



Potential of mangaba (*Hancornia speciosa*), mango (*Mangifera indica* L.), and papaya (*Carica papaya* L.) seeds as sources of bioactive compounds¹

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ABSTRACT

The bioactive compounds and the antioxidant capacities of mangaba, mango and papaya oils were investigated. Determinations of fatty acid composition, tocopherol, phytosterols, phenolic compounds profile, total carotenoids, and antioxidant activity were carried out in the oils of mangaba, mango and papaya seeds. The analysis of antioxidant activity was performed by the methods DPPH[•], ABTS^{•+}, FRAP, and β -carotene/linoleic acid. Only essential fatty acid C18:2 was detected, in an average of 6.2%. In contrast, the main fatty acids quantified were oleic, palmitic, and stearic. The amount of phytosterols in mangaba (1951.7 mg kg⁻¹), papaya (3540.3 mg kg⁻¹), and mango (4565.7 mg kg⁻¹) oils was higher than that of conventional oils, such as soybean oil. α -tocopherol was the main tocopherol found in all oils analyzed. Quantities of phenolic compounds were found only in mango seed oil. Papaya seed oil showed high quantity of total carotenoids (49.90 μ g g⁻¹). The possible use of the seeds studied to produce oils appears to be favorable. The information available in this study is of great importance for investigations regarding the use of vegetable oils as raw material for food, pharmaceutical, and chemical industries.

Keywords: antioxidant capacity; oil; seeds; waste.

INTRODUCTION

The importance of studying more about agroindustrial fruit waste, as a source of bioactive compounds, is related to the appreciation of these raw materials and their residues for obtaining new products of high added value. Recent studies demonstrate the importance of converting agro-industrial waste into biomolecules such as bioactive peptides, carotenoids, phenolic compounds, proteins, and enzymes (Socaci *et al.*, 2017; Nazzaro *et al.*, 2018; Rodrigues *et al.*, 2019). Fruits are widely processed by industries. However, when waste is utilized, it practically does not add any value to the fruits. The production of high-quality special oil from waste can guarantee the supply of the food, pharmaceutical, chemical and cosmetic industries, meeting the needs for new alternative sources of oils. Besides that, it will also allow better utilization of the

fruits and the rational and efficient use of residues generated by industry avoiding, thus, waste (Wu *et al.*, 2011; Mirabella *et al.*, 2014).

Research on new sources of oils and their impact on food quality and diet have not been fully explored. Brazil is rich in species of native and / or exotic tropical fruits of great agro-industrial potential, such as mango, mangaba and papaya, consumed, mainly as industrialized products, such as juices, for example. For this reason, a great volume of waste from these fruits is generated daily by agroindustry and, frequently, has its use limited to animal food industry or is disposed in the ambience. Nevertheless, the residues present high potential, since they contain sugars, micronutrientes, fibers, oils, and other minor compounds with beneficial properties (Babbar *et al.*, 2011; Nagle *et al.*, 2011; Luzia & Jorge, 2013).

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Mangaba and papaya fruits are usually cultivated in Northeastern Brazil, while mango fruits are grown in different regions around the country. Mangaba cultivation is mainly destined to the processing of juice and frozen pulps. Mango is normally consumed *in natura* during its harvest or processed as concentrated juice or pulp. In Brazil, local varieties such as Bourbon, Rosa, Espada, Palmer, Ubá, among others, are predominant. In this study, Palmer variety was used. Papaya is much used in the elaboration of sweets, juices, and frozen pulps. For being sweet, this fruit is commonly consumed *in natura*, and Formosa variety, used in this study, is destined to processing.

Studies have reported that some seeds contain considerable quantities of oil (Górnás & Rudzińska, 2016; Anwar *et al.*, 2019). However, further research on the chemical composition and other properties of fruit seed oils is necessary to evaluate their potential as sources of quality raw material for the industry (Maier *et al.*, 2009). The presence of bioactive compounds may grant functional properties to oils extracted from fruit seeds, i.e., if frequently ingested, they may reduce the risk of certain diseases (Geranpour *et al.*, 2020; Rezig *et al.*, 2019).

The objective of this work was to evaluate the oils obtained from the extractions of disposed mangaba, mango, and papaya seeds, as to the content of bioactive compounds. In order to reach this goal, the following analyses were performed: fatty acid composition, tocopherols, phytosterols, and phenolic compounds profile, and determination of total carotenoids, and antioxidant capacity of oils.

MATERIAL AND METHODS

Residues

The fruit residues were obtained from Brazilian agroindustries in the States of São Paulo (Southeast region) and Sergipe (Northeast region). One lot of each of the samples was collected between October, 2011 and March, 2012 (Table 1). The seeds were put in sieves and washed with running water until all visible pulp residues had been removed. During this cleaning phase, all shrunken, cracked, and split seeds were disposed of. The seeds were dried in an oven with air circulation (Marconi, model MA 035) at 40 °C. Drying time ranged from 2 days, for mangaba and papaya seeds, to 1 week, for mango seeds. Seed yield varied according to the composition of the residue: presence of fibers, pulp and peel remains and seed moisture, ranging from 10% for mango to 40% for mangaba. The seeds were then packed in glass flasks, sealed, and stored at room temperature until they were used.

Oil extraction

For cold extraction, a mixture of solvents was used: chloroform:methanol:water (2:1:0.8) (v/v/v) respectively and 1:14.5 (solid:solvent) during 30 min (Bligh & Dyer, 1959). The oils were frozen in airtight glass bottles.

Fatty acids composition

Lipid fractions of seeds (100 mg) were transesterified to methyl esters with KOH in methanol and hexane (AOCS, 2009). Fatty acid methyl esters (FAMES) were determined by CG 3900 gas chromatography (Varian Inc., Walnut Creek, CA, USA), equipped with flame ionization detector, split injector. The FAMES were separated using a CP-Sil 88 fused silica capillary column (60 m x 0.25 mm i. d., 0.20 µm film thickness, Chrompack, Varian Inc., Walnut Creek, CA, USA). The temperature curve started at 90 °C, for 4 min, heated at 10 °C min⁻¹ until reaching 195 °C, and remained constant for 16 min. The injector and the detector temperatures were 230 °C and 250 °C, respectively. The carrier gas was hydrogen. The amount of each fatty acid was expressed in percentage (%).

Tocopherols

Tocopherols composition was determined by AOCS Ce 8-86 (2009), using HPLC system (Varian Inc., Walnut Creek, CA, USA) with fluorescence detection. 20 µl of the extract formed by 400 mg of oil diluted in n-hexane were injected. Conditions of the analysis: λ excitation 290 nm and λ emission 330 nm. A normal phase column (Microsorb 100 Si, 250 mm 4.6 mm internal diameter with 0.5 mm particle size) was used with hexane/isopropanol (99.5/0.5 v/v) as a mobile phase and 1.2 mL min⁻¹ flow. Quantification was based on an external standard method. The contents of tocopherols were expressed as mg kg⁻¹ of oil.

Phytosterols

Phytosterols were measured using gas chromatography with prior saponification of the sample (Duchateau *et al.*, 2002). The analysis was performed using a GC-2010 Plus gas chromatograph (Shimadzu, Chiyoda-ku, Tokyo, Japan), with flame ionization detector, split injector. Parameters used: fused silica capillary column (30 m x 0.25 mm i. d.), and film thickness of 0.25 µm, (Restek RTX 5, Shimadzu, Chiyoda-ku, Tokyo, Japan). The temperature of column started at 100 °C for 2 minutes, heated at 15 °C min⁻¹ to 260 °C, and maintained constant for 35 minutes. The temperatures used in the injector and in the detector were 280 and 320 °C, respectively. The carrier gas was hydrogen. Samples of 1.0 µL were injected with split ratio of 1:50. The quantification of each isomer was performed by internal standardization (5α-cholestane-

3 β -ol) based on the areas of the peaks. The phytosterols were expressed in mg kg⁻¹.

Phenolic compounds

Phenolic compounds were obtained from the lipid fraction (Parry *et al.*, 2005). The analysis was carried out through HPLC (model Prominence, Shimadzu, Nakagyo-ku, Kyoto, Japan) with diode array detector (Kim *et al.*, 2006). Analysis conditions: analytical column 5C18 (250 x 4.6 mm i. d., particles of 5 μ m, Nakagyo-ku, Kyoto, Japan), mobile phase composed by 2% acetic acid in water (v/v) (solvent A) and methanol (solvent B). Gradient programming: 100-70% A in 30 min, 70-0% A in 10 min, and 0-100% A in 10 min; 1.2 mL min⁻¹ flow and 20 μ L injection volume. The quantification was performed by external standardization based on the areas of the peaks, using standards of gallic, caffeic, and salicylic acids, epicatechin, and quercetin, detected in 280 nm, and also of gentisic and *p*-coumaric acids and of catechin, detected in 320 nm. The phenolic compounds were expressed in mg/kg.

Total carotenoids

To determine the total carotenoid content, the scanning spectrophotometry technique was used (Shimadzu, Kyoto, Japan), model Uv-Vis mini 1240. Quantification was calculated using the absorption in the wavelength of maximum absorption and with absorptivity value of 2592, in petroleum ether (Rodriguez-Amaya, 2001). The values were expressed as μ g of β -carotene per gram of oil (μ g β -carotene g⁻¹).

Antioxidant capacity measurements in the seed oils

DPPH[•], The concentration of antioxidant required to inhibit 50% of the DPPH[•] radical, calculated from a standard ethyl acetate curve (10, 25, 50, 75 and 100 mg/mL). 1 mL of each dilution was mixed with 4 mL of DPPH[•] (10⁻⁴ M). The components were vortexed for 0.5 h and the absorbance of the mixture was then measured at 517 nm using a UV-Vis spectrophotometer. EC₅₀ value was expressed in mg mL⁻¹ (Brand-Williams *et al.*, 1995; Kalantzakis *et al.*, 2006).

Originally, DPPH[•] assay uses methanol as solvent of the components involved in the reaction. However, methanol does not dissolve oils, thus, the use of appropriate solvent is necessary. The effect of the solvents n-hexane, chloroform, acetone, petroleum ether, and ethyl acetate was tested and the best results were obtained with ethyl acetate (Espín *et al.*, 2000).

ABTS^{•+} radical method, as reference, synthetic antioxidant Trolox was used in concentrations from 0.05 to 2.0 mmol L⁻¹. The results were expressed as μ mol Trolox 100 g⁻¹ (Re *et al.*, 1999; Pellegrini *et al.*, 2001).

FRAP (Ferric Reducing Antioxidant Power) method, the measure was performed at 595 nm. The antioxidant capacity result was expressed as μ mol ferrous sulfate 100 g⁻¹ of oil (Szydłowska-Czerniak *et al.*, 2011).

β -carotene/linoleic acid method, a portion of the β -carotene solution (0.2 mg/mL in chloroform) was blended to 50 mg of linoleic acid and 200 mg of Tween 40 and the chloroform entirely evaporated with nitrogen. β -

Table 1: Popular name, scientific name, description of the fruits and residues used in this study

Popular name	Scientific name	Fruit description	Residue origin and description
Papaya Formosa	<i>Carica papaya</i> L.	Thin skin, ranging from green to intense yellow, long shape, fleshy and soft pulp of orange-reddish color, very sweet. The central cavity is filled with numerous small, round, black seeds.	Fruit processing industry, Sao Paulo State, Southeastern Brazil. Approximately 5 kg of residues were provided in October, 2011. The remaining fibers were removed manually. The fruits were processed in Sao Paulo State, although cultivated in Bahia State, Northeastern Brazil.
Mango Palmer	<i>Mangifera indica</i> L.	Classified as a drupe fruit, which is fleshy and contains only one seed protected by a hard endocarp. Its pulp is firm, with no fiber, and of mild and sweet flavor.	Fruit processing industry, Minas Gerais State, Southeastern Brazil. Approximately 10 kg of residues were collected right after the juice processing. Separation of seeds from endocarp was performed with the assistance of a stainless-steel knife. The broken seeds were disposed of.
Mangaba	<i>Hancornia speciosa</i> var. <i>pubescens</i>	Green-yellowish fruits, with juicy, viscous, aromatic, sweet pulp.	Fruit processing industry, Sergipe State, Northeastern Brazil. 10 kg of residues were obtained in March, 2012, and consisted of only seeds.

carotene/linoleic acid emulsion were mixed to distilled water saturated with oxygen and 0.5 mL of the ethanolic solution of the sample (20 mg/mL) in test tubes. The absorbance at 470 nm was measured every 15 minutes, for 2 hours at 50 °C. The results were expressed in oxidative inhibition (I):

$$I (\%) = \frac{(DR_c - DR_s)}{(DR_c)} \times 100$$

where DR_c is the degradation rate of the control and DR_s is the degradation rate of the sample. The degradation rate is the difference between the absorbances at times zero and 120 minutes. The degradation rate kinetic curve graph versus time allowed the calculation of the kinetic factor (Marco, 1968; Miller, 1971).

With the curve of the control and the curve of the sample the values of F1 and F2 were calculated, using this equation, where tg is the tangents of the curve:

$$F = \frac{tg_{sample}}{tg_{control}}$$

The coefficient resulting from the division between the opposite cathetus (obtained by the difference between the absorbances in the time evaluated) and the adjacent cathetus (obtained from the difference between times) was considered the value related to the tangents. F1 value was calculated in the interval from 15 to 45 min, while F2 was calculated from 75 to 105 min.

Statistical analysis

All experiments were executed in triplicate, expressed as means ± SD (standard deviation) and submitted to ANOVA and to Tukey test at 5% significance ($p > 0.05$), by using the Statistica program (Statsoft Inc., Tulsa, USA) version 7.0.

RESULTS AND DISCUSSION

Fatty acid profile

The fatty acid profile of the fruit seed oils is presented in Table 2. The lipid fractions obtained in the extractions of mango, mangaba, and papaya seeds presented yields of 7.0, 11.8, and 23.5%, respectively. Studies performed previously presented yields of 29.2% in papaya seed oil (Malacrida *et al.*, 2011). These yields are higher if compared with oilseeds such as corn and soy, which present lipid contents of 3.1-5.7% and 18-20%, respectively (O'Brien, 2004).

The results in Table 2 show that the main fatty acids present in oil are monounsaturated, especially oleic acid (C18:1). The main saturated fatty acids are palmitic (C16:0), in mangaba and papaya oils, and stearic (C18:0), in mango oil. The fatty acid composition of mangaba and papaya oils is similar to that of olive oil (55-83% of oleic acid, 7.5-20% of palmitic acid, and 0.5-5% of stearic acid) and of peanut oil (35-69% of oleic acid, 8-14% of palmitic acid, and 1-4.5% of stearic acid) (Codex Alimentarius Commission, 2009). The predominance of oleic acid is also observed in nut oils like almond (43-75%), cashew (57-64.2%), hazelnut (76-82%), macadamia (34-75%) pecan (40.6-75%) and pistachio (52-70%) (Maestri *et al.*, 2020).

Differently from the other samples, mango seed oil presented higher concentration of stearic acid, which is not common among vegetable oils. However, other researchers who also analyzed mango seed oil found higher concentration of this saturated fatty acid. In a research performed with seeds of the variety kibangou, native to Congo, the oil extracted by Folch method resulted in 40% of stearic acid, while the extractions by Bligh & Dyer and Soxhlet resulted in, respectively, 37.5 and 37.9% of stearic acid in mango seed oils (Nzikou *et al.*, 2008; Vieira *et al.*, 2009). It is possible to conclude that, regardless of the extraction method, the amount of stearic acid in mango seed oil is higher than palmitic acid.

Table 2: Fatty acid profile of oils extracted from fruit seeds

	Mangaba	Mango	Papaya
Fatty acid (%)			
C16:0	19.1 ± 0.0 ^a	7.8 ± 0.0 ^c	16.5 ± 0.0 ^b
C18:0	8.2 ± 0.0 ^b	29.2 ± 0.1 ^a	4.6 ± 0.0 ^c
C18:1 n-9	63.9 ± 0.0 ^b	52.7 ± 0.0 ^c	72.2 ± 0.0 ^a
C18:2 n-6	7.4 ± 0.1 ^a	5.9 ± 0.0 ^b	5.3 ± 0.0 ^b
C20:0	0.7 ± 0.0 ^b	1.7 ± 0.0 ^a	0.3 ± 0.0 ^c
SFA	28.3 ± 0.1	40.7 ± 0.0	22.0 ± 0.0
MUFA	64.1 ± 0.0	53.3 ± 0.0	72.7 ± 0.0
PUFA	7.5 ± 0.1	5.9 ± 0.0	5.3 ± 0.0
UFA/SFA	2.52	1.45	3.55

Means ± standard deviation of the analyses performed in triplicate followed by the same letter do not differ by Tukey test ($p > 0.05$). nd: not detected.

SFA: saturated fatty acids; MUFA: monounsaturated fatty acids; UFA: unsaturated fatty acids; PUFA: polyunsaturated fatty acids. nd < 5%.

The high content of oleic acid in mangaba, mango, and papaya seed oils is also similar to what is found in canola (70%) and sunflower (84%) high oleic oils (Codex Alimentarius Commission, 2009). These oils present enough stability to be used in frying processes and in spraying of snacks, cookies, cereals, dried fruits, and bakery products, in which the oil is useful to maintain the technological quality of the product (Corbett, 2003). Besides that, this author claims that lipids with high concentration of monounsaturated fatty acids can be used in the cosmetic industry as moisturizers, bath oils, hair conditioner, and make up.

The polyunsaturated fatty acids (PUFA) unlike in most of the vegetable oils, such as soybean (70%), corn (67%), and sunflower (83%), were found in small concentrations, between 5.3-7.5%, which could provide better oxidative stability to the oils. Although the relative amount of polyunsaturated fatty acids is an important factor for the thermal stability of oils, it can also be affected by the presence of antioxidants in the chemical composition of the oil, like phenolic compounds and tocopherols. The polyunsaturated fatty acids have physiological benefits such as the maintenance of the immune system in inflammatory processes and are able to carry out antimicrobial action (DebMandal *et al.*, 2011).

Bioactive compounds

The bioactive substances in fruit seeds are described in Table 3. The total quantities of phytosterols were 1951.7,

3540.3, and 4565.7 mg kg⁻¹ in mango, papaya, and mangaba seed oils, respectively, similarly to values found in some nuts for example almond, brazil nut, pecan, pistachio and walnut (Maestri *et al.*, 2020). In all samples, β -sitosterol stood out among other phytosterols. In accordance with Codex Alimentarius Commission (2009), the average β -sitosterol value in vegetable oils is 60%. In this study, about 78% of the composition of total sterols in the oils evaluated is formed by β -sitosterol, which confirms the prevalence of this sterol in the unsaponifiable matter of vegetable oils.

Phytosterols have the hypocholesterolemic property because, when consumed, they are able to reduce the absorption of cholesterol. Daily consumption of 1.6-2.0 g day⁻¹ of phytosterols and phytostanols can reduce cholesterol absorption by the intestine in up to 30%, besides decreasing the level of plasma LDL-cholesterol in 8-10% (Marangoni & Poli, 2010). Among commercial oils, soybean and sunflower oils present between 1800-4600 mg kg⁻¹ (Codex Alimentarius Commission, 2009). Therefore, it is possible to affirm that, when comparing the levels of total phytosterols of oils obtained in this study with those normally consumed, the seed oils analyzed can be considered alternative sources of phytosterols. In a study carried out with mango seed oil, the level of total phytosterols found was equivalent to 22.5% of the total unsaponifiable matter of oil, while tocopherols represented 11.9% of the unsaponifiable constituents (Abdalla *et al.*, 2007).

Table 3: Bioactive compounds present in the fruit seed oils

	Mangaba	Mango	Papaya
Phytosterol (mg kg ⁻¹)			
Campesterol	nd	nd	243.1 ± 0.02 ^a
Stigmasterol	nd	504.4 ± 0.01 ^a	220.9 ± 0.01 ^b
β -sitosterol	3471.1 ± 0.01 ^a	1447.3 ± 0.01 ^c	3069.1 ± 0.02 ^b
Stigmastanol	1094.6 ± 0.01 ^a	nd	nd
Totals	4565.7 ± 0.02	1951.7 ± 0.02	3540.3 ± 0.02
Tocopherols (mg kg ⁻¹)			
α -tocopherol	36.77 ± 0.06 ^a	14.37 ± 0.12 ^c	27.20 ± 0.51 ^b
β -tocopherol	nd	nd	3.97 ± 0.12 ^a
Totals	36.77 ± 0.06	14.37 ± 0.12	31.17 ± 0.06
Phenolic compounds (mg kg ⁻¹)			
Galic acid	nd	118.96 ± 1.03 ^a	nd
Salicylic acid	nd	78.14 ± 0.92 ^a	nd
Quercetin	nd	11.03 ± 0.29 ^a	nd
Epicatechin	nd	28.46 ± 0.04 ^a	nd
Totals carotenoids (μ g β -carotene g ⁻¹)	15.91 ± 0.70 ^b	0	49.90 ± 1.17 ^a

Means ± standard deviation of the analyses performed in triplicate followed by the same letter do not differ by Tukey test ($p > 0.05$). nd: not detected.

Detection limit: campesterol \leq 52.0 mg kg⁻¹; stigmasterol \leq 56.0 mg kg⁻¹; stigmastanol \leq 42.5 mg kg⁻¹.

Detection limit: β -tocopherol \leq 1.10 mg kg⁻¹.

Detection limit: galic ac., salicylic ac., epicatechin and quercetin \leq 5 mg kg⁻¹

The amounts of total tocopherols were 14.37, 31.17, and 36.77 mg kg⁻¹ in mango, papaya, and mangaba seed oils, respectively, similarly to macadamia oil (Maestri *et al.*, 2020). These values are lower than what found in traditionally consumed oils such as corn (314-3116 mg kg⁻¹), soybean (252-3627 mg kg⁻¹), and sunflower (401-1021 mg kg⁻¹) (Codex Alimentarius Commission, 2009). In a study performed with papaya seeds, 74.71 mg kg⁻¹ of total tocopherols were found for the lipid fraction (Malacrida *et al.*, 2011). In this study the seed oil was obtained by extraction using petroleum ether in a Soxhlet extractor, which can justify the difference between the values found. Comparing our results with others that have been cited in the literature, regardless of the total amount of tocopherols, it is possible to affirm that the predominant isomer in mango seed oil is α -tocopherol, as well as in papaya seed oil (Kamal-Eldin & Appelqvist, 1996; Malacrida *et al.*, 2011). Diets containing α -tocopherol are recommended for consumption by humans, since this isomer carries high vitamin E biological activity. Generally, high concentrations of tocopherols are correlated with high content of polyunsaturated fatty acids, as tocopherols act as natural antioxidants. Thus, the low quantity of tocopherols found in the oils analyzed can be explained by the low content of polyunsaturated fatty acids, especially linoleic acid (Tuberoso *et al.*, 2007).

Phenolic compounds were only quantified in mango seed oil, and gallic acid stood out (118.96 mg kg⁻¹). In refined vegetable oils from oilseeds, phenolic compounds appear in relatively low concentrations, since great part of these compounds is removed during refining stages. For this reason, few studies elucidate the investigation of these compounds in refined oils. Thus, researches on the composition of phenolics are restricted to crude oils.

In the review by Bodoira and Maestri *et al.* (2020), the authors concluded that innovative extraction techniques such as microwaves, ultrasound and compressed fluids are being used to obtain phenolic compounds because they are ecologically cleaner techniques. In general, phenolic compounds exist naturally in a wide variety of foods of vegetable origin, such as fruits, legumes, seeds, flowers, and leaves, and are part of the human diet. However, fruits are normally richer in phenolics than other vegetables. The amount of phenolic compounds in each food is quite variable, even among cultivars of the same species (Yang *et al.*, 2011).

Although the chromatographic analysis does not indicate the presence of isolated compounds in mangaba and papaya seed oils, it was possible to quantify total phenolic compounds by spectrophotometry in all oils because this analysis is able to detect several phenolic

groups present in the oil, including extractable proteins, although this overestimation in oils is minimal. In a research performed with papaya seed oil, 957.60 mg kg⁻¹ of total phenolic compounds were identified (Malacrida *et al.*, 2011).

The results regarding total carotenoids are also shown in Table 3. Mangaba and papaya seed oils presented 15.91 and 49.90 μ g of β -carotene g⁻¹, respectively, while mango seed oil did not show detectable level of total carotenoids. Oils of high carotenoid concentration, like palm oil, which presents total level of 38.5 μ g g⁻¹, present technological potential, since these pigments contain antioxidant activity, protecting the oil from lipid oxidation (Szydłowska-Czerniak *et al.*, 2011) and nutritional qualities because as they are sources of vitamin A. Therefore, papaya seed oil can be considered a good source of vitamin.

No data was found in the literature about the analysis of phenolic compounds and total carotenoids regarding mango and mangaba seed oils.

Antioxidant capacity measurements

Table 4 shows the average antioxidant capacities for the methods DPPH[•], ABTS^{•+}, FRAP, and β -carotene/linoleic acid. The antioxidant capacity of the oils by the method of DPPH[•] free radical was expressed by efficient concentration (EC₅₀), that is, the necessary amount of antioxidant to reduce free radical initial concentration in 50% in a way that, the lower the EC₅₀ value, the more effective the antioxidant agent. Overall, mango seed oil presented better results in DPPH[•], ABTS^{•+}, and FRAP tests.

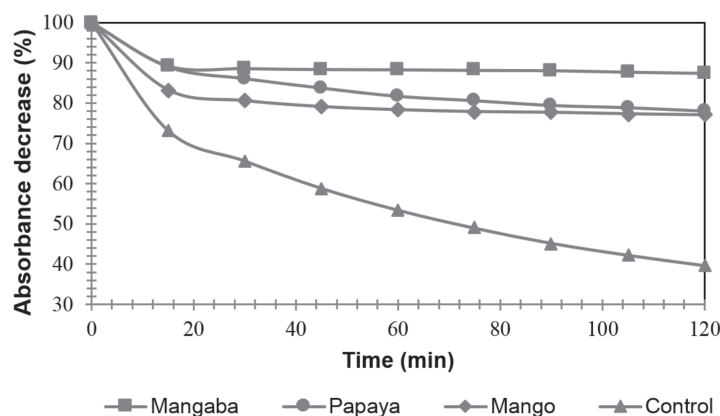
As FRAP system is a method that is incompatible with organic solvents, it is commonly used in order to analyze the antioxidant activity of the most polar fractions of vegetable oils, which is rich in phenolic compounds. FRAP assay is a non-competitive mechanism, since it does not necessarily need a free radical, as reactive species of oxygen. Carbonyl compounds and metals participate as oxidants in this sort of assay. Thus, they are considered less representative of the food real conditions, when compared to DPPH[•] and ABTS^{•+} tests (Prior *et al.*, 2005). The values of the antioxidant capacities of the samples ranged from 184.76 to 226.17 μ mol ferrous sulfate 100 g⁻¹ oil, which were higher in blackberry, blueberry, kiwi, and strawberry seed oils, 30, 26, 29, and 24 μ mol ferrous sulfate 100 g⁻¹ oil, respectively (Hoed *et al.*, 2011).

In the analysis of β -carotene / linoleic acid, tocopherols tend to perform better as antioxidants when compared to phenolic compounds due to the greater solubility in the water-oil emulsion matrix (Miraliakbari & Shahidi, 2008). The results on the oxidative inhibitions were consistent with the tocopherol level presented by each sample, in a way that mangaba seed oil, which showed higher quantity

Table 4: Antioxidant capacity of fruit seed oils

	Mangaba	Mango	Papaya
EC ₅₀ (mg mL ⁻¹)	155.87 ± 2.59 ^a	11.57 ± 0.57 ^c	34.83 ± 0.23 ^b
ABTS ⁺ (μmol Trolox 100 g ⁻¹)	121.45 ± 2.69 ^b	169.02 ± 1.19 ^a	113.23 ± 1.79 ^c
FRAP (μmol FeSO ₄ 100 g ⁻¹)	184.76 ± 4.34 ^c	226.17 ± 2.34 ^a	214.12 ± 1.72 ^b
β-carotene/linoleic (%)	74.6 ± 1.2 ^a	53.2 ± 2.1 ^c	58.3 ± 2.3 ^b
F1	0.06	0.30	0.32
F2	0.08	0.13	0.37

Means ± standard deviation of the analyses performed in triplicate followed by the same letter do not differ by Tukey test (p > 0.05).

**Figure 1:** Kinetic curves of the antioxidant capacity of fruit seed oils.

of total tocopherols, also showed the best effect in oxidative inhibition (74.6%), followed by papaya (58.3%) and mango (53.2%) samples. The oxidative inhibitions of the fractions of nut oils extracted with hexane were compared with the fractions obtained with chloroform-methanol, confirming better performance of the polar fraction: 79.2, 62.5, 48.5, and 45.2% for pecan nut, Brazil nut, pistachio nut, and hazelnut oils, respectively (Miraliakbari & Shahidi, 2008).

Additional information about the efficiency of samples was obtained with the values of F1 and F2 (Table 4), calculated by using the kinetic oxidation curves (Figure 1). The first part of the analysis (between 15 and 45 min after the beginning of the reaction), measured the efficiency of the antioxidant to inhibit the chain reaction by neutralizing the peroxide radicals. In sequence, the participation of antioxidants in secondary oxidation reactions was measured in the second half of the analysis (between 75 and 90 min after the beginning of the reaction). The more distant the values of F1 and F2 are from 1.0, the higher the antioxidant efficiency (Yanishlieva & Marinova, 1995). According to the results, the performance of the antioxidants presents in mangaba and papaya seed oils was more efficient in the reduction of peroxide formation (F1), acting as primary antioxidants.

Only mango seed oil presented F2 values lower than F1, which indicates the efficiency of the antioxidants present in this sample in acting through secondary

mechanisms, interfering in the reactions of formation of secondary products from the oxidation reaction. The correlations between the oxidative inhibition percentage (I) and F1 and F2 values were -0.82 and -0.75, respectively. The negative correlation confirms the inverse relation between I and F values.

The results show that the oils extracted from seeds present oxidative inhibition capacity, showing to be efficient in the initial times (F1) as well as in further times of the oxidative process (F2).

CONCLUSION

In summary, the present study presents the composition of bioactive compounds of oils extracted from mangaba, mango, and papaya seeds.

The oils analyzed do not present significant quantities of essential fatty acids, such as n-6 and n-3. However, they present high quantity of monounsaturated and saturated fatty acids. It was proved that the oils are significant sources of phytosterols and present antioxidant activities, which protect them from oxidative damages. However, before considering these oils to be adequate for application in foods, toxicological studies are necessary in order to guarantee their safety.

The information available in this study is of great importance for investigations regarding the use of vegetable oils as raw material for food, pharmaceutical, and chemical industries.

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