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(Organizadores)

Produção e Controle de Produtos Naturais 2

Atena Editora
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APRESENTAÇÃO

A utilização de plantas como medicamento provavelmente é tão antiga quanto o surgimento do homem, pois sempre existiu uma grande preocupação com as doenças durante toda a história da humanidade. No Brasil, a cultura indígena, possui uma sabedoria tradicional, passada de geração a geração acerca das propriedades dessas plantas. Apesar de muitas plantas serem úteis para a medicina, existem algumas tóxicas ou venenosas, sendo necessário conhecer as características de cada uma. Se fazendo importante os estudos científicos, tendo em vista a grande diversidade de flora do Brasil.

O leitor irá encontrar nesta obra estudos que abordam diversas propriedades das plantas medicinais, como sua ação antioxidante, antimicrobiana, analgésica e ainda a utilização dos óleos essenciais como conservantes de alimentos. Também sua utilização na defesa contra raios UV, utilizando compostos químicos naturais de plantas.

O e-book "Produção e Controle de Produtos Naturais 2", possui 9 artigos científicos, e ressalta a importância de dar seguimento ao conhecimento acerca das pesquisas da flora brasileira, que contribuem para o crescimento e o desenvolvimento da pesquisa, preservação da utilização das plantas, levando o leitor a uma reflexão. Desejamos uma ótima leitura!

Raissa Rachel Salustriano da Silva-Matos
Vanessa Reis Cardoso
Kleber Veras Cordeiro

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CAPÍTULO 6

EFFECT OF FROZEN STORAGE ON THE COMPOSITION OF ESSENTIAL OILS FROM ARAÇÁ, MAROLO AND MIXED PULPS

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EFEITO DO ARMAZENAMENTO CONGELADO NA COMPOSIÇÃO DOS ÓLEOS ESSENCIAIS DE POLPAS DE ARAÇÁ, MAROLO E MISTA

RESUMO: Frutos exóticos do Cerrado brasileiro como araçá (*Psidium guineense*) e marolo (*Annona crassiflora*) são comercializados em feiras regionais como polpas cujo consumo está aumentando continuamente devido à preferência do consumidor por hábitos alimentares saudáveis. Neste trabalho, os óleos essenciais (OEs) de polpas de araçá, marolo e mista (1:1) foram investigados visando avaliar se o armazenamento congelado por 12 meses preserva a qualidade geral das polpas frescas. Os OEs foram obtidos por hidrodestilação e analisados por CG-DIC e CG-EM. Os hidrocarbonetos sesquiterpênicos constituíram os principais constituintes do araçá, enquanto ésteres foram majoritários no marolo. A polpa mista preservou os voláteis das polpas originais, com uma leve tendência aos voláteis do marolo. Alguns poucos constituintes minoritários só ocorrem nessa polpa. A análise por redundância (RDA) resultou em 89,2% de variância explicada. A RDA1 separou as polpas do araçá (terpenos) daquelas do marolo (ésteres), enquanto a RDA2 estabeleceu os

constituintes minoritários associados com a polpa mista. A curva de resposta principal (PRC) mostrou que a variabilidade nos OEs foi causada majoritariamente pela origem da polpa (87,8%) com pouca influência do tempo de armazenamento (2,3%). Assim, as polpas congeladas armazenadas por 12 meses se assemelharam a polpas frescas, com pequenas alterações em alguns constituintes e retiveram os constituintes voláteis semelhantes aos frutos frescos.
PALAVRAS-CHAVE: Frutos exóticos, frutos processados, variabilidade química, voláteis.

ABSTRACT: Brazilian Cerrado exotic fruits such as araçá (*Psidium guineense*) and marolo (*Annona crassiflora*) are sold at regional fairs as pulps, whose consumption is on the rise due to consumer preference for healthy eating habits. In this study, essential oils (EOs) from araçá, marolo and mixed (1:1) pulps were examined to assess whether a 12-month frozen storage preserves the overall quality of fresh pulps. EOs were obtained by hydrodistillation and analyzed by GC-FID and GC-MS. Sesquiterpene hydrocarbons were the main constituents in araçá, whereas esters were the main constituents in marolo. Volatiles from original pulps were preserved in the mixed pulp, with a closer association with marolo. Few minor constituents are found only in this pulp. Redundancy analysis (RDA) resulted in 89.2% of explained variance. RDA1 separated araçá pulp (terpenes) from those of marolo (esters), while RDA2 established minor chemical constituents associated with the mixed pulp. Principal response curves (PRC) showed that chemovariation in EOs was mainly caused by pulp origin (87.8%), with storage time playing a minor role (2.3%). Pulps that were stored frozen for 12 months resembled fresh pulps, with small changes in some constituents, and retained volatiles, similarly to fresh fruit.

KEYWORDS: Exotic fruits, processed fruit, chemical variability, volatiles.

1 I INTRODUCTION

The Brazilian Cerrado has a rich biodiversity and is home to species whose fruits have a high nutritional value. Currently more than 58 species of native fruits are found in the region, which ensures food diversification and enrichment for the local population (AQUINO & OLIVEIRA, 2006). However, most fruits are highly perishable, with seasonal and extractive production (FINCO et al., 2012). As an alternative to increase shelf life, artisanal fruit processing seeks to prevent postharvest loss and offers a differentiated product for consumption. Among the native fruits viewed as commercially exploitable are araçá (*Psidium guineense* Sw.) and marolo (*Annona crassiflora* Mart.), particularly due to their pleasant sensory characteristics and nutritional and functional potential. Moreover, they are well received by consumers both in natura and in the processed form of pulps, jams, ice creams and juices (ARRUDA & PASTORE, 2019; FRANZON et al., 2009).

A product's shelf life is determined by how long it remains in good sensory and microbiological conditions for consumption, without compromising taste and health. These conditions depend on physical, chemical and microbiological transformations during technological processing and storage (SILVA & ABUD, 2017). Essential oils (EOs), generally safe (ECFR, 2019) and widely known for their antimicrobial activity (TONGNUANCHAN & BENJAKUL, 2014), are alternatives to synthetic preservatives in increasing shelf life. In this scenario, processed frozen pulps acquire special importance, since they maintain sensory appeals such as exotic aroma and flavor, combined with the microbiological control promoted by EOs. In fact, frozen pulp storage is one way of preserving fruit freshness with maximum food safety and a substantial increase in shelf life (SILVA & ABUD, 2017), although these qualities are affected during storage.

Previous studies have shown that *P. guineense* pulp extracts have antibacterial activity (ANESINI & PEREZ, 1993; GONZÁLEZ et al., 2005) and terpenes or esters as major volatiles (PERALTA-BOHÓRQUEZO et al., 2010). EOs from marolo have mainly terpenes (SIRENA et al., 2014). In turn, fresh pulp show changes in terpene and ester compositions, with only esters at the end of fruit ripening (SILVA et al., 2013), whereas lyophilized pulp provides esters and alcohols as its main constituents (BEZERRA et al., 2018). Some studies have indicated that pulp extracts have antioxidant, antimicrobial, molluscicide and anti-Alzheimer activity (ARRUDA & PASTORE, 2019).

To our knowledge, the effects of frozen storage on the volatile profile of these pulps have so far not been described. Therefore, this study aims to assess whether the frozen storage of araçá, marolo and mixed (1:1) pulps could be a suitable means of preserving the overall quality of fresh fruits, with emphasis on the variability of EOs analyzed over a one-year period.

2 I MATERIAL AND METHODS

2.1 Fruit Collection, Pulp Preparation and Frozen Storage

Ripe fruits of araçá and marolo were respectively collected in March 2007 in Ingaí and Contagem, both cities in Minas Gerais state, Brazil. Fruits were selected, prewashed, sanitized in sodium hypochlorite solution (100 mg/L, 20 min) and pulped using stainless steel spoons. Fresh pulp was packed in low density polyethylene bags (100 g/package) using a manual dispenser and immediately sealed after air expulsion. Sealed bags were frozen and stored in a freezer (-18°C) for 12 months.

2.2 Extraction and Analysis of Essential Oils (EOs)

Pulps in frozen storage for 0, 2, 4, 6, 8 and 12 months were thawed at room temperature and EOs were extracted by hydrodistillation in a Clevenger apparatus (2 h), dried with anhydrous Na_2SO_4 and kept in a freezer (-18°C). EOs were analyzed by gas chromatography-mass spectrometry (GC/MS) on a QP5050A (Shimadzu) using a DB5 capillary column (30 m x 0.25 mm x 0.25 μm); flow rate of 1.0 ml/min (He) and heating at a programmed temperature (60-246°C at 3°C/min); sample injection of 0.4 μl (20% hexane) and split ratio of 1:50. Ionization energy was 70 eV; mass range was 40-400 Da at 1.0 scan/s. Injector and interface temperatures were 220°C and 240°C, respectively. A Varian CP3900 with a flame ionization detector (GC/FID) was used for compositional analysis. Chromatographic conditions were the same as those of GC/MS. The carrier gas was N_2 and relative percentages were determined from peak areas without use of correction factors. Identification of oil constituents was performed by comparing mass spectra with those of NIST (1988) and ADAMS (2018) libraries, as well as by comparing mass spectra and retention indices (ADAMS, 2017). Arithmetic retention indices (DOOL & KRATZ, 1963) were calculated by co-injection with a linear hydrocarbon (C_8-C_{32}) mixture.

2.3 Statistical Analysis

Average multiple comparisons were established by analysis of variance (ANOVA), with pulp and storage time as factors using SAS (SAS Institute Inc., version 6.0, 1996). Normality and homoscedasticity were checked with Shapiro-Wilk and Hartley tests, respectively, followed by a Tukey *post hoc* test. *P*-values < 0.05 were considered significant. For multivariate analysis, oil constituents were organized in a response matrix, with samples in rows and chemical percentages as variables in columns. An explanatory matrix contained the same samples in rows and two categorical variables, representing pulp origin and storage time in columns. Redundancy analysis (RDA) was performed with the interaction between pulp origin and storage time as explanatory variables. Monte Carlo permutation tests (999 permutations) were used to assess the significance of canonical axes. Principal response curve (PRC) was applied to investigate the effects in EOs and their changes over time (VAN DEN BRINK & TER BRAAK, 1999). In PRC, sampling months were used as covariables and interaction time and treatment (pulps) were used as explanatory variables. Monte Carlo permutation tests (999 permutations) were performed on the entire time sequence to compare treatments (araçá and marolo pulps) and a control (mixed pulp). To verify whether treatment outcome at a given storage period varied significantly, treatment effects at each time period were also assessed via permutation (499 permutations). Variables with weights ranging from -0.5 to +0.5 suggest random fluctuations and are not shown. Prior to multivariate analysis, the response matrix was log(x+1)-transformed, centralized and analyzed in R (R Foundation for Statistical Computing, version 3.4.4, 2018).

3 I RESULTS AND DISCUSSION

Forty compounds were identified in EOs, accounting for 69%-100% of volatile constituents in pulp samples (Table 1).

Oil constituent	Pulp	Frozen storage time / months							Mean
(RI[b])		0	2	4	6	8	10	12	
a-Pinene[c]	Mixed	12.2^{Aab}	2.4^{Ab}	4.5^{Aab}	3.3^{Aab}	16.1^{Aa}	7.5^{Aab}	5.3^{Aa}	
(935)	Araçá	4.8^{Aa}	4.6^{Aa}	5.9^{Aa}	8.2^{Aa}	3.3^{Ba}	5.4^{Aa}	14.6^{Aa}	
	Marolo	-	-	-	-	-	-	-	
b-Pinene[c]	Mixed	3.3	0.6	0.8	0.8	3.0	1.4	1.2	1.6^{B}
(978)	Araçá	1.0	0.9	2.2	1.6	1.8	1.5	3.8	1.8^{A}
	Marolo	-	-	-	-	-	-	-	
	Mean	2.2^{bc}	0.7^{c}	1.5^{abc}	1.2^{abc}	2.4^{a}	1.4^{abc}	2.5^{ab}	
Ethyl hexanoate[d]	Mixed	8.6^{Aa}	5.4^{Aa}	5.2^{Ba}	13.4^{Aa}	18.1^{Aa}	7.9^{Aa}	5.5^{Ba}	
(997)	Araçá	-	-	-	-	-	-	-	
	Marolo	9.5^{Ab}	12.6^{Ab}	35.9^{Aa}	21.8^{Ab}	8.1^{Ab}	11.8^{Ab}	20.4^{Ab}	
Limonene	Mixed	-	-	-	-	-	-	-	
(1030)	Araçá	-	-	0.9^{a}	0.6^{a}	1.2^{a}	0.9^{a}	1.8^{a}	
	Marolo	-	-	-	-	-	-	-	
Methyl octanoate[d]	Mixed	6.6	6.6	5.3	7.6	9.8	8.7	7.2	7.4^{B}
(1123)	Araçá	-	-	-	-	-	-	-	
	Marolo	11.5	10.3	19.8	15.2	16.8	17.1	18.2	15.6^{A}
	Mean	9.1^{a}	8.5^{a}	12.6^{a}	11.4^{a}	13.3^{a}	12.9^{a}	12.7^{a}	
a-Terpineol[c]	Mixed	-	-	-	-	-	-	-	
(1191)	Araçá	0.7^{a}	0.9^{a}	0.8^{a}	0.7^{a}	1.7^{a}	0.5^{a}	1.0^{a}	
	Marolo	-	-	-	-	-	-	-	
Ethyl octanoate[c]	Mixed	18.1	22.4	19.2	20.9	19.8	23.4	22.8	20.9^{B}
(1197)	Araçá	-	-	-	-	-	-	-	
	Marolo	43.7	37.3	22.3	44.2	48.9	47.6	48.7	41.8^{A}
	Mean	30.9^{a}	29.9^{a}	20.7^{a}	32.5^{a}	34.4^{a}	35.5^{a}	35.8^{a}	
Methyl decanoate[c]	Mixed	0.3^{a}	0.3^{a}	0.1^{a}	0.2^{a}	0.1^{a}	0.3^{a}	0.4^{a}	
(1326)	Araçá	-	-	-	-	-	-	-	
	Marolo	-	-	-	-	-	-	-	
a-Copaene	Mixed	1.1	1.2	1.0	1.6	0.7	1.2	1.2	1.1^{B}
(1378)	Araçá	2.9	2.7	2.8	2.9	2.9	2.9	2.5	2.8^{A}
	Marolo	-	-	-	-	-	-	-	
	Mean	2.0^{a}	2.0^{a}	1.9^{a}	2.2^{a}	1.8^{a}	2.1^{a}	1.8^{a}	
Ethyl decanoate[d]	Mixed	1.4	1.8	1.8	1.1	0.9	1.8	1.9	1.5^{B}
(1395)	Araçá	-	-	-	-	-	-	-	
	Marolo	5.5	4.9	2.5	2.5	3.6	4.8	3.6	3.9^{A}

	Mean	3.5^{a}	3.4^{a}	2.2^{a}	1.8^{a}	2.3^{a}	3.3^{a}	2.7^{a}	
(*E*)-Caryophyllene	Mixed	8.8	10.6	10.4	9.2	6.3	9.9	10.4	9.4^{B}
(1420)	Araçá	22.1	23.3	22.1	20.8	20.7	21.5	19.4	21.4^{A}
	Marolo	3.4	2.6	0.7	1.9	t	t	0.1	1.2^{C}
	Mean	11.4^{ab}	12.2^{a}	11.1^{ab}	10.7^{ab}	9.0^{b}	10.5^{ab}	10.0^{ab}	
b-Gurjunene	Mixed	0.3^{a}	-	-	0.1^{a}	-	0.3^{a}	-	
(1434)	Araçá	-	-	0.3^{a}	0.3^{a}	0.7^{a}	0.6^{a}	-	
	Marolo	-	-	-	-	-	-	-	
	Mean								
Aromadendrene	Mixed	1.2	1.4	1.2	0.9	0.7	1.4	1.3	1.2^{B}
(1443)	Araçá	3.2	2.9	3.1	2.7	3.6	3.6	2.9	3.1^{A}
	Marolo	-	-	-	-	-	-	-	
	Mean	2.2^{a}	2.1^{a}	2.2^{a}	1.8^{a}	2.2^{a}	2.5^{a}	2.1^{a}	
a-Humulene[d]	Mixed	1.8	1.9	0.9	1.4	1.1	1.3	1.5	1.4^{B}
(1457)	Araçá	3.6	3.7	3.3	2.9	3.2	3.3	2.9	3.3^{A}
	Marolo	-	-	-	-	-	-	-	
	Mean	2.7^{a}	2.8^{a}	2.1^{a}	2.1^{a}	2.2^{a}	2.3^{a}	2.2^{a}	
3-Hexenyl heptanoate[e]	Mixed	1.7	2.9	3.2	2.0	0.4	2.2	1.9	2.1^{B}
(1462)	Araçá	-	-	-	-	-	-	-	
	Marolo	11.0	11.5	3.2	3.0	4.5	6.2	3.1	6.1^{A}
	Mean	6.3^{a}	7.2^{a}	3.2^{a}	2.5^{a}	2.5^{a}	4.2^{a}	2.5^{a}	
9-*epi*-(*E*)-Caryophyllene	Mixed	0.3^{a}	0.3^{a}	-	-	-	0.2^{a}	0.4^{a}	
(1465)	Araçá	-	-	-	-	-	-	-	
	Marolo	-	-	-	-	-	-	-	
b-Selinene[c]	Mixed	4.7	6.1	6.6	4.7	3.3	5.7	6.1	5.3^{B}
(1493)	Araçá	13.2	12.7	13.0	11.7	12.3	12.5	11.1	12.4^{A}
	Marolo	-	-	-	-	-	-	-	
	Mean	9.0^{a}	9.4^{a}	9.8^{a}	8.2^{a}	7.8^{a}	9.1^{a}	8.6^{a}	
a-Selinene[c]	Mixed	5.5	6.9	7.9	6.3	3.7	6.7	6.8	6.2^{B}
(1503)	Araçá	12.8	12.0	12.3	12.8	12.3	13.7	10.1	12.3^{A}
	Marolo	-	-	-	-	-	-	-	
	Mean	9.1^{a}	9.4^{a}	10.1^{a}	9.5^{a}	8.0^{a}	10.2^{a}	8.4^{a}	
b-Bisabolene[d]	Mixed	0.8	1.0	1.4	1.8	0.3	0.9	1.0	1.0^{B}
(1507)	Araçá	2.1	1.7	1.8	1.7	2.2	1.9	1.7	1.9^{A}
	Marolo	-	-	-	-	-	-	-	
	Mean	1.5^{a}	1.4^{a}	1.6^{a}	1.7^{a}	1.2^{a}	1.4^{a}	1.4^{a}	
g-Cadinene	Mixed	-	-	-	-	-	-	-	
(1514)	Araçá	-	-	-	-	-	-	-	

	Marolo	3.4^{a}	2.6^{ab}	1.3^{c}	-	-	-	-	
b-Curcumene[d]	Mixed	0.5	0.6	0.6	2.0	0.2	0.6	0.6	0.7^{B}
(1516)	Araçá	0.8	0.9	1.1	1.3	1.8	1.3	1.0	1.2^{A}
	Marolo	-	-	-	-	-	-	-	
	Mean	0.6^{a}	0.8^{a}	0.9^{a}	1.6^{a}	1.0^{a}	1.0^{a}	0.8^{a}	
d-Cadinene[c]	Mixed	0.8	1.2	2.3	0.5	0.3	0.6	0.6	1.0^{B}
(1524)	Araçá	2.6	2.5	1.8	2.7	1.9	1.9	1.5	2.1^{A}
	Marolo	1.0	0.9	0.4	t	t	t	t	0.3^{C}
	Mean	1.5^{a}	1.5^{a}	1.5^{a}	1.1^{a}	0.7^{a}	0.9^{a}	0.8^{a}	
Zonarene[c]	Mixed	2.0	2.8	3.5	2.8	1.3	2.2	2.8	2.5^{B}
(1528)	Araçá	5.7	5.7	5.3	3.5	6.7	5.7	4.6	5.3^{A}
	Marolo	-	-	-	-	-	-	-	
	Mean	3.8^{a}	4.2^{a}	4.4^{a}	3.1^{a}	4.0^{a}	3.9^{a}	3.7^{a}	
(*E*)-g-Bisabolene	Mixed	0.7	0.8	0.6	0.5	0.2	0.8	0.7	0.6^{B}
(1537)	Araçá	1.1	1.6	1.8	1.4	1.9	1.7	1.4	1.6^{A}
	Marolo	-	-	-	-	-	-	-	
	Mean	0.9^{a}	1.2^{a}	1.2^{a}	1.0^{a}	1.1^{a}	1.3^{a}	1.1^{a}	
a-Cadinene	Mixed	1.0	0.9	0.8	0.5	0.3	1.1	0.9	0.8^{B}
(1540)	Araçá	2.2	1.6	2.3	1.9	2.4	2.8	1.8	2.1^{A}
	Marolo	-	-	-	-	-	-	-	
	Mean	1.6^{a}	1.2^{a}	1.6^{a}	1.2^{a}	1.4^{a}	1.9^{a}	1.3^{a}	
Selina-3,7(11)-diene	Mixed	0.8	1.1	1.1	0.7	0.4	1.0	1.1	0.9^{B}
(1547)	Araçá	2.6	2.3	2.5	2.1	2.4	2.5	2.1	2.4^{A}
	Marolo	-	-	-	-	-	-	-	
	Mean	1.7a	1.7^{a}	1.8^{a}	1.4^{a}	1.4^{a}	1.8^{a}	1.6^{a}	
Germacrene B[c]	Mixed	0.4^{a}	0.3^{a}	0.3^{a}	1.7^{a}	t	0.3^{a}	0.4^{a}	
(1559)	Araçá	-	-	-	2.4	-	0.3	-	
	Marolo	-	-	-	-	-	-	-	
	Mean								
(*E*)-Nerolidol	Mixed	1.0^{B}	1.5^{A}	1.5^{A}	0.6^{B}	0.4^{B}	1.2^{B}	1.6^{A}	1.1^{B}
(1566)	Araçá	2.0^{Aa}	2.0^{Aa}	2.0^{Aa}	1.9^{Aa}	1.9^{Aa}	2.0^{Aa}	1.7^{Aa}	1.9^{A}

	Marolo	-	-	-	-	-	-	-	
	Mean	1.5^{a}	1.8^{a}	1.8^{a}	1.3^{a}	1.2^{a}	1.6^{a}	1.7^{a}	
Caryophyllene oxide	Mixed	-	-	-	-	-	-	-	
(1583)	Araçá	-	0.4^{a}	-	0.3^{a}	-	-	-	
	Marolo	1.3^{a}	0.5^{a}	0.4^{a}	1.1^{a}	-	-	-	
	Mean								
Globulol[d]	Mixed	1.2	1.1	1.7	1.3	0.2	1.4	1.4	1.2^{A}
(1587)	Araçá	2.1	2.4	1.1	1.3	0.5	1.5	0.7	1.4^{A}
	Marolo	-	-	-	-	-	-	-	
	Mean	1.7^{ab}	1.8^{a}	1.4^{ab}	1.3^{ab}	0.3^{b}	1.5^{ab}	1.1^{ab}	
Ethyl dodecanoate[c]	Mixed	0.5	0.4	2.6	t	t	0.3	0.4	0.6^{A}
(1594)	Araçá	0.9	0.5	0.2	0.2	0.4	0.9	0.6	0.5^{A}
	Marolo	-	-	-	-	-	-	-	
	Mean	0.7^{a}	0.4^{a}	1.4^{a}	0.1^{a}	0.2^{a}	0.6^{a}	0.5^{a}	
Humulene epoxide II	Mixed	-	-	-	-	-	-	-	
(1609)	Araçá	-	-	-	-	-	-	-	
	Marolo	0.8^{a}	-	-	-	0.1^{a}	0.3^{a}	0.2^{a}	
1-*epi*-Cubenol[c]	Mixed	0.5^{a}	0.9^{a}	0.6^{a}	1.6^{a}	0.2^{a}	0.5^{a}	0.7^{a}	
(1630)	Araçá	-	-	-	-	-	-	-	
	Marolo	-	-	-	-	-	-	-	
allo-Aromadendrene	Mixed	0.2^{ab}	1.0^{a}	0.8^{a}	0.4^{ab}	0.1^{b}	0.3^{ab}	0.8^{a}	
(1642)	Araçá	-	-	-	-	-	-	-	
	Marolo	-	-	-	-	-	-	-	
epi-a-Muurolol[c]	Mixed	0.3^{a}	1.2^{a}	0.8^{a}	0.2^{a}	0.6^{a}	t	0.7^{a}	
(1645)	Araçá	-	-	-	-	-	-	-	
	Marolo	-	-	-	-	-	-	-	
a-Muurolol[c]	Mixed	0.5^{abc}	1.2^{ab}	1.5^{a}	0.2^{c}	0.1^{c}	0.4^{bc}	1.4^{a}	
(1650)	Araçá	-	-	-	-	-	-	-	
	Marolo	-	-	-	-	-	-	-	
Selin-11-en-4a-ol	Mixed	2.7	5.0	4.5	2.5	1.2	2.7	3.8	3.2^{B}
(1660)	Araçá	6.0	6.3	6.0	5.7	5.3	5.1	4.8	5.6^{A}
	Marolo	-	-	-	-	-	-	-	

	Mean	4.3^{ab}	5.7^{a}	5.2^{a}	4.1^{ab}	3.2^{b}	3.9^{ab}	4.3^{ab}	
epi-b-Bisabolol	Mixed	1.3	2.0	1.9	0.9	0.5	1.4	1.8	1.4^{B}
(1673)	Araçá	2.7	2.9	3.0	2.3	2.9	2.7	2.3	2.7^{A}
	Marolo	-	-	-	-	-	-	-	
	Mean	2.0^{a}	2.5^{a}	2.4^{a}	1.6^{a}	1.7^{a}	2.1^{a}	2.1^{a}	
Eudesm-7(11)-en-4-ol	Mixed	0.4	0.6	0.4	1.1	t	0.2	0.5	0.4^{A}
(1701)	Araçá	0.3	0.3	0.3	1.2	0.3	t	t	0.4^{A}
	Marolo	-	-	-	-	-	-	-	
	Mean	0.4^{a}	0.5^{a}	0.3^{a}	1.2^{a}	0.2^{a}	0.1^{a}	0.2^{a}	
(2*Z*,6*E*)-Farnesol	Mixed	0.8	1.3	0.7	0.5	0.3	0.9	1.4	0.8^{B}
(1725)	Araçá	1.6	1.9	1.9	1.0	1.9	1.9	1.5	1.7^{A}
	Marolo	-	-	-	-	-	-	-	
	Mean	1.2^{ab}	1.6^{a}	1.3^{ab}	0.7^{b}	1.2^{ab}	1.4^{ab}	1.4^{ab}	
Monoterpene	Mixture	15.5	3	5.2	4.1	19.1	8.9	6.5	8.9^{A}
hydrocarbons[c]	Araçá	5.8	5.5	9.0	10.4	6.4	7.7	20.2	9.3^{A}
	Marolo	-	-	-	-	-	-	-	
	Mean	10.7^{ab}	4.2^{b}	7.1^{ab}	7.3^{ab}	12.7^{a}	8.3^{ab}	13.3^{a}	
Oxygenated	Mixture	-	-	-	-	-	-	-	
monoterpenes[c]	Araçá	0.7^{a}	0.9^{a}	0.8^{a}	0.7^{a}	1.7^{a}	0.5^{a}	1.0^{a}	
	Marolo	-	-	-	-	-	-	-	
Sesquiterpene	Mixture	30.6	37.8	39.5	34.8	18.8	34.5	36.7	33.2^{B}
hydrocarbons[c]	Araçá	74.8	73.5	73.6	71.0	74.9	76.1	63.0	72.4^{A}
	Marolo	7.8	6.1	2.4	1.9	t	t	0.1	2.6^{C}
	Mean	37.7^{a}	39.2^{a}	38.5^{a}	35.9^{a}	31.2^{a}	36.9^{a}	33.2^{a}	
Oxygenated	Mixture	8.5	15.0	13.6	8.8	3.3	8.8	13.2	10.2^{B}
sesquiterpenes[c]	Araçá	15.0	15.9	14.1	13.6	12.7	13.2	11.0	13.7^{A}
	Marolo	2.1	0.5	0.4	1.1	0.1	0.3	0.2	0.7^{C}
	Mean	8.5^{ab}	10.5^{a}	9.4^{ab}	7.9^{ab}	5.4^{b}	7.4^{ab}	8.1^{ab}	
Esters[d]	Mixed	37.1	39.7	37.2	45.1	49.1	44.7	40.1	41.5^{B}
	Araçá	0.9	0.5	0.2	0.2	0.4	0.9	0.6	0.5^{C}
	Marolo	81.2	76.8	83.7	86.6	82.0	87.5	93.9	84.5^{A}
	Mean	39.7^{a}	39.0^{a}	40.4^{a}	44.0^{a}	43.8^{a}	44.4^{a}	44.9^{a}	

Table 1: Average content[a] of EO constituents from araçá, marolo and mixed (1:1) pulps over frozen storage time.

[a]Percentage on original values; [b]Retention index; [c]rank, [d]arcsine and [e]log-transformed in ANOVA.

Averages with the same small letters in rows and same capital letters in columns did not share significant differences at 5% based on Tukey test; t = trace (< 0.1%).

Pulps' EOs showed a predominance of esters (0-96.2%, mean of 42.3%) and sesquiterpene hydrocarbons (0-79.4%, 36.1%), particularly in marolo (84.5%) and araçá (72.4%), respectively. ANOVA indicated interaction between the two factors only for a-pinene and methyl hexanoate, with the highest contents at around six months of storage for mixed (16.1%) and marolo (35.9%) pulps, respectively. For other volatiles, terpenes and esters had significantly higher percentages in araçá and marolo, respectively, without any influence of storage time. In turn, b-pinene and total monoterpene hydrocarbons had a significant increase from the eighth month of storage onwards. In contrast, (*E*)-caryophyllene, selin-11-en-4a-ol and total oxygenated sesquiterpenes showed reduction at the same period, with both variations occurring regardless of pulp origin. Despite being a minor component, a-terpineol occurred only in araçá, which suggests an enzymatic degradation in the mixed pulp. Constituents with low contents such as a-muurolol, 1-*epi*-cubenol, *epi*-a-cubenol, *allo*-aromadendrene and methyl decanoate only occurred in the mixed pulp, with most of them not influenced by storage time.

Terpenes (60.8%, 82 compounds) and esters (69.5%, 58 compounds) have been identified as the main components in the *P. guineense* pulp via solvent extraction-distillation (SED) and solid phase microextraction (SPME), respectively (PERALTA-BOHÓRQUEZO et al., 2010). (*E*)-Caryophyllene (8.6%) and selin-11-en-4a-ol (5.9%) were predominant in SDE, and ethyl butyrate (7.4%) and ethyl hexanoate (2.5%) in SPME. Marolo has previously shown mainly oxygenated sesquiterpenes (SIRENA et al., 2014). However, in this study, ripe fruit pulp extracted by SPME showed only esters, mainly methyl and ethyl derivatives of hexanoate, octanoate and decanoate (SILVA et al., 2013). Terpenes were also identified, but only in the stages prior to full fruit ripening. Alcohols and esters, such as 2,3-butanediol (32.8%), ethyl hexanoate (21.2%), acetic acid (7.9%), ethyl octanoate (6.8%), 1,2-propanediol (5.4%) and methyl octanoate (4.7%), also predominated in the lyophilized pulp (BEZERRA et al., 2018). Variations in volatiles can be attributed to different extraction techniques (TONGNUANCHAN & BENJAKUL, 2014), as in the results described above. Postharvest process and storage conditions also affect volatile composition (DAMIANI et al., 2009; SHASHIREKHA et al., 2008). Volatiles may also be released from glycosidically linked non-volatile precursors by enzymatic or acid hydrolysis (HERRMANN, 2010), which may account for minor constituents observed only in the mixed pulp.

RDA indicated that correlations between EOs and the two factors were higher in the first two canonical axes (0.994 and 0.972), with 89.2% of the variation being explained by pulp origin and storage time interactions (Figure 1).

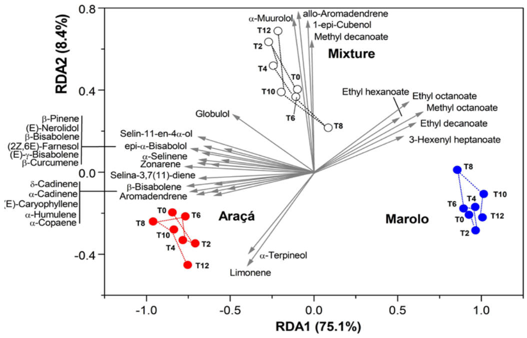

Figure 1: RDA diagram of araçá, marolo and mixed pulps according to EO variation along frozen storage (T0-T12). Fitted oil constituents (> 50%) are represented by long arrows.

RDA1 contributed with 75.1% (*F*-Fisher = 20.3; *P* < 0.001) of total explained variation and showed a clear separation between marolo – mainly characterized by higher ester contents (hexanoate, octanoate and decanoate of ethyl or methyl) – from araçá pulps, mainly characterized by higher terpene contents. RDA2 explained 8.4% of total variation (*F* = 3.9; *P* < 0.001) and distinguished mixed pulp samples mainly by higher contents of methyl decanoate, a-muurolol, *allo*-aromadendrene and 1-*epi*-cubenol, as well as by lower levels in monoterpenes such as limonene and a-terpineol. Thus, RDA1 described the variation of major constituents in araçá (terpenes) and marolo (esters) pulps, whereas RDA2 was associated with minor constituents, particularly in the mixed pulp. The RDA diagram suggests a small influence of storage time, with sample distribution predominantly influenced by pulp origin, a result already indicated by ANOVA. In RDA, however, the contribution of minor constituents for mixed pulp separation is clearly established. Since the projection of temporal effects is often not linear in factorial planes, principal response curves (PRC) were applied to assess metabolite differences and their changes over time (Figure 2).

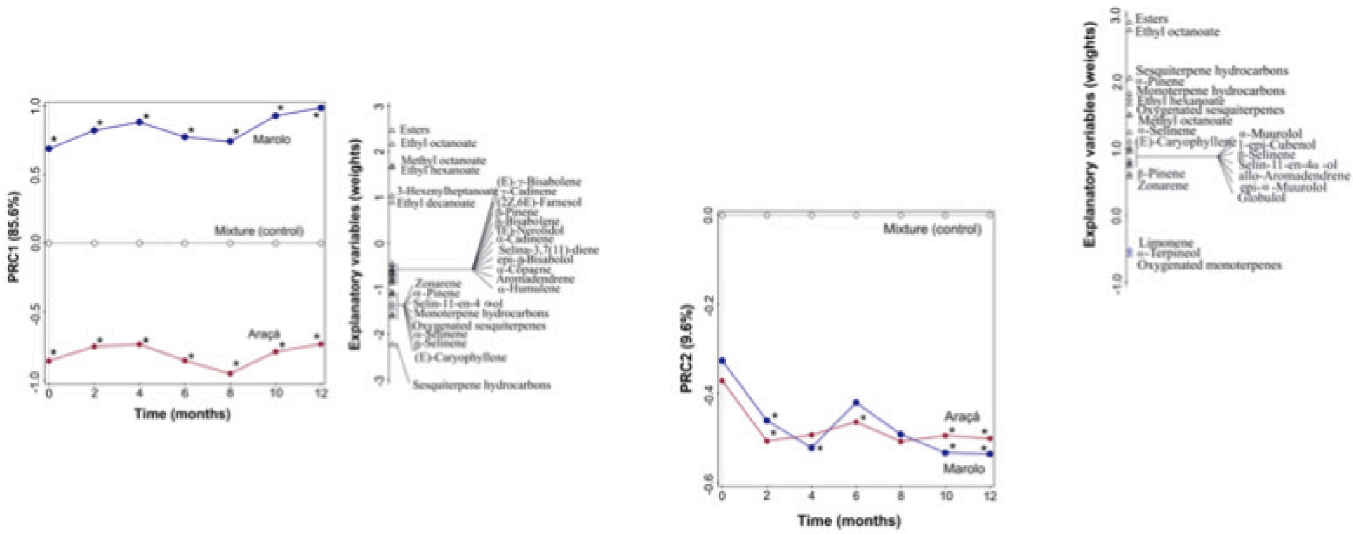

Figure 2. First and second principal response curves (PRC) diagram indicating variations in EO contents according to fruit pulps along frozen storage time.

PRCs showed that the treatment (pulps) x time interaction accounted for 89.9% in EO variation, with 87.8% being attributable to pulp effect, of which 95.2% ($P = 0.02$) were represented by the first two diagrams (PRC1: 85.6%, $F = 140$; PRC2: 9.6%, $F = 25.1\%$). Storage time contributed with 2.3% of the variance. In PRC1, the most important variables for distinguishing between marolo and araçá (treatments) and mixed pulp (control) were esters, with high levels in marolo, and mainly sesquiterpene hydrocarbons in araçá ($P < 0.02$). In PRC2, limonene, a-terpineol and oxygenated monoterpenes were the main variables for treatment distinctions, with higher levels in marolo and araçá ($P < 0.03$), particularly in the last quarter of storage time. Volatile dynamics during pulp storage, with small changes in minor constituents, was similar to that of Cerrado fruits like pequi, custard and red mombin (DAMIANI et al., 2009; SHASHIREKHA et al., 2008; TODISCO et al., 2014), but differed from mangaba, which showed higher compositional changes (GONÇALVES et al., 2018).

4 I CONCLUSIONS

Forty volatiles were identified in the EOs of araçá, marolo and mixed pulps. Esters were identified mainly in marolo, whereas terpenes were the major component in araçá. In the mixed pulp, EOs were slightly more related to marolo, with some minor constituents being identified only in this mixture. Volatile changes were mainly associated with pulp origin, while storage contributed very little to chemovariations. Pulps in frozen storage for 12 months resembled fresh pulps, with minor changes in some constituents, and retained volatiles similarly to fresh fruits. These findings endorse artisanal fruit processing and frozen pulp storage to preserve fruits' native aroma and flavor.

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ÍNDICE REMISSIVO

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