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Article

Seasonal Influence on Volatile Composition of *Psidium friedrichsthalianum* Leaves, Sampled in the Brazilian Amazon

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Abstract: *Psidium friedrichsthalianum* (Myrtaceae) is a small tree with antioxidant activity in its fruits and antimicrobial activity in its leaves and thin branches. The present study analyzed the seasonal variability in the yield and essential oil composition of a *P. friedrichsthalianum* population in Belém, Brazil. Essential oils were obtained by hydrodistillation and analyzed by gas chromatography (GC) coupled to mass spectrometer (MS) and flame ionization detector (FID). Chemometric analyses were carried out to verify the climatic influence on the production and composition of the essential oil. The average oil yield in the dry season (August–February) was 0.5 ± 0.0%, and in the rainy season (March–May), it was 0.8 ± 0.0%, with statistical differentiation. There was a moderate correlation between oil yield and the collection area's relative humidity (r = 0.63). The PCA and HCA analyses did not show differentiation between the *P. friedrichsthalianum* oil samples during the dry and rainy seasons. However, the class of monoterpene hydrocarbons presented a negative correlation with temperature (r = −0.81) and humidity (−0.80) of the sampled area. In the PCA and HCA studies, the samples were classified into three groups: Group I (leaf oils) was characterized by a higher content of α-pinene (6.3–18.0%), β-elemene (9.9–14.8%), caryophyllene oxide (4.3–16.3%), and β-pinene (4.8–13.4%). Group II (leaf oils) was defined by a higher content of selin-11-en-4-α-ol (4.6–15.6%), β-elemene (9.9–14.8%), α-pinene (6.3–18.0%), and *E*-caryophyllene (3.1–8.7%). Group III (fruits volatile concentrate) was characterized by a higher content of α-pinene (17.6%), α-terpineol (13.7%), and selin-11-en-4-α-ol (10.0%). There was significant seasonal variability in *P. friedrichsthalianum*, whose responses are directly linked to abiotic factors such as precipitation, insolation, humidity, and temperature.

Keywords: Costa Rican guava; Myrtaceae; volatiles; mono- and sesquiterpenes; environmental factors

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1. Introduction

Myrtaceae has around 1200 species, comprising 29 genera of trees, shrubs, and subshrubs, emphasizing *Eugenia*, *Myrciaria*, and *Psidium* found in Brazilian territory. Many scientific reports about its pharmacological and cosmetic applications are present in the literature [1,2]. The *Psidium* genus comprises 266 species, widely distributed worldwide in tropical and subtropical regions. In Brazil, *Psidium* has 60 species of trees, from large to small sizes. Among them, *P. guineense* Sw., known as "araçá-mirim", *P. acutangulum* Mart. ex DC., popularly called "araçá-pera", and *P. guajava* L., the traditional "guava", all used in the treatment of coughs, diarrhea, stomach pain, vomiting, fever, and flu [3,4].

Myrtaceae essential oils have high variability in volatile compounds and have outstanding biological activities [1]. Essential oils from *Psidium* species have antiproliferative, antioxidant, fungicidal, antibacterial, phytotoxic, larvicidal, anti-inflammatory, and cytotoxic properties [1,5]. In addition, *Psidium* oils are abundant in terpene compounds, with great emphasis on monoterpene hydrocarbons limonene and α-pinene [6,7].

Psidium friedrichsthalianum (O. Berg) Nied. (syn. *Calyptropsidium friedrichsthalianum* O. Berg), known as "Costa Rican guava" or "sour guava", is a small tree with fruits with antioxidant activity and widely used to prepare juices, jellies, and sweets [8,9]. This species originates from Central America, but its cultivation is currently carried out in several tropical countries, including Colombia, Brazil, and Ecuador [10]. Phytochemical and pharmacological studies with leaf and bark extracts of *P. friedrichsthalianum* reported significant antimicrobial potential [11].

The present work aimed to analyze the seasonal variability in a *Psidium friedrichsthalianum* population sampled in Belém, Pará state, Brazil, based on the analysis of yield and composition of its essential oils from August 2021 to May 2022 (10 months), using chemometric tools.

2. Materials and Methods

2.1. Plant Material and Climatic Data

The leaves (250 g) and fruits (100 g) of a cultivated population of *Psidium friedrichsthalianum* were randomly collected in Belém city, Pará state, Brazil (coordinates: 1°26′14.2″ S/48°26′30.2″ W). The mature leaves for the seasonal study were sampled on day 10 of each month, at 8 am, from August 2021 to May 2022. For its volatile concentrate analysis, the fruits were collected in November 2021, the month of fruiting of the species. Plant identification was performed by comparison with an authentic specimen of *Psidium friedrichsthalianum*. A specimen sample (MSF001848) was incorporated into the Herbarium Marlene Freitas da Silva at Universidade do Estado do Pará, Belém, State of Pará, Brazil. The specimen was collected in agreement with Brazilian laws concerning the protection of biodiversity (Sisgen A47AD8F).

The climatic parameters (insolation, relative air humidity, and rainfall precipitation) of the mentioned area were obtained for each month from the website of the Instituto Nacional de Meteorologia (INMET, http://www.inmet.gov.br/portal/, accessed on 5 December 2022), of Brazilian Government (INMET, 2022). Meteorological data were recorded through the automatic station A-201, located in Belém, Pará state, Brazil, equipped with a Vaisala system, model MAWS 301 (Vaisala Corporation, Helsinki, Finland).

2.2. Essential Oil and Volatile Concentrate Extraction

The leaves were dried for seven days at room temperature, then pulverized. The dried leaves (100 g) were subjected to hydrodistillation (in duplicate) using a Clevenger-type apparatus (3 h). The dry plant weights were used to calculate the oil yields (in duplicate). The moisture content of the leaves samples was calculated in an infrared moisture balance for water loss measurement. The fresh fruits were cut, homogenized (20 g), and subjected to a distillation-simultaneous extraction (DES) system using a Nickerson and Likens type extractor, in addition to water (150 mL) and n-pentane (2 mL) as solvents, for 2 h (in duplicate), to obtain its volatile concentrate (Vc). The oils (leaves) and the volatile concentrate (fruits) were stored in dark bottles for later chromatographic analysis.

2.3. Oils and Volatile Concentrate Composition Analysis

The analyses of the oils and volatile concentrate were performed by GC-MS. A Shimadzu instrument Model QP-2010 ultra (Shimadzu, Tokyo, Japan) was used. An Rtx-5MS (30 m × 0.25 mm; 0.25 μm film thickness) fused silica capillary column (Restek, Bellafonte, PA, USA) was used as the stationary phase. The carrier gas was helium adjusted to 1.0 mL/min at 57.5 Kpa. One μL of *n*-hexane solution (oil and volatile concentrate, 5 μL: *n*-hexane, 500 μL) was injected in split mode (split ratio 1:20). The injector and interface temperature was 250 °C, oven programmed temperature was 60 to 240 °C (3 °C/min), followed by an isotherm of 10 min. EIMS (electron ionization mass spectrometry) at 70 eV.

The ion source temperature was 200 °C. The mass spectra were obtained by scanning every 0.3 s. The mass fragments were from 35 to 400 *m*/*z*. The retention index was calculated for all components using C8-C40 *n*-alkanes series (Sigma-Aldrich, Milwaukee, WI, USA) according to the van den Dool and Kratz linear equation [12]. Individual components were identified by comparing their retention indices and mass spectra (molecular mass and fragmentation pattern) with those in the GCMS-Solution system libraries [13,14]. The quantitative data regarding the volatile constituents were obtained using a Shimadzu GC 2010 Series, operated under similar conditions to the Shimadzu GC-MS system. The relative amounts of individual components were calculated by peak-area normalization using the flame ionization detector (GC-FID). GC-FID and GC-MS analyses were performed in duplicate.

2.4. Statistical Analysis

The statistical analysis was performed according to Santos et al. [6]. The significance was assessed by a Tukey test ($p < 0.05$). The GraphPad Prism software, version 5.0 was used to calculate the Pearson correlation coefficients (r). The principal component analysis (PCA) was applied to the oil components (>3.0%). The hierarchical cluster analysis (HCA) was carried out considering the Euclidean distance and the Ward linkage [15].

3. Results and Discussion

3.1. Seasonal Effect on Oil Yields

Climatic factors, such as insolation, precipitation, temperature, and relative humidity, were monitored from August 2021 to May 2022 to evaluate their influence on the production and composition of the essential oil of *P. friedrichsthalianum*. The insolation values varied between 105.4 (March) and 256.1 h (August), the monthly precipitation from 163.4 (October) to 527.4 mm (March), the temperature from 25.9 °C (January) to 27.6 °C (October), and the relative air humidity from 82.1% (October) to 93.0% (April). The dry period in the region where the plant occurs comprised the months from August to February, with an average precipitation of 253.7 ± 58.4 mm, and the rainy period from March to May, with an average precipitation of 472.5 ± 60.2 mm (Figure 1). In previous work, in the seasonal study of the essential oil composition of *Lippia alba*, the dry period occurred from August to February, and the rainy period from March to May [16].

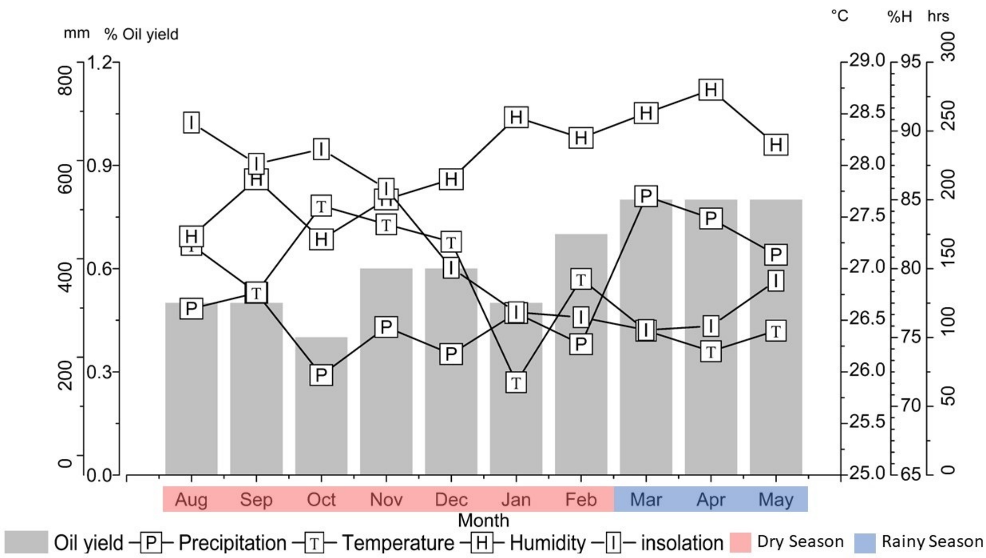

Figure 1. Relationship between climatic factors and *Psidium friedrichsthalianum* leaves essential oil yield during the seasonal study.

The climate in the Brazilian Amazon is represented only by the dry and rainy seasons. With a hot and humid climate, the Amazon region has the highest rainfall from December to April, characterized by the rainy season, and the lowest rainfall from June to November, represented by the dry season. The year's remaining months are considered transition periods between these two seasons [17,18]. However, from one year to another, these two seasons may change depending on the atmospheric phenomena that affect tropical regions [19].

In the present seasonal study, the leaves essential oil yields of *P. friedrichsthalianum* ranged from 0.4% (October) to 0.8% (March to May), averaging 0.6 ± 0.1% for the annual period (Figure 1). The essential oil yield showed a significant difference (Tukey, $p < 0.05$) during the dry (0.5 ± 0.0%) and rainy (0.8 ± 0.0%) periods. Concerning the climatic factors vs. the essential oil yield, no significant correlation was observed (Tukey, $p > 0.05$) with the temperature (r = −0.32), while with the relative humidity (r = 0.63), the oil yield showed a moderate correlation. There was also a strong and negative correlation between the oil yield and the insolation (r = −0.70), as seen in Table 1.

Table 1. Correlation between the yield, principal components, and classes of compounds of the *Psidium friedrichsthalianum* oil and the climatic factors.

Oil Yield/Components	Temperature	Humidity	Insolation	Precipitation
Oil yield	−0.32	0.63 *	−0.70 *	0.57
Caryophyllene oxide	0.51	0.57	0.16	0.63 *
β-Pinene	0.26	0.36	−0.24	−0.43
α-Pinene	−0.44	0.33	−0.70 *	0.01
β-Elemene	0.86 *	0.88 *	0.44	0.60 *
α-Terpineol	−0.99 *	−0.99 *	−0.66 *	−0.65 *
β-Selinene	−0.75 *	−0.72 *	−0.59 *	−0.41
Selin-11-en-4-α-ol	−0.22	−0.27	0.16	−0.05
Monoterpene hydrocarbons	−0.29	−0.26	−0.49	−0.32
Oxygenated monoterpenes	−0.79 *	−0.78 *	−0.47	−0.38
Sesquiterpene hydrocarbons	0.41	0.36	0.36	0.10
Oxygenated sesquiterpenes	0.28	0.35	0.13	0.42

* Significant correlation ($p < 0.05$).

A previous study evaluating the effect of seasonality on the leaves essential oil of a *Psidium acutangulum* DC. population, collected in Belém, Pará, Brazil, did not show a significant difference in the oils yield between the dry period (0.7 ± 0.3%) and the rainy period (0.9 ± 0.2%) [6]. On the other hand, during the seasonal study of *Psidium salutare* (Kunth). O. Berg leaves in Northeast Brazil, its leaf oil yield showed different percentages during the dry (0.15%) and rainy (0.73%) seasons, with no significant correlation with the precipitation [20].

3.2. Seasonal Effect on P. friedrichsthalianum Oil Composition

Table 2 lists eighty-nine (89) chemical constituents identified by GC and GC-MS in the EOs from the leaves and volatile concentrate of *P. friedrichsthalianum*, in ascending order of their respective retention indices. These constituents comprise about 89.5% of the oils analyzed in the seasonal study and 85.0% of the components from the fruits' volatile concentrate. The predominant classes of compounds in the leaf oil samples were sesquiterpene hydrocarbons (19.1% to 45.7%), followed by oxygenated sesquiterpenes (18.8 to 39.4%), monoterpene hydrocarbons (13.2 to 34.6%), and oxygenated monoterpenes (1.3 to 9.6%). As for the volatile concentrate of the fruits, there was a predominance of monoterpene hydrocarbons (31.2%), followed by oxygenated sesquiterpenes (20.9%), sesquiterpene hydrocarbons (17.5%), and oxygenated monoterpenes (15.4%). The main constituents identified in the leaf oils of the seasonal study were α-pinene (6.3 to 18.0%), caryophyllene oxide (4.3 to 16.3%), selin-11-en-4-α-ol (4.6 to 15.6%), β-elemene (9.9 to 14.9%), β-pinene (4.8 to 13.4%), bicyclogermacrene (6.1 to 7.3%), linalool (0.1 to 7.1%), and spathulenol (1.9 to 5.9%). In the volatile concentrate of the fruits, there was a predominance of α-pinene (17.6%), α-terpineol (13.7%), selin-11-en-4-α-ol (10.0%), β-pinene (7.1%), β-selinene (6.0%), and *E*-caryophyllene (5.0%). The chemical structures of these compounds are shown in Figure 2.

Table 2. Seasonal study of leaves essential oils (19 August–20 May) and fruits volatile concentrate (19 November) composition of *P. friedrichsthalianum*.

RI_C	RI_L	Oil Yield (%)	0.5	0.5	0.4	0.6	0.6	0.5	0.7	0.8	0.8	0.8	Vc (%)
		Month/Constituents (%)	**Aug**	**Sep**	**Oct**	**Nov**	**Dec**	**Jan**	**Feb**	**Mar**	**Apr**	**May**	
926	924 [a]	α-Thujene	n.d.	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	n.d.
934	932 [a]	α-Pinene	6.3	9.1	14.0	17.2	11.5	10.8	18.0	12.9	14.9	10.8	17.6
947	945 [a]	α-Fenchene	n.d.	0.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.1
949	946 [a]	Camphene	n.d.	0.1	n.d.	n.d.	n.d.	0.1	n.d.	n.d.	0.1	n.d.	0.2
974	969 [a]	Sabinene	0.9	0.2	0.5	0.6	0.5	0.6	0.8	0.5	0.5	0.4	n.d.
978	974 [a]	β-Pinene	4.8	6.9	11.0	11.9	9.5	8.9	13.4	9.8	10.5	8.4	7.1
991	988 [a]	Myrcene	n.d.	0.5	1.1	0.5	1.0	0.5	0.6	0.7	0.6	0.8	1.1
1017	1014 [a]	α-Terpinene	n.d.	0.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.2
1024	1020 [a]	*p*-Cymene	0.4	0.4	0.1	0.2	n.d.	0.3	0.2	0.2	0.2	0.1	n.d.
1028	1024 [a]	Limonene	0.7	1.4	1.5	1.4	1.4	1.3	1.5	1.3	1.2	1.2	2.2
1031	1026 [a]	1,8-Cineole	n.d.	n.d.	n.d.	n.d.	0.1	n.d.	n.d.	0.2	n.d.	n.d.	n.d.
1046	1044 [a]	*E*-β-Ocimene	n.d.	n.d.	0.1	n.d.	0.1	n.d.	n.d.	n.d.	n.d.	0.1	0.2
1058	1054	γ-Terpinene	0.1	0.1	n.d.	n.d.	0.1	n.d.	n.d.	n.d.	n.d.	0.1	0.3
1072	1067 [a]	*cis*-Linalool oxide (furanoid)	0.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.2	n.d.
1088	1084 [a]	*trans*-Linalool oxide (furanoid)	0.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.1	n.d.
1089	1086 [a]	Terpinolene	n.d.	0.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	2.2
1100	1095 [a]	Linalool	0.5	0.1	0.4	0.3	0.5	1.7	0.9	0.7	0.6	7.1	0.2
1113	1114 [a]	*endo*-Fenchol	0.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.5
1126	1122 [a]	α-Campholenal	0.3	n.d.	n.d.	0.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1137	1135 [a]	Nopilone	0.2	n.d.	n.d.	0.1	n.d.	0.1	n.d.	n.d.	n.d.	n.d.	n.d.
1139	1135 [a]	*trans*-Pinocarveol	1.3	n.d.	0.1	0.7	0.1	0.6	0.3	0.3	0.6	n.d.	n.d.
1145	1140 [a]	*trans*-Verbenol	1.5	n.d.	n.d.	0.4	n.d.	0.3	n.d.	0.1	0.3	n.d.	n.d.
1162	1160 [a]	Pinocarvone	0.7	n.d.	n.d.	0.2	n.d.	0.4	0.2	0.2	0.4	n.d.	n.d.
1166	1165 [a]	Borneol	0.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.3
1177	1174 [a]	Terpinen-4-ol	0.1	0.3	0.1	0.1	0.1	0.2	0.1	0.1	0.1	n.d.	0.7
1191	1186 [a]	α-Terpineol	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.3	0.4	13.7
1196	1195 [a]	Myrtenal	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.3	0.3	0.5	n.d.	n.d.
1197	1197 [b]	Myrtenol	1.4	n.d.	n.d.	0.7	n.d.	0.7	n.d.	n.d.	n.d.	n.d.	n.d.
1209	1204 [a]	Verbenone	0.9	n.d.	n.d.	0.1	n.d.	0.2	n.d.	n.d.	0.1	n.d.	n.d.
1219	1215 [a]	*trans*-Carveol	0.2	n.d.	n.d.	0.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1221	1218 [a]	*endo*-Fenchyl acetate	0.1	0.1	n.d.	n.d.	0.1	0.1	n.d.	0.1	0.1	n.d.	n.d.
1243	1241 [b]	Methyl phenethyl ketone	n.d.	0.1	0.2	0.3	0.1	0.1	n.d.	0.2	0.3	n.d.	n.d.
1286	1287 [a]	Bornyl acetate	0.4	0.2	0.2	0.2	0.2	0.4	0.1	0.3	0.3	0.1	n.d.
1300	1298 [a]	*trans*-Pinocarvyl acetate	n.d.	0.1	0.1	0.1	0.1	n.d.	0.1	0.2	0.2	0.1	n.d.
1323	1325 [a]	*p*-Mentha-1,4-dien-7-ol	1.0	n.d.	n.d.	0.2	n.d.	n.d.	n.d.	0.1	n.d.	n.d.	n.d.
1326	1326 [b]	Myrtenyl acetate	0.2	0.1	0.1	0.1	0.1	0.2	0.1	0.2	0.2	0.1	n.d.
1338	1335 [a]	δ-Elemene	n.d.	0.3	0.3	0.1	0.4	n.d.	n.d.	0.1	n.d.	0.3	n.d.
1351	1345 [a]	α-Cubebene	n.d.	0.1	n.d.	0.1	n.d.	n.d.	n.d.	0.1	n.d.	0.1	n.d.
1377	1374 [a]	α-Copaene	2.2	2.6	2.2	3.1	2.5	2.8	2.6	2.7	2.1	2.3	0.9
1385	1387 [a]	β-Bourbonene	0.4	n.d.	n.d.	n.d.	n.d.	0.5	0.3	n.d.	0.4	n.d.	n.d.
1394	1389 [a]	β-Elemene	11.4	9.9	13.0	14.9	14.8	11.0	14.7	14.5	10.7	14.8	1.8
1422	1417 [a]	*E*-Caryophyllene	n.d.	8.5	8.3	3.6	8.7	1.9	4.4	6.4	3.1	8.3	5.0
1430	1430 [a]	β-Copaene	0.1	0.1	0.1	0.1	0.1	0.1	n.d.	0.1	0.1	0.1	n.d.
1436	1432 [a]	*trans*-α-Bergamotene	n.d.	0.1	n.d.	0.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1440	1439 [a]	Aromadendrene	0.4	0.2	0.2	0.4	0.3	0.4	0.1	0.3	0.3	0.2	n.d.
1455	1452 [a]	α-Humulene	n.d.	1.3	1.2	0.7	1.3	0.4	0.5	1.0	0.6	1.1	0.7
1458	1454 [a]	*E*-β-Farnesene	n.d.	0.1	n.d.	n.d.	0.1	n.d.	n.d.	0.1	n.d.	n.d.	n.d.
1462	1464 [a]	9-*epi*-*E*-Caryophyllene	0.1	0.4	0.3	0.3	0.4	0.3	n.d.	0.3	0.2	0.3	n.d.
1477	1476 [a]	Selina-4,11-diene	n.d.	n.d.	n.d.	n.d.	0.3	n.d.	n.d.	n.d.	n.d.	n.d.	2.0
1478	1478 [a]	γ-Muurolene	0.6	0.7	0.6	0.8	0.5	0.8	0.5	0.8	0.7	0.6	n.d.
1482	1480 [a]	Germacrene D	n.d.	2.6	2.4	n.d.	2.9	n.d.	n.d.	0.4	n.d.	2.6	n.d.
1488	1489 [a]	β-Selinene	2.2	3.7	1.3	1.7	3.0	3.4	3.0	3.3	1.3	3.4	6.0
1493	1493 [a]	*trans*-Muurola-4(14),5-diene	n.d.	0.2	0.2	n.d.	0.2	n.d.	n.d.	n.d.	n.d.	0.1	n.d.
1496	1498 [b]	*epi*-Cubebol	0.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.0	n.d.	n.d.
1498	1500 [a]	Bicyclogermacrene	n.d.	6.1	7.3	n.d.	6.4	n.d.	n.d.	n.d.	n.d.	6.5	n.d.
1501	1500 [a]	α-Muurolene	0.2	0.5	0.5	0.3	0.4	0.4	0.1	0.3	0.3	0.3	n.d.
1506	1509 [a]	α-Bulnesene	n.d.	0.6	n.d.	0.1	1.1	n.d.	n.d.	0.5	n.d.	n.d.	n.d.
1516	1514 [a]	Cubebol	n.d.	0.8	n.d.	1.1	1.1	n.d.	n.d.	1.1	1.1	0.7	n.d.
1525	1522 [a]	δ-Cadinene	n.d.	2.5	1.9	n.d.	1.9	n.d.	n.d.	n.d.	n.d.	1.9	1.1
1534	1533 [a]	*trans*-Cadina-1,4-diene	n.d.	0.1	0.1	n.d.	0.1	n.d.	n.d.	n.d.	n.d.	0.1	n.d.
1539	1537 [a]	α-Cadinene	0.9	0.1	n.d.	0.1	0.1	n.d.	n.d.	0.1	n.d.	n.d.	n.d.

Table 2. *Cont.*

RI_C	RI_L	Oil Yield (%)	0.5	0.5	0.4	0.6	0.6	0.5	0.7	0.8	0.8	0.8	Vc (%)
		Month/Constituents (%)	**Aug**	**Sep**	**Oct**	**Nov**	**Dec**	**Jan**	**Feb**	**Mar**	**Apr**	**May**	
1542	1539 [a]	α-Copaen-11-ol	n.d.	0.1	n.d.	0.1	0.1	0.2	n.d.	0.1	0.1	n.d.	n.d.
1550	1548 [a]	Elemol	0.2	0.1	0.1	0.2	0.2	0.2	n.d.	0.2	0.2	0.1	n.d.
1558	1559 [a]	Germacrene B	0.2	0.1	0.1	n.d.	0.2	0.2	n.d.	n.d.	0.1	0.1	n.d.
1565	1561 [a]	*E*-Nerolidol	n.d.	0.1	0.1	0.1	0.1	0.1	n.d.	0.1	0.1	0.1	n.d.
1568	1566 [a]	Maaliol	0.5	0.2	0.1	0.2	0.2	0.3	n.d.	0.2	0.2	0.2	n.d.
1571	1570 [a]	Caryophyllenyl alcohol	0.4	0.4	0.2	0.1	0.3	0.2	n.d.	0.3	0.3	0.2	n.d.
1579	1577 [a]	Spathulenol	5.0	2.0	n.d.	2.4	3.7	5.7	5.9	4.0	3.1	2.6	1.9
1585	1582 [a]	Caryophyllene oxide	16.3	4.7	4.3	11.2	4.3	13.6	13.6	9.5	12.4	4.4	n.d.
1588	1590 [a]	β-Copaen-4α-ol	n.d.	0.3	0.3	0.1	0.3	0.3	n.d.	0.3	0.3	0.2	n.d.
1593	1592 [a]	Viridiflorol	1.0	0.5	0.4	0.5	0.4	0.8	0.4	0.5	0.5	0.5	2.8
1595	1595 [a]	Cubeban-11-ol	0.3	0.3	0.3	0.2	0.3	0.3	0.1	0.3	0.3	0.2	0.4
1599	1600 [a]	Guaiol	n.d.	0.2	0.2	n.d.	0.2	n.d.	n.d.	0.1	n.d.	0.1	n.d.
1604	1602 [a]	Ledol	n.d.	0.8	n.d.	0.6	n.d.	0.6	0.3	0.8	0.7	0.6	n.d.
1610	1608 [a]	Humulene epoxide II	1.7	0.3	0.3	1.1	n.d.	1.2	0.7	0.9	1.0	0.2	n.d.
1619	1618 [a]	Junenol	n.d.	0.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1630	1630 [a]	Muurola-4,10(14)-dien-1β-ol	0.8	1.6	1.2	0.8	1.3	1.4	1.1	1.5	1.4	1.0	n.d.
1632	1630 [a]	γ-Eudesmol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	1.7
1638	1636 [b]	Caryophylla-4(12),8(13)-dien-5β-ol	0.3	0.5	0.5	0.2	0.6	0.5	0.2	0.6	0.4	0.5	0.8
1644	1640 [a]	*epi*-α-Muurolol (= τ-Muurolol)	1.5	1.9	1.8	1.6	1.7	1.8	1.7	1.9	2.0	1.7	2.0
1649	1644 [b]	-Muurolol (= Torreyol)	1.5	1.7	1.5	1.3	1.3	1.4	1.4	1.5	1.7	1.3	1.3
1658	1651	Selin-11-en-4α-ol	8.0	15.6	7.5	n.d.	4.6	6.8	7.6	5.3	9.1	5.5	10.0
1669	1668 [a]	*trans*-Calamenen-10-ol	0.1	n.d.	n.d.	0.2	n.d.	0.2	n.d.	n.d.	0.1	n.d.	n.d.
1676	1675 [a]	Cadalene	0.4	0.1	n.d.	n.d.	n.d.	n.d.	n.d.	0.1	0.2	n.d.	n.d.
1677	1676 [a]	Muskatone	0.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1687	1685 [a]	α-Bisabolol	n.d.	0.3	n.d.	0.3	0.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1691	1688 [a]	Shyobunol	n.d.	n.d.	n.d.	n.d.	0.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
1691	1692 [a]	Acorenone	0.6	n.d.	n.d.	n.d.	n.d.	0.4	n.d.	n.d.	n.d.	n.d.	n.d.
1738	1739 [a]	Oplopanone	n.d.	n.d.	n.d.	0.2	n.d.	0.2	n.d.	n.d.	n.d.	n.d.	n.d.
Monoterpene hydrocarbons			13.2	19.2	28.4	31.9	24.2	22.6	34.6	25.5	28.1	22.0	31.2
Oxygenated monoterpenes			9.6	1.3	1.5	4.0	1.7	5.3	2.4	3.3	4.0	8.1	15.4
Sesquiterpene hydrocarbons			19.1	40.9	40.0	26.5	45.7	22.2	26.2	31.1	20.1	43.1	17.5
Oxygenated sesquiterpenes			39.4	32.9	18.8	22.5	21.4	36.2	33.0	29.2	36.0	20.1	20.9
Total (%)			81.3	94.3	88.7	84.9	93.0	86.3	96.2	89.1	88.2	93.3	85.0

RI_C = Calculated retention index; RI_L = Literature retention index; Vc = Volatile concentrate; [a] = Adams (2007); [b] = Mondello (2011); n.d. = not detected; Main constituents in bold; Standard deviation was less than 2.0 (n = 2).

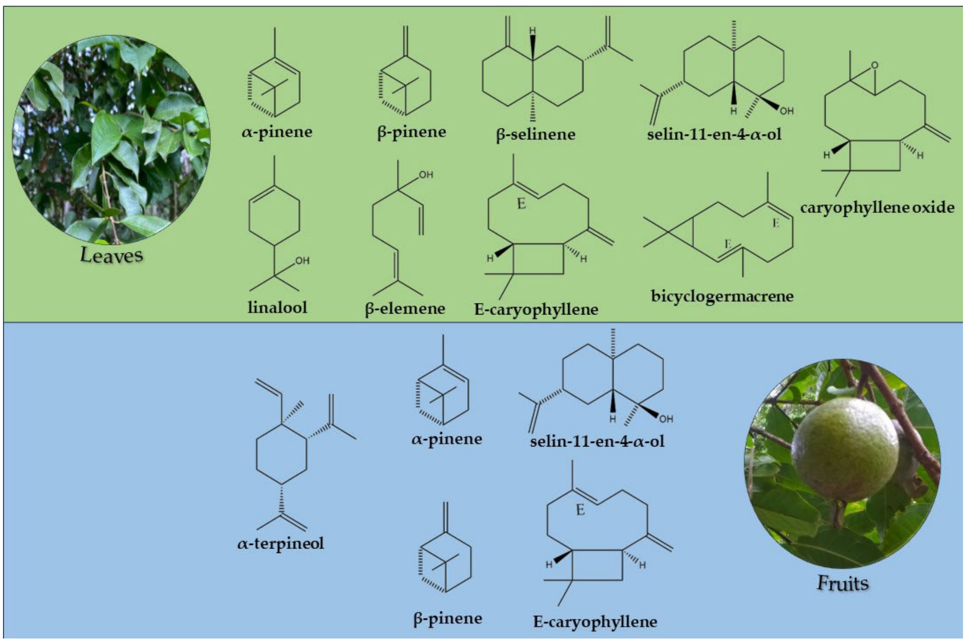

Figure 2. Chemical structures of main constituents identified in the oils and fruits of *P. friedrichsthalianum*.

The chemical constituents that significantly correlated with climatic factors were α-pinene with insolation (r = −0.70), the caryophyllene oxide with precipitation (r = 0.63), the β-elemene with mean temperature (r = 0.86), relative humidity (r = 0.88), and precipitation (r = 0.60), the α-terpineol with temperature (−0.99), relative humidity (−0.99), insolation (r = −0.66), and precipitation (r = −0.65), the β-selinene with temperature (−0.75), relative humidity (−0.72), and insolation (r = −0.59). The constituents that did not significantly correlate with climatic factors were selin-11-en-4-α-ol and β-pinene. On the other hand, the class of oxygenated monoterpenes showed a strong negative and significant correlation with temperature (r = −0.79) and relative humidity (−0.78) (see Table 1).

3.3. Multivariate Analysis of *P. friedrichsthalianum*

Hierarchical cluster analysis (HCA) and principal component analysis (PCA) were plotted with volatile constituents above 3%. Applying hierarchical cluster analysis (HCA) provided the dendrogram shown in Figure 3, which presents the *P. friedrichsthalianum* oil volatiles in three groups and zero similarity. Group I comprised oils from August, November, January, February, March, and April. Group II included September, October, December, and May oils. Group III concerned only the volatile concentrate of the fruits.

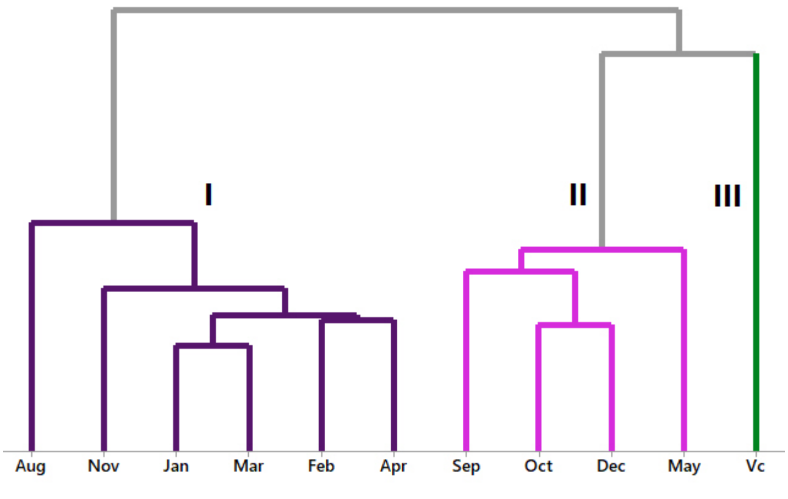

Figure 3. HCA analysis of main volatiles from *P. friedrichsthalianum*.

Principal Component Analysis (PCA) (Figure 4) clarified 79.81% of the data variability. The PC1 component explained 36.33% and was positively correlated with α-pinene (r = −0.11), α-terpineol (r = −0.50), and β-selinene (r = −0.39). The PC2 component explained 24.54% and showed a negative correlation with α-pinene (r = −0.13), β-pinene (r = −0.09), β-elemene (r = −0.07), α-copaene (r = −0.10), and spathulenol (r = −0.45). The PC3 component explained 18.94% of the data and showed a positive correlation with α-pinene (r = 0.68), β-pinene (r = 0.60), α-terpineol (r = 0.14), β-elemene (r = 0.03), and *E*-caryophyllene (r = 0.19). As with the HCA, the analysis of the PCA confirmed the formation of three distinct groups. Group I was characterized by the highest content of α-pinene (6.3–18.0%), β-elemene (9.9–14.9%), caryophyllene oxide (4.3–16.3%), and β-pinene (4.8–13.4%). Group II was characterized by the highest content of selin-11-en-4-α-ol (4.6–15.6%), β-elemene (9.9–14.9%), α-pinene (6.3–18.0%), and *E*-caryophyllene (3.1–8.7%). Group III was characterized by the highest content of α-pinene (17.6%), α-terpineol (13.7%), and Selin-11-en-4-α-ol (10.0%).

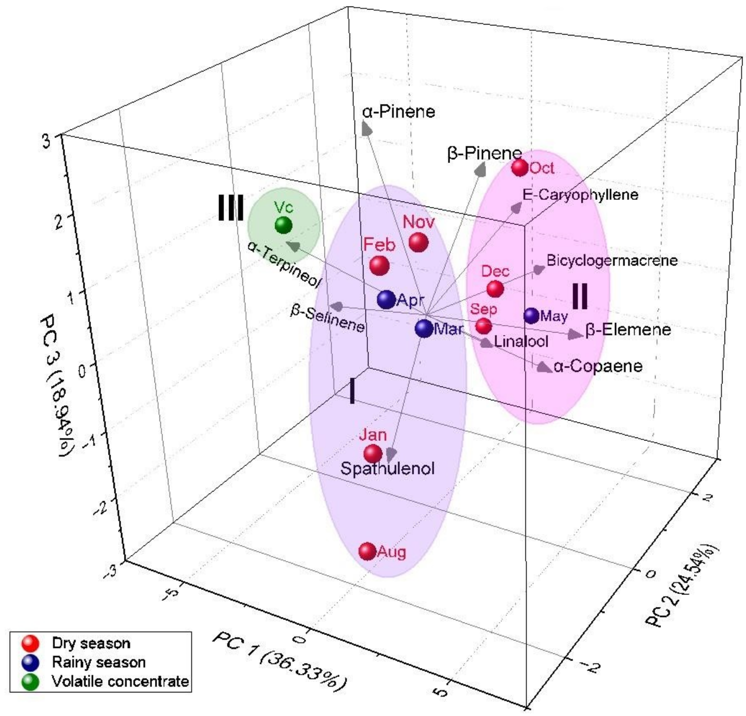

Figure 4. PCA analysis of main volatiles from *P. friedrichsthalianum*.

PCA and HCA analyses did not differentiate between *P. friedrichsthalianum* oil samples during dry and rainy seasons. A previous study about the seasonality of *Psidium acutangulum* leaves essential oils from Brazil showed no sample separation from dry and rainy seasons [6]. Indeed, some species show variation in the constituents contents but cannot be separated in chemometric analyses due to their metabolism not correlating with climatic parameters or other factors, biotic or abiotic, which may interfere with metabolic pathways [6,15]. However, correlations were observed between climatic parameters and constituents of oils and their classes of compounds, as mentioned before (see Table 1).

About eighteen *Psidium* species are grown worldwide, and the chemical compositions of more than one hundred of their essential oils have been reported in the literature, with significant variability of volatile constituents and according to seasonality and collection sites [1]. Previously, the essential oils composition of the leaves and the volatile concentrate of the fruits of *P. friedrichsthalianum* were reported: The leaves of a specimen collected in San Jose, Costa Rica, having *E*-caryophyllene, α- and β-pinene, and β-elemene as main constituents [21], the fruits of a specimen sampled in Havana, Cuba, with the predominance of *E*-caryophyllene, α-terpineol, α-pinene, α- and β-selinene, δ-cadinene, and α-copaene [22], and the leaves of a specimen collected in Alegre, Espírito Santo, Brazil, having *E*-caryophyllene, caryophyllene oxide, α-humulene, and α-copaene as significant components [23].

The extracts of leaves and fruits of *P. friedrichsthalianum*, the Costa Rican guava, proved to be a rich source of phenolic compounds, mainly quercetin derivatives, and proanthocyanidins derived from epicatechin units, besides other compounds such as ellagitannins, and benzophenones [24,25].

4. Conclusions

The main constituents identified in the leaf oils of the seasonal study of *Psidium friedrichsthalianum* were α-pinene, caryophyllene oxide, selin-11-en-4-α-ol, β-elemene, β-pinene, bicyclogermacrene, linalool, and spathulenol. In the volatile concentrate of the fruits, there was a predominance of α-pinene, α-terpineol, selin-11-en-4-α-ol, β-pinene, β-selinene, and *E*-caryophyllene. The essential oil exhibited a significantly strong correlation with humidity and insolation, and the constituents of the oil were correlated with climatic parameters. Furthermore, the class of monoterpene hydrocarbons showed a moderate negative correlation with temperature and humidity. Thus, the present study contributes to the knowledge on the chemical variability of *P. friedrichsthalianum* essential oils.

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