gas Chromatography coupled to Quadrupole Mass Spectrometry analyser well know as GC/MS, Shimatzu, model QP 5000. The analyte compounds have been separate by capillary column DB-5, within $30\text{m} \times 0,25\text{mm} \times 0,25\mu\text{m}$, with polished-dimetyl-siloxan (5% fenil) stationary phase composition, therefore, lightly polar. Helium was used as carrier gas and gave a column head pressure of 12 p.s.i. and an average flux of 1 mL/min. The operation followed the following conditions: 2-min hold at 75°C , a $15^\circ\text{C}/\text{min}$ ramp until 200°C , a $20^\circ\text{C}/\text{min}$ ramp until 250°C and an 2 min hold at 250°C . Temperature of the detector of 250°C ; gas of drags: helium with linear speed of $32\text{cm}/\text{s}$. The race with mass detector was carried through in the form scan, of mass of 50 the 250 m/z ; energy of 70 eV. The identification of the analytes was made by comparison of the mass spectra standard NIST-92 library. The gas chromatograph was plotted and the retention time of each analyte was identify by mass spectra data and finally plotted in Table 2 and 3.

3 Results and Conclusion

The gas chromatogram gotten for the analysis of the pure Açai Oil not radiated is shown in Figure 1. The main constituent had been fatty acids saturated: palmitic, myristic and lauric and the insaturated ones: oleic and linoleic.

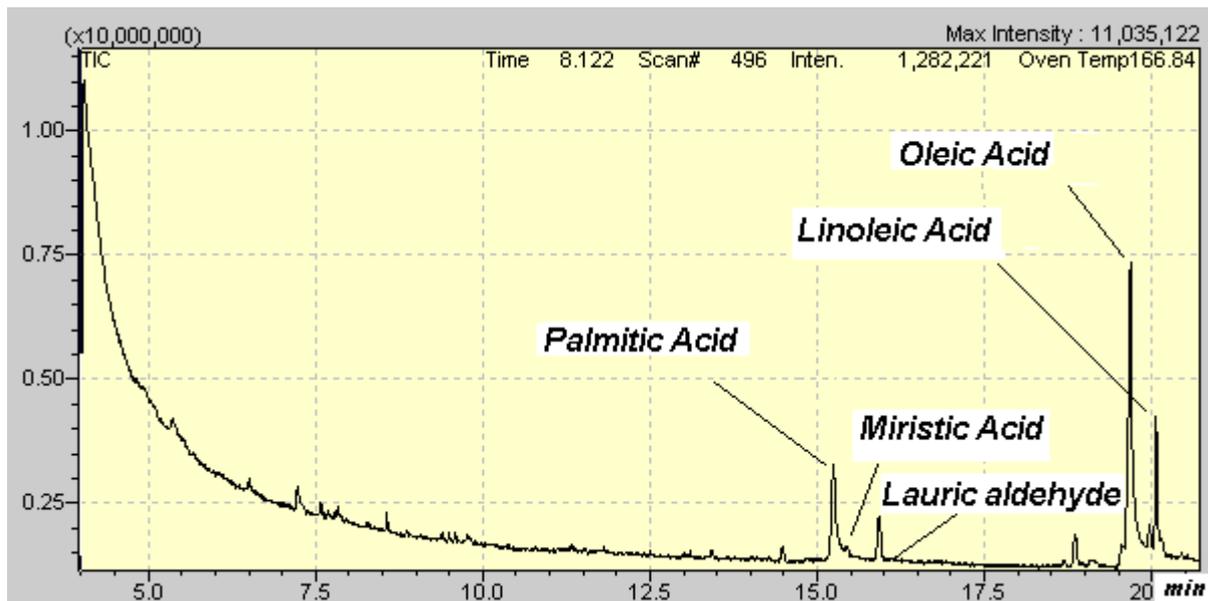


Figure 1: Açai oil chromatogram without irradiation.

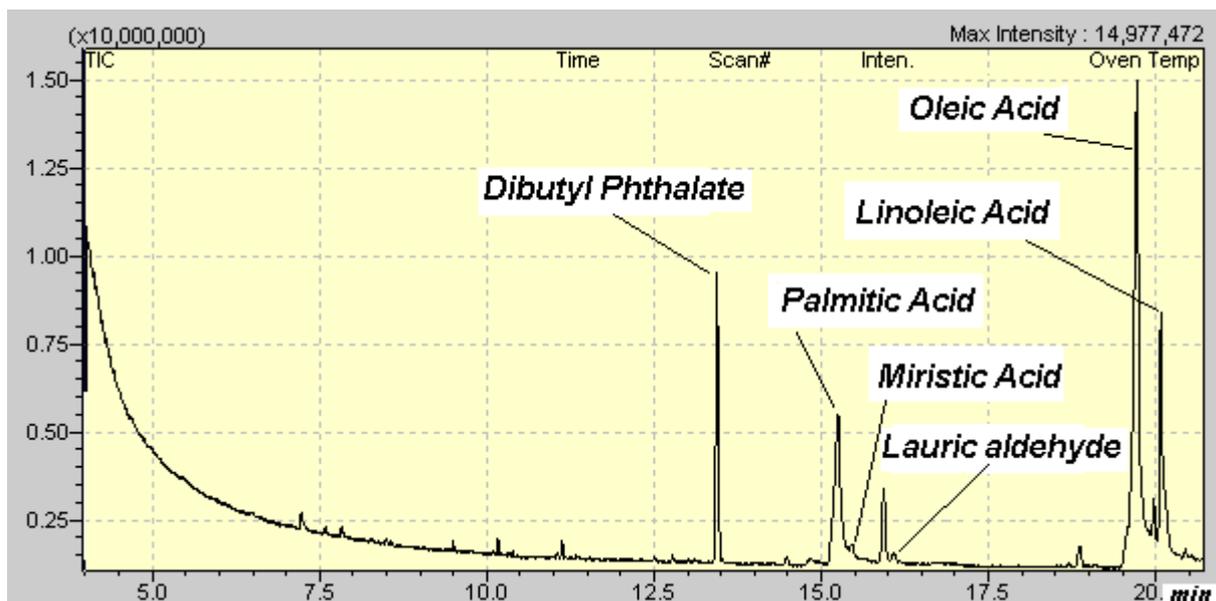


Figure 2: Açai oil chromatogram irradiated within 25 kGy

TABLE 1: Fatty acids analysis from Açaí oil by GC/MS. Sample non irradiated.

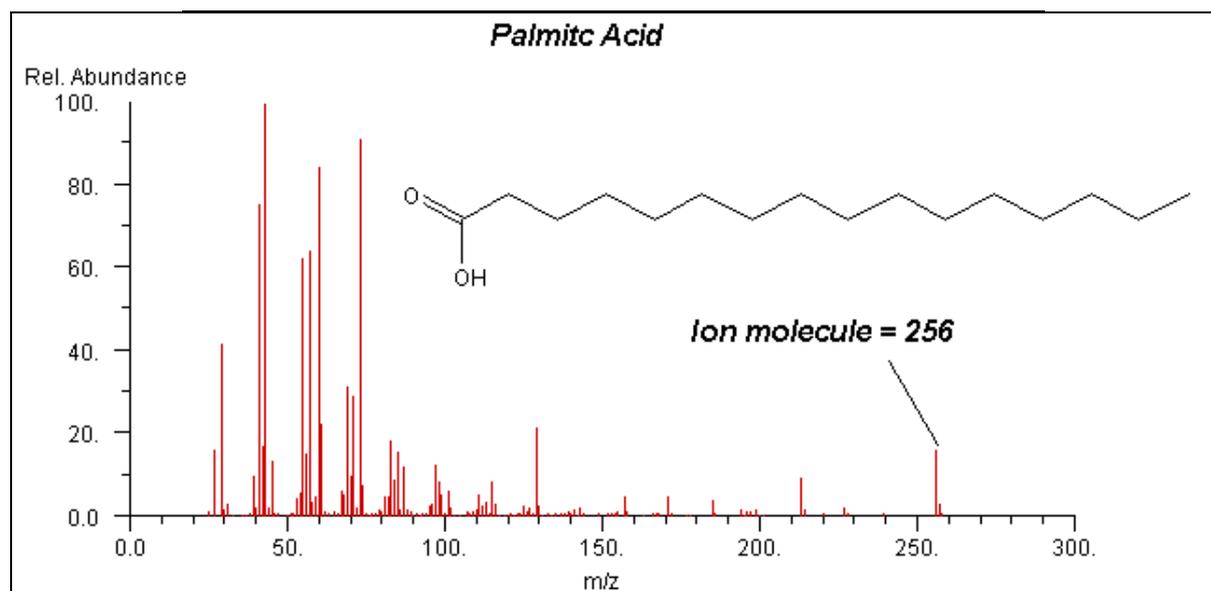
R.T. (min)	COMPOUND	FORMULA	M.W.	AREA (TIC)	R.I.(%)	CAS
15,2	Palmitic Acid	C ₁₆ H ₃₂ O ₂	256	10037612	32,2	57-10-3
15,4	Miristic Acid	C ₁₄ H ₂₈ O ₂	228	1204918	3,9	544-63-8
15,9	Ethyl Ester Palmitic Acid	C ₁₀ H ₁₆	284	4063860	13,1	628-97-7
16,1	Lauric Aldehyde	C ₁₂ H ₂₄ O	284	195564	0,6	112-54-9
18,8	Methyl Ester Oleic	C ₁₉ H ₃₆ O ₂	296	2482392	8,0	112-62-9
19,7	Oleic Acid	C ₁₈ H ₃₈ O ₂	282	31131622	100,0	112-80-1
19,9	Linoneic Acid Chloride	C ₁₈ H ₃₁ ClO	298	3070993	9,9	7459-33-8
20,0	Ethyl Oleic	C ₁₈ H ₃₈ O ₂	310	8445239	27,1	111-62-6

TABLE 2: Fatty acids analysis from Açaí oil by GC/MS. Sample irradiated.

R.T. (min)	COMPOUND	FORMULA	M.W.	AREA (TIC)	R.I.(%)	CAS
15,2	Palmitic Acid	C ₁₆ H ₃₂ O ₂	256	31284651	37,3	57-10-3
15,4	Miristic Acid	C ₁₄ H ₂₈ O ₂	228	4381154	5,2	544-63-8
15,9	Ethyl Ester Palmitic Acid	C ₁₀ H ₁₆	284	9179540	11,0	628-97-7
16,1	Lauric Aldehyde	C ₁₂ H ₂₄ O	284	1116193	1,3	112-54-9
18,8	Methyl Ester Oleic	C ₁₉ H ₃₆ O ₂	296	2775850	3,3	112-62-9
19,7	Oleic Acid	C ₁₈ H ₃₈ O ₂	282	83760841	100,0	112-80-1
19,9	Linoneic Acid Chloride	C ₁₈ H ₃₁ ClO	298	7293915	8,7	7459-33-8
20,0	Ethyl Oleic	C ₁₈ H ₃₈ O ₂	310	32207517	38,5	111-62-6

TABLE 3: Intensities relative areas difference of the sample irradiated to non irradiated

COMPOUND	Irradiated	non irradiated	Difference
Palmitic Acid	37,3	32,2	5,1
Miristic Acid	5,2	3,9	1,4
Ethyl Ester Palmitic Acid	11,0	13,1	-2,1
Lauric Aldehyde	1,3	0,6	0,7
Methyl Ester Oleic	3,3	8,0	-4,7
Oleic Acid	100,0	100,0	0,0
Linoneic Acid Chloride	8,7	9,9	-1,2
Ethyl Oleic	38,5	27,1	11,3

**Figure 3: Palmitic Acid mass spectra.**

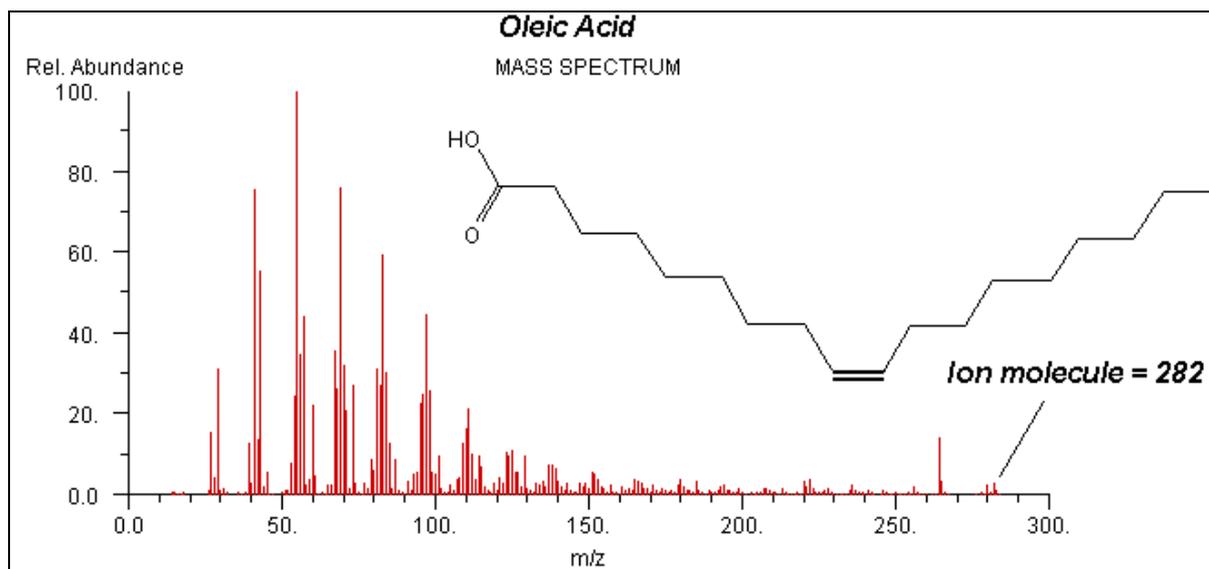


Figure 4: Oleic Acid mass spectra.

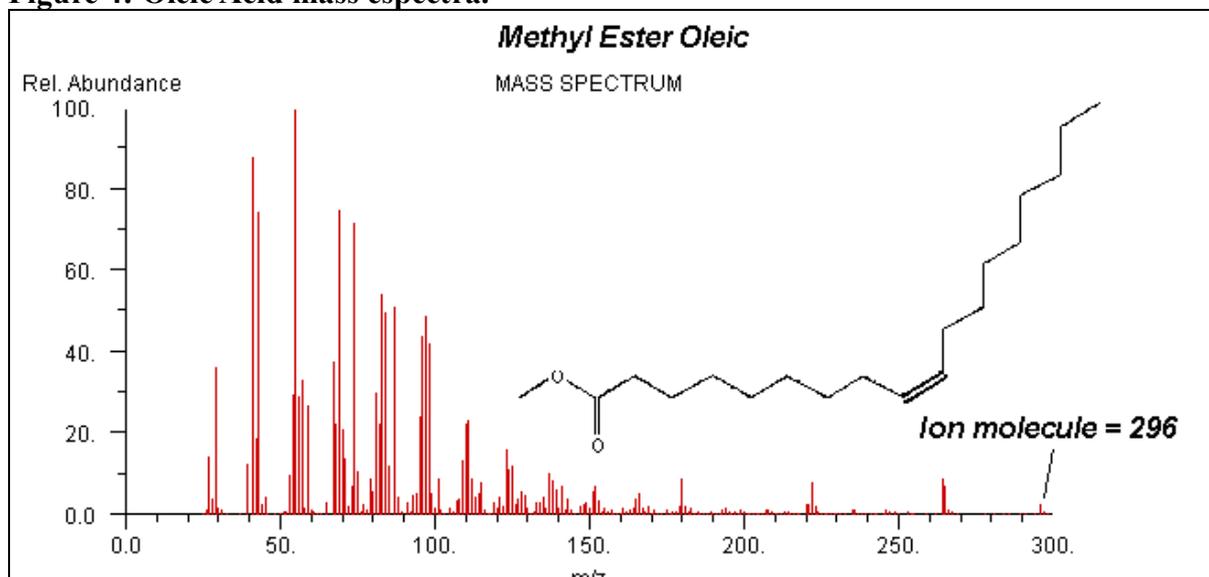


Figure 3 : Methyl ester oleic mass spectra

REFERENCES

BARRY, B. Liberação transdérmica de fármacos. In: AULTON, M.E. *Delineamento de formas farmacêuticas*. 2. ed. São Paulo: Artmed, 2005. Cap. 33, p. 504-536.

LUBRANO, C.; ROBIN, J. R.; KHAIAT, A. Composition em acides grãs, stérols et tocophérols d'huiles de pulpe de fruits de six espèces de palmiers de Guyane. *Oléagineux*, v. 49, n.2, 1994. p. 59-65.

DEWICK M. PAUL Medicinal Natural Products

BUSTILLOS VEGA OSCAR, SASSINE ANDRÉ MARCH RAYMONS A espectrometria de massas quadrupolar

ROGEZ HERVÉ Açaí: Preparo, Composição e Melhoramentos da conservação