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Article

Antioxidant Capacity, Total Phenolic Content, Fatty Acids and Correlation by Principal Component Analysis of Exotic and Native Fruits from Brazil

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As capacidades antioxidante de sete frutas nativas e exóticas do Brasil foram avaliadas usando os métodos DPPH$^{\bullet}$, ABTS$^{\bullet+}$ e FRAP, além da determinação do conteúdo de fenólicos totais e composição de ácidos graxos. Murici e dovialis apresentaram os maiores conteúdos de compostos fenólicos (243,42 e 205,98 mg EAG 100 g^{-1}, respectivamente), e maiores capacidades antioxidante pelo método de FRAP (24,97 e 23,70 µmol Fe^{2+} g^{-1}, respectivamente). Pelos métodos de DPPH$^{\bullet}$ e ABTS$^{\bullet+}$, dovialis apresentou a maior capacidade antioxidante, 9,59 e 10,41 ET g^{-1}, respectivamente. Os maiores teores dos ácidos alfa-linolênico e linoleico foram encontrados na siriguela (107,86 mg AG g^{-1} LT) e tomatinho do mato (215,50 mg AG g^{-1} LT), respectivamente. A análise de componentes principais (PCA) dos ácidos graxos gerou três significantes PCs, que representaram 99,75% do conjunto de dados da variância. Os dados de PCA das análises de antioxidantes geraram dois significantes PCs, representando 97,00% do total de variância.

The antioxidant capacities of seven exotic and native fruits from Brazil were evaluated using DPPH$^{\bullet}$, ABTS$^{\bullet+}$ and FRAP assays, in addition to their total phenolic content and fatty acid composition. *Murici* and *dovialis* presented the highest total phenolic contents (243.42 and 205.98 mg GAE 100 g^{-1}, respectively), and the highest antioxidant capacities by the FRAP assay (24.97 and 23.70 µmol Fe^{2+} g^{-1}, respectively). In the DPPH$^{\bullet}$ and ABTS$^{\bullet+}$ assays, *dovialis* presented the highest antioxidant capacity, 9.59 and 10.41 TE g^{-1}, respectively. The highest alpha-linolenic and linoleic acid contents were found in *siriguela* (107.86 mg FA g^{-1} TL) and *tomatinho do mato* (215.50 mg FA g^{-1} TL), respectively. The principal component analysis (PCA) of fatty acids yielded three significant PCs, which accounted for 99.75% of the data set total variance. The PCA data of the antioxidant analyses yielded two significant PCs, which accounted for 97.00% of the total variance.

Keywords: fruits, antioxidant capacity, fatty acids, alpha-linolenic acid, principal component analysis

Introduction

Reactive oxygen species (ROS) represent the most important class of radical species generated in living systems. ROS are an umbrella term that includes both oxygen radicals ($^{\bullet}OH$, $ROO^{\bullet}$ and $O_2^{\bullet-}$) and certain non-radical (H_2O_2) oxidizing agents and/or compounds that are easily converted into radicals.[1] The overproduction of ROS and the insufficiency of antioxidant mechanisms result in oxidative stress, a deleterious process that can be an important mediator of damage to cell structures, including lipids, membranes, proteins and DNA.[2]

ROS are correlated with chronic health problems such as cancer, cardiovascular disease, neurodegenerative diseases, inflammation, atherosclerosis and aging.[3,4] The interest in foods containing antioxidants has increased because they are able to retard oxidation, which is a normal process of body functions.[5]

Brazil is a country that has favorable geographical and climate characteristics for the production of fruits.[6] However, a large number of native and exotic fruit species remains unexploited despite their potential interest to the agricultural industry and as sources of local income.[7]

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The increasing consumption of fruits is associated not only to a matter of taste and personal preference, but also to a concern with health improvement through the enhancement of the nutritional composition of food sources rich in essential nutrients and micronutrients, such as fiber, vitamins, minerals and secondary phenolic compounds.[7,8]

The antioxidant capacity of fruits vary according to their composition in phenolic compounds, vitamins C and E, carotenoids, flavonoids and other polyphenols.[9] In addition to antioxidant compounds, fruit has essential polyunsaturated fatty acids, linoleic acid (LA, 18:2n-6) and alpha-linolenic acid (LNA, 18:3n-3). These fatty acids are considered strictly essential because they cannot be synthesized by the human body and must be supplied through the diet.[10]

FRAP (ferric reducing antioxidant power), $ABTS^{\bullet+}$ (2,2'-azino-bis-3-ethylbenzthiazoline-6-sulphonic acid) and $DPPH^{\bullet}$ (1,1-diphenyl-2-picrylhydrazyl) assays are the most widely used methods for determining the antioxidant capacity of *in vitro* fruit. The results obtained depend upon the method used.[7,11] These methods differ in terms of assay principles and experimental conditions. Because multiple reaction characteristics and mechanisms are usually involved, no single assay accurately quantifies all antioxidants in a mixed or complex system.[12] Thus, the use of two or more methods has been shown to provide greater confidence in the elucidation of the complete profile of the total antioxidant capacity of foodstuff.[13]

The aim of this study was to evaluate the determination of the antioxidant capacity of seven exotic and native fruits from Brazil by $DPPH^{\bullet}$, $ABTS^{\bullet+}$ and FRAP assays and their total phenolic content (TPC) and fatty acid composition using principal component analysis (PCA).

Experimental

Chemical reagents

The reagents used were $DPPH^{\bullet}$, ABTS, 6-hydroxy-2,5,7,8-tetramethyl chroman-2-carboxylic acid (Trolox), 2,4,6-tris(2-pyridyl)-*s*-triazine (TPTZ) methyl tricosanoate (23:0), fatty acid methyl ester mixture standard 189-19 and Folin-Ciocalteu phenol reagent from Sigma-Aldrich (São Paulo, Brazil). Potassium persulfate from Neon, ferrous sulfate heptahydrate and gallic acid from Vetec and sodium carbonate from J. T. Baker were also used. All solvents and chemicals were of analytical grade.

Sample preparation

The respective botanical identifications and geographical origin of the seven exotic and native fruits from Brazil under investigation are provided in Table 1. Fresh fruit samples (ca. 2 kg for each fruit) were acquired from a farm located in Monte Alegre city, São Paulo state (23°35'31"S and 48°38'38"W). The fruits were washed with tap water and the peels and seeds were removed manually. The pulps of the different fruits were chopped and homogenized in a blender until obtain a uniform sample before analysis.

Extraction of antioxidants

The extracts were prepared using approximately 10.00 g of homogenized sample in 100.0 mL of ethanol under magnetic stirring for 4 h. After filtration, the extracts were concentrated under reduced pressure at 40 ºC to determine their antioxidant capacity by the $DPPH^{\bullet}$, $ABTS^{\bullet+}$, FRAP assays and their TPC. The extract solutions for the different fruits for each methodology were prepared with the appropriate solvents. The absorbance values obtained were in accordance with the range of the respective method calibration curves. The results are expressed in fresh weight (FW).

$DPPH^{\bullet}$ (free radical-scavenging) assay

The $DPPH^{\bullet}$ scavenging capacity was measured using the method described by Brand-Williams *et al.*[14] with modifications.[12] Briefly, the fruit extract solutions (25 µL) were added to 2 mL of a 6.25×10^{-5} mol L^{-1} $DPPH^{\bullet}$ methanol solution. The absorbance of the resulting solutions was measured at 517 nm after gently mixing and then letting the solutions stand at room temperature for 30 min. Methanolic

Table 1. List of the seven exotic and native fruits from Brazil included in this study

Common name	Scientific name	Family	Origin
Araçá boi	*Eugenia stipitata*	Myrtaceae	Brazil
Cajamanga	*Spondias dulcis*	Anacardieceae	Islands of Polynesia
Siriguela	*Spondias purpurea L.*	Anacardiacea	Central America
Dovialis	*Dovyalis caffra*	Flacourtiaceae	South Africa
Landim	*Posoqueira acutifólia*	Rubiaceae	Brazil
Murici	*Byrsonima crassifolia* (L.) Kunth	Malpighiaceae	Brazil
Tomatinho do mato	*Cyphomandra divaricata*	Solanaceae	Brazil

solutions of known Trolox concentrations in the range of 0-2000 μmol L^{-1} were used for calibration. The results were expressed as μmol Trolox equivalents (TE) g^{-1} FW using a calibration curve ($y = 0.686 - 2.90 \times 10^{-4} x$, $r^2 = 0.997$).

$ABTS^{\bullet+}$ assay

The $ABTS^{\bullet+}$ assay was based on a method developed by Re *et al*.[15] with modifications.[7] $ABTS^{\bullet+}$ radical cations were produced by reacting 7.0 mmol L^{-1} of an ABTS stock solution with 145.0 mmol L^{-1} of potassium persulfate and allowing the mixture to stand in the dark at room temperature for 12-16 h before use. The $ABTS^{\bullet+}$ solution was diluted with ethanol to obtain absorbance at 0.70 ± 0.02 at 734 nm. Absorbance was recorded 6 min after the addition of 30 μL of either fruit extract solutions or a Trolox standard to 3 mL of a diluted $ABTS^{\bullet+}$ solution and mixing. Known concentrations of ethanolic solutions of Trolox in the range of 0-2000 μmol L^{-1} were used for calibration ($y = 0.682 - 2.91.10^{-4} x$, $r^2 = 0.999$), and the results were expressed as μmol Trolox equivalents (TE) g^{-1} FW.

FRAP (ferric reducing antioxidant power) assay

The FRAP assay was determined as previously described by Benzie and Strain[16] with modifications. The FRAP reagent was prepared by mixing of acetate buffer (0.3 mol L^{-1}, pH 3.6), TPTZ (10.0 mmol L^{-1}) and $FeCl_3$ (20.0 mmol L^{-1}) solutions in the ratio 10:1:1, respectively. 100 μL fruit extract solutions and 300 μL of distilled water were added to 3.0 mL of the FRAP reagent, which was kept in the dark for 30 min at 37 °C. The absorbance was measured in comparison with a blank at 593 nm. Aqueous solutions of known Fe(II) concentrations in the range of 0-1500 μmol L^{-1} ($FeSO_4.7H_2O$) were used for the calibration curve ($y = 0.006 + 6.55.10^{-4} x$, $r^2 = 0.999$), and the results were expressed as μmol Fe^{2+} g^{-1} FW.

Total phenolic content (TPC)

TPCs of fruit extracts were analyzed using Folin-Ciocalteu reagent.[17] Fruit extract solutions (250 μL) were mixed with 250 μL of the Folin-Ciocalteu reagent (diluted in distilled water, 1:1 v/v), 500 μL of a sodium carbonate saturated solution and 4 mL of distilled water. After 25 min of rest, the mixture was centrifuged for 10 min at 3000 rpm (1638 g) and the absorbance was read on a spectrophotometer at 725 nm. Methanolic solutions of known gallic acid concentrations in the range of 0-250 mg L^{-1} were used for calibration. The results were expressed as mg gallic acid equivalents (GAE) 100 g^{-1} FW using the calibration curve ($y = -0.0273 + 0.00517 x$, $r^2 = 0.999$).

Chromatographic analysis

Total lipids (TL) were extracted by the Bligh and Dyer method.[18] Fatty acid methyl esters (FAME) were prepared by methylation of TL as described by Joseph and Ackman.[19] Methyl esters were separated by gas chromatography in a Trace Ultra 3300 model (Thermo Scientific) equipped with flame ionization detector (FID) and a cyanopropyl capillary column (100 m × 0.25 mm i.d., 0.25 μm film thickness, CP-7420). The gas flow rates used were 1.2 mL min^{-1} carrier gas (H_2), 30 mL min^{-1} make-up gas (N_2), and 35 and 350 mL min^{-1} flame gases (H_2 and synthetic air, respectively). The sample splitting rate was 1:80 and the samples (2 μL) were injected in triplicate. The operational parameters were as follows: detector and injection port temperature of 240 °C, column temperature of 185 °C for 7.5 min, programmed to increase at 4 °C min^{-1} to 235 °C and kept at this temperature for 1.5 min. The peak areas were determined by the ChromQuest 5.0 software. For fatty acid identification, retention times were compared with those of standard methyl esters.

Quantification (in mg fatty acid g^{-1} of TL) was made against tricosanoic acid methyl ester as an internal standard (23:0), as described by Joseph and Ackman.[19] Theoretical FID correction factor values were used to obtain concentration values.[20] Fatty acid contents were calculated in mg g^{-1} of TL by using equation 1:

$$FA = \frac{A_X \, W_{IS} \, CF_X}{A_{IS} \, W_X \, CF_{AE}} 100 \quad (1)$$

where FA is mg of fatty acids *per* g of TL, A_X is the peak area (fatty acids), A_{IS} is the peak area of internal standard (IS) methyl ester of tricosanoic acid (23:0), W_{IS} is the mass (mg) of IS added to the sample (in mg), W_X is the sample mass (in mg), CF_X is the theoretical correction factor, and CF_{AE} is the conversion factor necessary to express the results as mg of fatty acids rather than as methyl esters.

Statistical analysis

All analyses were carried out in triplicate. The results were submitted to PCA using Statistica 7.0 software. Data pre-treatment was not necessary.

Results and Discussion

Antioxidant capacity and total phenolic content

In this study, seven exotic and native fruits from Brazil (Table 1) were investigated for their TPC and antioxidant

capacity using DPPH$^{\bullet}$, ABTS$^{\bullet+}$ and FRAP methods. The results are shown in Table 2.

Murici (243.42 mg GAE 100 g^{-1}) and *dovialis* (205.98 mg GAE 100 g^{-1}) presented the highest TPC, and *landim* the lowest value (28.76 mg GAE 100 g^{-1}). Comparing our results with results reported by Barreto *et al.*,[21] *murici* and *dovialis* presented higher TPC than *buriti* (*Mauritia vinifera*), banana (*Musa x paradisiaca L.*), *marimari* (*Geoffroea striata* (Willd.) Morong.) and egg fruit (*Pouteria campechiana* (Kunth) Baehni) other tropical fruits from Brazil.

Almeida *et al.*[22] found 159.9 mg GAE 100 g^{-1} for edible part of *murici*, being this value lower than the value found by us. Souza *et al.*[6] and Barreto *et al.*[21] reported higher values for *murici* pulp, 334.37 and 384.5 mg GAE 100 g^{-1}, respectively. This variation may happen because the composition of fruit depends on factors like climate conditions, geographic location, stage of maturation, variety and extraction method.[21,23]

The antioxidant capacity of the fruit extracts analyzed by the DPPH$^{\bullet}$ assay varied from 0.79 to 9.59 μmol TE g^{-1}. The lowest antioxidant capacity was observed in *landim*, followed by *tomatinho do mato*, *cajamanga*, *araça boi*, *murici*, *siriguela* and *dovialis*. In comparison, *dovialis*, *siriguela* and *murici* presented antioxidant capacity higher than some commercial cultivars of citrus from Brazil that ranged from 2.656 to 4.567 μmol TE g^{-1} FW measured by DPPH$^{\bullet}$ assay.[24]

The analyzed fruits displayed a range of antioxidant capacity of 1.82-10.41 μmol TE g^{-1} measured by the ABTS$^{\bullet+}$ method, and 1.38-24.97 μmol Fe^{2+} g^{-1} measured by the FRAP method. The antioxidant capacity rank based on the ABTS$^{\bullet+}$ method was: *tomatinho do mato* < *araça boi* < *cajamanga* = *landim* < *siriguela* < *murici* < *dovialis*, and by using the FRAP method: *landim* < *cajamanga* < *tomatinho do mato* < *araça boi* < *siriguela* < *dovialis* < *murici*.

Fu *et al.*[25] evaluated the antioxidant capacity of ethanolic extracts (water-ethanol, 1:1, v/v) of 62 fruits by the FRAP and ABTS$^{\bullet+}$ methods. Comparatively to our results, *dovialis*, *murici* and *siriguela* presented a higher antioxidant capacity than jackfruit (2.57 μmol Fe^{2+} g^{-1} and 2.37 μmol TE g^{-1}), litchi (7.22 μmol Fe^{2+} g^{-1} and 4.63 μmol TE g^{-1}), avocado (2.76 μmol Fe^{2+} g^{-1} and 1.16 μmol TE g^{-1}) and grapefruit (6.74 μmol Fe^{2+} g^{-1} and 3.04 μmol TE g^{-1}) measured by FRAP and ABTS$^{\bullet+}$ methods, respectively.

The DPPH$^{\bullet}$, FRAP and ABTS$^{\bullet+}$ methods indicated that *siriguela*, *murici* and *dovialis* have the highest levels of antioxidants probably due to their highest TPC.

Correlation between study variables

The correlations between the results of the DPPH$^{\bullet}$, FRAP and ABTS$^{\bullet+}$ methods and TPCs are shown in Figure 1.

A positive correlation was found between TPC-DPPH$^{\bullet}$ (0.8277), TPC-ABTS$^{\bullet+}$ (0.8835) and TPC-FRAP (0.9153). These results suggest that phenolic compounds, such as phenolic acids and flavonoids, may be important contributors to the antioxidant capacity. Other studies such as those by Rufino *et al.*,[7] Almeida *et al.*[22] and Vasco *et al.*[23] report a relationship between TPC and antioxidant capacity.

The correlations between DPPH$^{\bullet}$-ABTS$^{\bullet+}$, FRAP-DPPH$^{\bullet}$ and FRAP-ABTS$^{\bullet+}$ were high, 0.9554, 0.9251 and 0.8663, respectively. Ma *et al.*[12] evaluated the fruits of eight mango tree genotypes for antioxidant capacity and found high linear correlation coefficients between the DPPH$^{\bullet}$, FRAP and ABTS$^{\bullet+}$ methods.

According to Huang *et al.*,[26] antioxidant capacity methods can be divided into two types, hydrogen atom transfer (HAT) reaction and electron transfer (ET) reaction-based methods, depending how the radicals are deactivated by the antioxidants. HAT-based methods measure the classical ability of an antioxidant to scavenge free radicals by hydrogen donation and form stable compounds. ET-based methods detect the ability of an antioxidant to transfer one electron and reduce any compound. The TPC determination by the Folin-Ciocalteu reagent, ABTS$^{\bullet+}$, FRAP and DPPH$^{\bullet}$ methods are considered ET methods. This classification can explain the high correlation coefficients shown in Figure 1,

Table 2. Antioxidant capacity and total phenolic content (TPC) in ethanolic extracts of fruits from Brazil based on fresh weight (FW)[a]

Fruit	TPC / (mg GAE 100 g^{-1})	DPPH$^{\bullet}$ / (μmol TE g^{-1})	ABTS$^{\bullet+}$ / (μmol TE g^{-1})	FRAP / (μmol Fe^{2+} g^{-1})
Araça boi	51.91 ± 0.12	2.66 ± 0.06	2.11 ± 0.01	8.64 ± 0.10
Cajamanga	45.25 ± 0.21	2.25 ± 0.07	2.21 ± 0.05	6.34 ± 0.13
Siriguela	94.46 ± 1.10	6.29 ± 0.10	4.88 ± 0.03	20.06 ± 0.24
Dovialis	205.98 ± 0.70	9.59 ± 0.40	10.41 ± 0.49	23.70 ± 1.02
Landim	28.76 ± 0.74	0.79 ± 0.00	2.21 ± 0.00	1.38 ± 0.06
Murici	243.42 ± 2.79	6.00 ± 0.10	6.80 ± 0.29	24.97 ± 0.22
Tomatinho do mato	56.38 ± 0.56	2.02 ± 0.10	1.82 ± 0.08	8.34 ± 0.06

[a]Mean value ± standard deviation; n = 3. GAE: gallic acid equivalents; TE: Trolox equivalents; DPPH$^{\bullet}$: 1,1-diphenyl-2-picrylhydrazyl; ABTS$^{\bullet+}$: 2,2'-azino-bis-3-ethylbenzthiazoline-6-sulphonic acid; FRAP: ferric reducing antioxidant power.

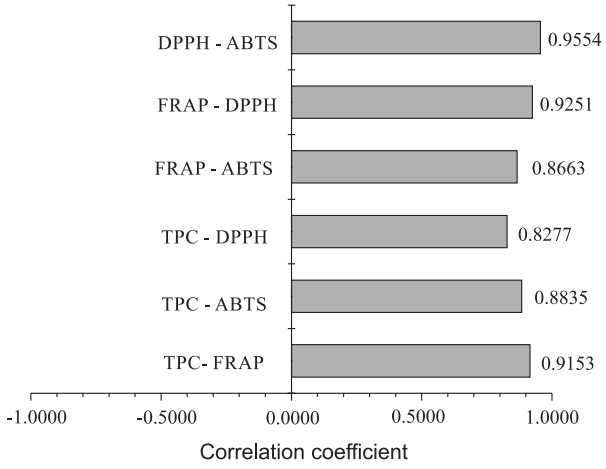

Figure 1. Correlation coefficients between the methods DPPH•, FRAP, ABTS•+ and total phenolic content (TPC).

all methods act through the same mechanism.

Fatty acids

The fatty acid (FA) composition of the investigated fruit is shown in Table 3. A total of twenty fatty acids in the pulp of the fruit was detected, quantified and characterized as saturated (SFA), monounsaturated (MUFA) or polyunsaturated (PUFA) fatty acids. These classes of fatty acids were also found by Santos *et al*.[27] in different parts of grapes and Yi *et al*.[28] in two varieties of grape pomace powder. The lowest content of total SFA was found in *cajamanga* (158.14 mg FA g^{-1} TL) and the highest content in *siriguela* (223.98 mg FA g^{-1} TL). However, the MUFA content presented a significant variation, between 32.46 and 240.08 mg FA g^{-1} TL for the *siriguela* and *murici* samples. The PUFA content of the fruit had a minimum value of 110.34 and a maximum value of 296.34 mg FA g^{-1} TL in landim and *tomatinho do mato*, respectively.

Palmitic acid (PA, 16:0) was the major SFA in all of the analyzed fruit. The main MUFA in fruit was oleic acid (OA, 18:1n-9), and the highest amount obtained was in *murici* (Table 3). According to Bellido *et al*.,[29] the ingestion of

Table 3. Fatty acid compositions in different fruits from Brazil quantified in mg FA g^{-1} total lipids[a]

Fatty acid	Composition / (mg FA g^{-1} total lipid)							
	Araça boi	*Cajamanga*	*Siriguela*	*Dovialis*	*Landim*	*Murici*	*Tomatinho do mato*	SD_{max}
12:0	0.42	2.30	6.59	3.99	8.16	1.55	0.06	0.01
14:0	3.62	7.29	17.38	15.28	8.09	2.92	3.08	0.04
16:0	136.05	119.48	160.26	126.43	149.66	142.52	139.68	0.59
16:1n-9	2.08	1.52	1.67	1.57	2.20	0.19	1.27	0.01
16:1n-7	23.81	2.88	3.02	9.81	15.42	1.79	6.48	0.06
16:1n-5	0.33	0.45	0.49	0.26	0.78	0.08	0.98	0.02
17:0	3.10	0.89	2.33	1.73	1.47	0.31	4.28	0.05
17:1	1.81	0.87	0.38	1.57	0.29	0.14	0.63	0.02
18:0	26.19	18.19	18.66	18.99	22.53	13.69	26.15	0.06
18:1n-9	150.03	179.57	23.27	142.87	180.15	231.75	62.02	0.40
18:1n-7	15.83	14.44	2.81	4.76	13.81	5.44	5.64	0.06
18:2n-6	148.52	88.83	168.50	88.60	57.59	103.72	215.50	0.31
18:3n-6	0.65	0.79	0.43	0.71	0.86	0.06	0.13	0.02
18:3n-3	10.21	98.92	107.86	102.50	47.45	9.21	75.08	0.15
20:0	2.00	2.19	4.02	1.86	5.01	2.40	3.43	0.08
20:1n-9	1.56	3.00	0.81	1.59	2.48	0.69	1.55	0.01
22:0	2.88	0.25	4.24	1.70	2.03	2.13	1.59	0.10
20:5n-3	1.50	2.81	4.99	4.14	3.97	1.44	5.36	0.13
24:0	0.63	7.53	10.51	5.97	2.92	30.89	10.81	0.10
22:6n-3	1.62	0.24	3.11	0.11	0.47	1.11	0.26	0.04
∑ SFA	174.89	158.14	223.98	175.95	199.87	196.42	189.07	0.62
∑ MUFA	195.44	202.73	32.46	162.42	215.12	240.08	78.57	0.42
∑ PUFA	162.50	191.60	284.89	196.05	110.34	115.55	296.34	0.44
∑ n-3	13.33	101.98	115.96	106.75	51.89	11.76	80.71	0.25
∑ n-6	149.17	89.63	168.93	89.30	58.45	103.78	215.63	0.31
n-3/n-6 ratio	0.09	1.14	0.69	1.20	0.89	0.11	0.37	0.00
PUFA/SFA ratio	0.93	1.21	1.27	1.11	0.55	0.59	1.57	0.00

[a]Results expressed as average total fatty acids of tree replicates. SFA: saturated fatty acid; AGMI: monounsaturated fatty acid; AGPI: polyunsaturated fatty acid; n-3: omega-3 fatty acid; n-6: omega-6 fatty acid; FA: fatty acid; SD_{max}: maximum standard deviation.

OA is related to the reduction of the level of low-density lipoproteins (LDL) and, consequently, the prevention of arteriosclerosis. All of the studied fruit are sources of OA, with values ranging from 23.27 to 231.75 mg FA g^{-1} TL of fruit.

The main PUFA were alpha-linolenic acid (LNA, 18:3n-3) in *dovialis* (102.50 mg FA g^{-1} TL) and *siriguela* (107.86 mg FA g^{-1} TL), and linoleic acid (LA, 18:2n-6) in *landim*, *siriguela*, *tomatinho do mato*, *araça boi* and *murici*. The major concentrations of LA were found in *tomatinho do mato*, 215.50 mg FA g^{-1} TL. LA and LNA are essential fatty acids metabolized by the same sequential denaturation and elongation enzyme systems, which results in the production of long-chain polyunsaturated fatty acids (LC-PUFA) of the n-3 and n-6 series.[30]

The n-3/n-6 ratio reference value in the human diet varies between 0.1 and 0.2. In the last few years, some studies have proposed that this ratio has moved from 0.033 to 0.05 in Western diets, a value considered extremely low since the ideal value is between 0.5 and 1.0.[30] Thus, *landim* and *siriguela* samples presented ideal n-3/n-6 ratio values, whereas *araça boi* and *murici* showed concentrations in excess of n-6 fatty acids, and *cajamanga* and *dovialis* had extreme amounts of n-3 fatty acids (Table 3). The n-3/n-6 ratio is considered crucial for the conversion of LNA into long-chain n-3 PUFA, as n-6 PUFA (LA) also competes for Δ-6-desaturase enzyme.[31]

PCA analysis

Multivariate analysis can summarize the variability of a complex data set and present it in a most interpretable form, such as principal components. The PCA analysis of antioxidants and fatty acid analyses of different fruits

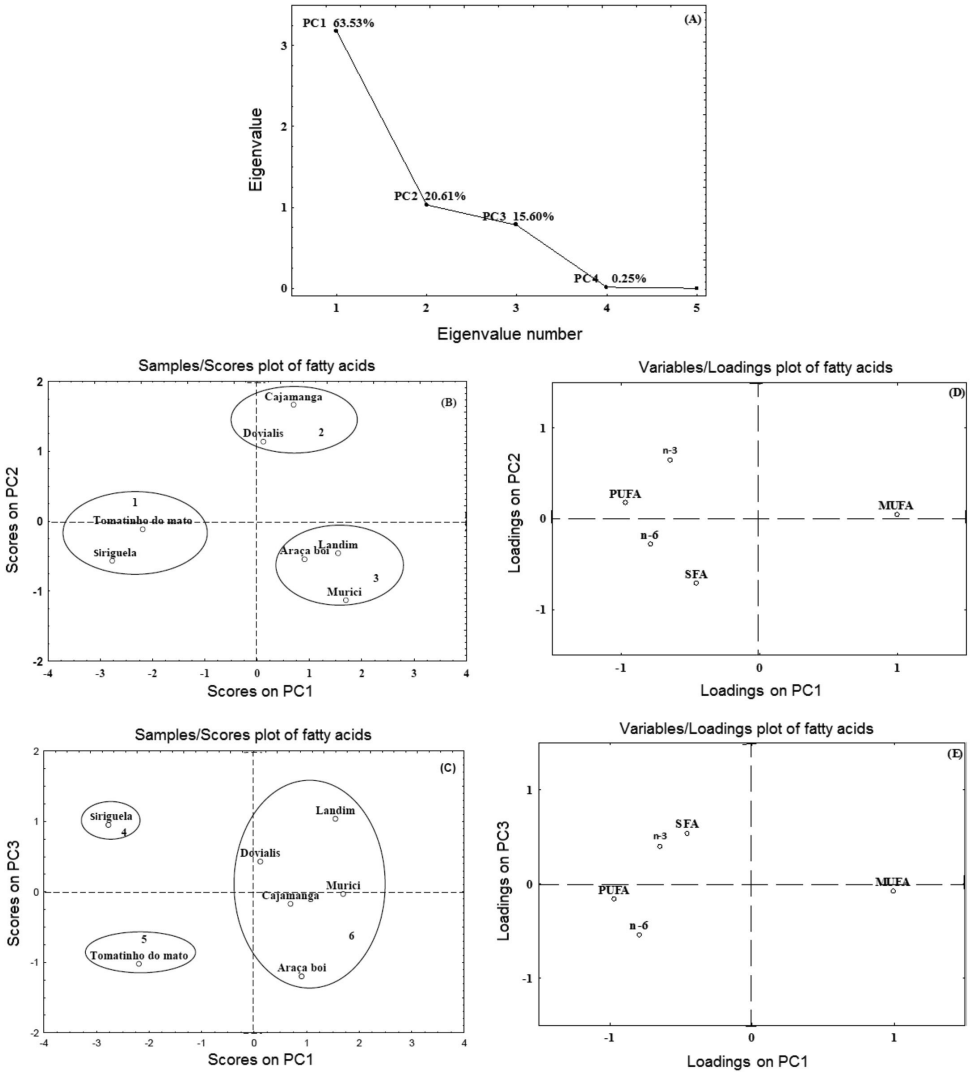

Figure 2. Eigenvalue number (a), scores plot of fatty acids for PC1 × PC2 (b) and PC1 × PC3 (c), loadings PC1 × PC2 (d) and loadings PC1 × PC3 (e) to different fruits.

were carried out because this matrix is a very complex mixture.[32] Figures 2a and 3a show that the eigenvalues and approximately 100% of the variance of the original data were explained by both analyses. Thus, three components were retained for the principal component analysis for the fatty acids and two components for the antioxidant analyses (TPC, DPPH$^{\bullet}$, ABTS$^{\bullet+}$ and FRAP assays).

The first component (PC1) for fatty acids (Figure 2a) explained 63.53% of the total variance of the data set, and the loadings indicated high positive contributions from MUFA and negative contributions from PUFA. The second component (PC2) was associated with 20.61% and the third component (PC3) explained 15.60% the total variance. The n-3 presented a positive contribution to both PCs, SFA and n-6 presented negative contributions to PC2 and PC3, respectively. The total variance of the data set for the fatty acid analysis was 99.75%.

Figures 2b-2e show the principal component analysis of fatty acids in the fruit samples. Analyzing Figures 2b and 2c, it is possible to observe that three groups were formed. In Figure 2b, the groups were: *tomatinho do mato* and *siriguela* (1), *cajamanga* and *dovialis* (2), *araça boi*, *landim* and *murici* (3), and in Figure 2c the groups were: *siriguela* (4), *tomatinho do mato* (5), *dovialis*, *landim*, *murici*, *cajamanga* and *araça boi* (6). The evaluation of the importance of the loadings (Figures 2d and 2e) for the separation of the score groups indicated that the major contributors to PC1 were MUFA and PUFA, respectively. The contributors to PC2 (Figure 2d) were n-3 and SFA, and to PC3 (Figure 2e) n-3 and n-6. Analyzing Figure 2b (score on PC1 × PC2), Figure 2d (loadings PC1 × PC2) and Figure 2e (loadings PC1 × PC3), PUFA was the variable responsible for the formation of group 1, for group 2, it was the sum of omega-3 fatty acids (n-3), and for group 3, it was MUFA. Moreover, the correlation between Figures 2b and 2c shows that variable n-3 contributed to group 4, for group 5, it was the sum of omega-6 fatty acids (n-6), and for group 6, it was both SFA and MUFA.

In the antioxidant analyses by TPC, DPPH$^{\bullet}$, ABTS$^{\bullet+}$ and FRAP assays, two components explained about 97.00% of the total variance (Figure 3a), PC1 (92.17%) and PC2 (4.82%). The DPPH$^{\bullet}$, ABTS$^{\bullet+}$ and FRAP variables contributed negatively to PC1. The loadings on PC2 indicated high contributions from DPPH$^{\bullet}$ and TPC, with positive and negative values, respectively.

Figures 3b and 3c show PCA, samples/score and variables/loadings of antioxidant analyses of the fruit samples. In Figure 3b, the formation of four groups can be observed: *dovialis* (7), *siriguela* (8), *murici* (9) and *cajamanga*, *landim*, *araça boi* and *tomatinho do mato* (10). The DPPH$^{\bullet}$ and ABTS$^{\bullet+}$ variables were responsible for the separation of group 7, FRAP and TPC for group 9, DPPH$^{\bullet}$, ABTS$^{\bullet+}$ and FRAP for group 8, with group 10 presenting the lowest values in all analyses.

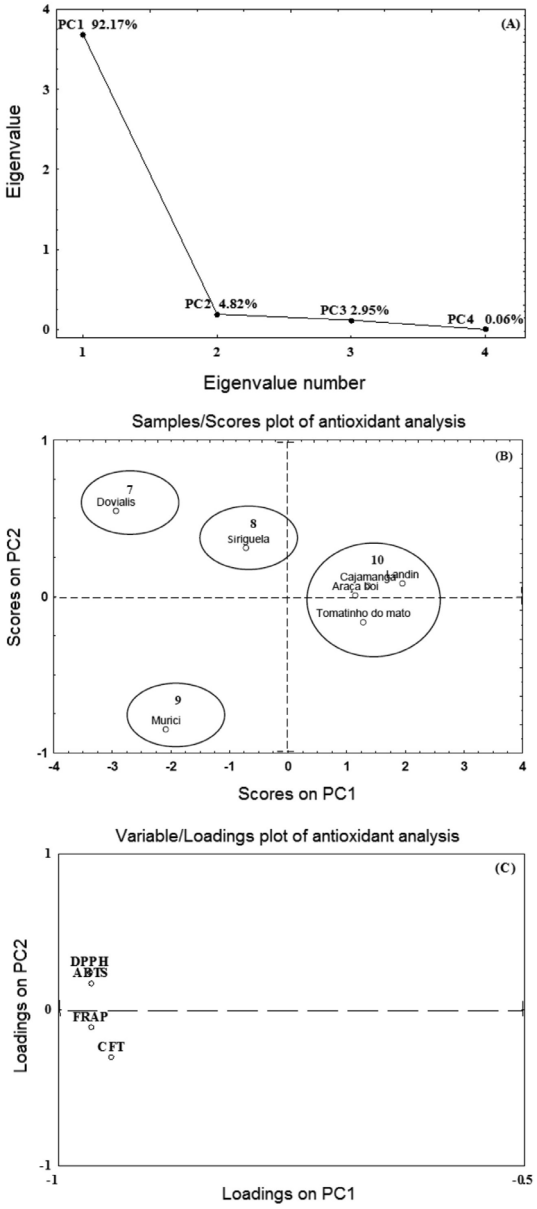

Figure 3. Eigenvalue number (A), scores (B) and loadings (C) plot antioxidant analyses for the first and second PC of different fruits.

Conclusions

This study revealed that exotic and native fruits from Brazil had essential omega-6 and -3 fatty acids as well as antioxidant capacity by different methods. Phenolic compounds showed to be contributors to the antioxidant capacity of these fruits since there was a positive correlation between total phenolic content and antioxidant capacity, as verified by the different methods used. The PCA analysis

showed the contribution of individual fatty acids and antioxidants to the total variability of the main component. Eigen analysis of the correlation matrix loadings of the three significant PCs for fatty acids explained more than 99% of the total data set variability and two significant PCs for antioxidant analyses explained about 97% of the total data set variability.

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