Chemical variability in the essential oil of leaves of Araçá (Psidium guineense Sw.), with occurrence in the Amazon

Pablo Luis B. Figueiredo1*, Renan C. Silva2, Joyce Kelly R. da Silva3, Chieno Suemitsu4, Rosa Helena V. Mourão5 and José Guilherme S. Maia1

Abstract
Background: Psidium guineense, known as Araçá, is a Brazilian botanical resource with commercial application perspectives, based on the functional elements of its fruits and due to the use of its leaves as an anti-inflammatory and antibacterial agent. The essential oils of leaves of twelve specimens of Araçá were analyzed by GC and GC-MS to identify their volatile constituents and associate them with the biological activities reputed to the plant.

Results: In a total of 157 identified compounds, limonene, α-pinene, β-caryophyllene, epi-β-bisabolol, caryophyllene oxide, β-bisabolene, α-copaene, myrcene, muurola-4,10(14)-dien-1-β-ol, β-bisabolol, and ar-curcumene were the primary components in descending order up to 5%. Hierarchical Cluster Analysis (HCA) and Principal Component Analysis (PCA) displayed three different groups with the following chemical types: limonene/α-pinene, β-bisabolene/epi-β-bisabolol, and β-caryophyllene/caryophyllene oxide. With the previous description of another chemical type rich in spathulenol, it is now understood that at least four different chemotypes for P. guineense should occur.

Conclusions: In addition to the use of the Araçá fruits, which are rich in minerals and functional elements, it should be borne in mind that the knowledge of the chemical composition of the essential oils of leaves of their different chemical types may contribute to the selection of varieties with more significant biological activity.

Keywords: Psidium guineense, Myrtaceae, essential oil composition, chemical variability

Background
Myrtaceae comprises 132 genera and 5671 species of trees and shrubs, which are distributed mainly in tropical and subtropical regions of the world, particularly South America, Australia and Tropical Asia [1]. It is one of the most prominent families in Brazil, represented by 23 genera and 1034 species, with occurrence in all regions of the country [2, 3]. Psidium is a genus with at least 60 to 100 species, occurring from Mexico and Caribbean to Argentina and Uruguay. Therefore, it is naturally an American genus, although P. guajava, P. guineense and P. cattleyanum are subtropical and tropical species in many other parts of the world [4].

*Correspondence: pablolbf@ufpa.br
1 Programa de pós-graduação em Química, Universidade Federal do Pará, 66075-900 Belém, PA, Brazil
Full list of author information is available at the end of the article
The leaf samples of twelve *Psidium guineense* specimens were collected in Pará state, Brazil. Collection site and voucher number of each specimen are listed in Table 1. The plant vouchers after the identification were deposited in the Herbaria of Embrapa Amazônia Oriental, in Belém (IAN) and Santarém (HSTM), Pará state, Brazil. The leaves were dried for two days in the natural environment and, then, subjected to essential oil distillation.

### Isolation and analysis of the composition of oils

The leaves were ground and submitted to hydrodistillation using a Clevenger-type apparatus (3 h). The oils were dried over anhydrous sodium sulfate, and their yields were calculated by the plant dry weight. The moisture content of the samples was calculated using an Infrared Moisture Balance for water loss measurement. The procedure was performed in duplicate.

### Table 1 Identification data and collection site of the specimens of *Psidium guineense*

| Samples  | Collection site         | Herbarium Nº | Local coordinates |
|----------|-------------------------|--------------|------------------|
| PG-01    | Curuçá, PA, Brazil      | IAN-195396   | 0°27'66.5"S/47°84'07"W |
| PG-02    | Curuçá, PA, Brazil      | IAN-195397   | 0°43'40.5"S/47°50'58"W |
| PG-03    | Curuçá, PA, Brazil      | IAN-195398   | 0°27'67.5"S/47°85'13"W |
| PG-04    | Curuçá, PA, Brazil      | IAN-195399   | 0°27'57.5"S/47°84'84"W |
| PG-05    | Curuçá, PA, Brazil      | IAN-195400   | 0°27'57.5"S/47°84'07"W |
| PG-06    | Santarém, PA, Brazil    | HSTM-3611    | 2°27'48.7"S/54°44'04"W |
| PG-07    | Monte Alegre, PA, Brazil| HSTM-6763    | 1°57'24.9"S/54°07'07.8"W |
| PG-08    | Monte Alegre, PA, Brazil| HSTM-6763    | 1°57'24.9"S/54°07'07.8"W |
| PG-09    | Santarém, PA, Brazil    | HSTM-6775    | 2°25'14.6"S/54°42'25.8"W |
| PG-10    | Santarém, PA, Brazil    | HSTM-3603    | 2°25'08.4"S/54°42'28.3"W |
| PG-11    | Santarém, PA, Brazil    | HSTM-6769    | 2°29'16.8"S/54°42'07.9"W |
| PG-12    | Ponta de Pedras, PA, Brazil | HSTM-6759 | 2°31'08.3"S/54°52'25.8"W |

The oils were analyzed on a GCMS-QP2010 Ultra system (Shimadzu Corporation, Tokyo, Japan), equipped with an AOC-20i auto-injector and the GCMS-Solution software containing the NIST (Nist, 2011) and FFNSC 2 (Mondello, 2011) libraries, a Rxi-5ms (30 m x 0.25 mm; 0.25 μm film thickness) silica capillary column (Restek Corporation, Bellefonte, PA, USA) was used. The conditions of analysis were: injector temperature of 250 °C; Oven temperature programming of 60-240 °C (3 °C/min); Helium as carrier gas, adjusted to a linear velocity of 36.5 cm/s (1.0 mL/min); split mode injection for 1 μL of sample (oil 5 μL : hexane 500 μL); split ratio 1:20; ionization by electronic impact at 70 eV; ionization source and transfer line temperatures of 200 and 250 °C, respectively. The mass spectra were obtained by automatic scanning every 0.3 s, with mass fragments in the range of 35-400 m/z. The retention index was calculated for all volatile components using a homologous series of C8-C20 n-alkanes (Sigma-Aldrich, USA), according to the linear equation of Van den Dool and Kratz (1963) [19]. The quantitative data regarding the volatile constituents were obtained by peak-area normalization using a GC 6890 Plus Series, coupled to FID Detector, operated under similar conditions of the GC-MS system. The components of oils were identified by comparing their retention indices and mass spectra (molecular mass and fragmentation pattern) with data stored in the GCMS-Solution system libraries, including the Adams library (2007) [20].

### Statistical analysis

The multivariate analysis was performed using as variables the constituents with content above than 5%. For the multivariate analysis, the data matrix was standardized by subtracting the mean and then dividing it by the standard deviation. For hierarchical cluster analysis, the complete linkage method and the Euclidean distance were used. Minitab software (free 390 version, Minitab Inc., State College, PA, USA), was used for these analyzes.

### Results and discussion

#### Yield and composition of the oils

*Psidium guineense* is a botanical resource that presents commercial application perspectives, based on its fruits and functional elements, as well as due to the use of its leaves as anti-inflammatory and antibacterial agent [6–14]. For this study were selected twelve Araçá specimens, with occurrence in various localities of Pará state (PA), Brazil (see Table 1), and which showed different composition for the leaf oils. The yields of the oils from these twelve Araçá samples ranged from 0.1 to 0.9%, where the higher yields were from specimens sampled in the Northeast of Pará, Brazil (0.4-0.9%), and the lower yields were...
from plants collected in the West of Pará, Brazil (0.1-0.3%). The identification of the constituents of the oils by GC and GC-MS was 92.5% on average, with a total of 157 compounds, where limonene (0.3-47.4%), α-pinene (0.1-35.6%), β-caryophyllene (0.1-24.0%), epi-β-bisabolol (6.5-18.1%), caryophyllene oxide (0.3-14.1%), β-bisabolene (0.1-8.9%), α-copaene (0.3-8.1%), myrcene (0.1-7.3%), muurola-4,10(14)-dien-1-β-ol (1.6-5.8%), β-bisabolol (2.9-5.6%), and ar-curcumene (0.1-5.0%) were the primary components, in descending order up to 5% (see Figure 1 and Table 2). In general, the constituents identified in oils belong to the terpenoids class, with the following predominance: monoterpene hydrocarbons (0.9-76.9%), oxygenated sesquiterpenes (5.2-63.5%), sesquiterpene hydrocarbons (5.6-46.7%), and oxygenated monoterpenes (1.9-8.8%).

Comparing these results with the composition of other essential oils described for the same plant, a specimen of *P. guineense* sampled in Arizona, USA, has also been found to contain β-bisabolene, α-pinene, and limonene as its primary constituents [14]. In addition, the oil from another specimen collected in Roraima, Brazil, presented β-bisabolol as the main component, followed by limonene and epi-α-bisabolol [15]. On the other hand, a specimen sampled in Mato Grosso do Sul, Brazil, presented an essential oil with a very high value of spathulenol [16]. Therefore, it is possible that there is a significant variation in the essential oils of different types of Araçá.

**Variability in oils composition**

The multivariate analysis of PCA (Principal Component Analysis) (Fig. 2) and HCA (Hierarchical Cluster Analysis) (Fig. 3) were applied to the primary constituents present in oils (content ≥ 5.0%), for the evaluation of chemical variability among the *P. guineense* specimens.

The HCA analysis performed with complete binding and Euclidean distance showed the formation of three different groups. These were confirmed by the PCA analysis, which accounted for 79.5% of the data variance. The three groups were classified as:

**Group I** Characterized by the presence of the monoterpenes α-pinene (13.4-35.6%) and limonene (3.7-37.2%),
### Table 2 Yield and volatile composition of twelve essential oil samples of *P. guineense*

| RI(C) | RI(L) | Constituents (%) | PG-01 | PG-02 | PG-03 | PG-04 | PG-05 | PG-06 | PG-07 | PG-08 | PG-09 | PG-10 | PG-11 | PG-12 |
|-------|-------|------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 848   | 846<sup>a</sup> | (2E)-Hexenal      | 0.3   | 0.1   |       |       |       |       |       |       |       |       |       |       |
| 850   | 850<sup>a</sup> | (2E)-Hexenol      |       | 0.2   | 0.1   |       |       |       |       |       |       |       |       |       |
| 933   | 932<sup>a</sup> | α-Pinene          | 35.6  | 26.1  | 17.7  | 13.4  | 34.0  | 26.4  | 2.0   | 0.8   | 1.0   | 13.0  | 0.1   | 0.6   |
| 946   | 948<sup>a</sup> | α-Fenchene        | 0.1   | 0.1   |       |       |       |       |       |       |       |       |       |       |
| 957   | 952<sup>a</sup> | Benzaldehyde      | 0.3   | 0.5   | 1.1   | 0.8   | 0.9   | 0.6   | 0.1   | 0.4   | 0.3   | 0.3   | 0.5   | 0.1   |
| 977   | 974<sup>a</sup> | β-Pinene          | 2.1   | 1.8   | 1.4   | 1.3   | 1.7   | 3.9   | 0.1   |       |       |       |       | 0.3   |
| 985   | 981<sup>a</sup> | 6-methyl-5-Hepten-2-one | 0.2   | 0.1   |       |       |       |       | 0.1   |       |       |       |       | 0.1   |
| 990   | 988<sup>a</sup> | Myrcene           | 0.2   | 1.4   | 1.2   | 1.4   | 1.3   | 1.6   | 0.1   | 0.1   | 0.6   | 0.7   | 0.1   | 1.7   |
| 1005  | 1003<sup>a</sup> | p-Mentha-1(7),8-diene | 0.5   | 0.9   | 1.0   | 0.7   | 0.3   | 0.1   | 0.2   | 0.7   | 1.2   |       | 0.1   |
| 1016  | 1014<sup>a</sup> | α-Terpine        | 0.1   | 0.1   |       |       |       |       |       |       |       |       |       |       |
| 1023  | 1020<sup>a</sup> | p-Cymene         | 0.3   | 0.5   | 1.0   | 0.7   | 1.4   | 0.5   | 0.2   | 0.3   | 0.4   | 0.3   | 0.1   | 0.6   |
| 1028  | 1024<sup>a</sup> | Limonene         | 3.7   | 30.7  | 30.4  | 26.5  | 37.2  | 14.0  | 4.3   | 9.6   | 23.4  | 47.4  | 0.3   | 5.4   |
| 1031  | 1032<sup>b</sup> | 1,8-Cineole      | 0.3   | 0.1   | 0.1   | 0.1   | 0.1   | 0.1   | 0.2   | 0.1   |       |       | 1.7   | 0.8   |
| 1035  | 1032<sup>a</sup> | (Z)-β-Ocimene    | 0.1   | 0.1   | 0.1   |       |       |       |       |       |       |       |       | 0.1   |
| 1046  | 1044<sup>a</sup> | (E)-β-Ocimene    | 0.1   | 0.2   | 0.1   | 0.1   | 0.1   | 0.8   |       |       |       |       |       | 0.1   |
| 1057  | 1054<sup>a</sup> | γ-Terpine        | 0.6   | 0.4   | 0.7   | 0.6   | 0.3   | 0.9   |       | 0.2   | 0.2   | 0.1   |       | 0.1   |
| 1088  | 1086<sup>a</sup> | Terpinolene      | 0.1   | 0.1   | 0.2   | 0.1   | 0.1   | 0.3   |       |       |       |       | 0.1   |       |
| 1100  | 1095<sup>a</sup> | Linalool         | 0.1   | 0.1   | 0.1   |       |       |       | 0.2   | 0.1   |       |       | 0.1   | 0.1   |
| 1114  | 1114<sup>a</sup> | endo-Fenchol     | 0.1   | 0.1   | 0.1   |       |       |       | 0.1   |       |       |       |       | 0.1   |
| 1116  | 1113<sup>b</sup> | 4,8-dimethyl-(E)-Nona-1,3,7-triene | 0.1   |       |       |       |       |       |       |       |       |       |       |       |
| 1120  | 1122<sup>a</sup> | trans-p-Mentha-2,8-dien-1-ol | 0.1   |       | 0.1   |       |       |       |       |       |       |       |       |       |
| 1125  | 1122<sup>a</sup> | α-Campholenal    | 0.1   | 0.1   | 0.1   |       |       |       |       | 0.1   |       |       |       |       |
| 1130  | 1131<sup>b</sup> | Limon ketone     |       |       |       |       |       |       |       |       |       |       |       | 1.6   |
| 1134  | 1133<sup>a</sup> | cis,p-Mentha-2,8-dien-1-ol | 0.1   |       | 0.1   |       |       |       |       |       |       |       |       | 0.1   |
| 1138  | 1136<sup>a</sup> | trans-p-Mentha-2-en-1-ol | 0.4   |       | 0.4   | 0.1   | 0.4   | 0.4   | 0.2   |       |       |       |       |       |
| 1139  | 1135<sup>a</sup> | trans-Pinocarveol |       |       |       | 0.4   | 0.1   |       |       |       |       |       |       |       |
| 1148  | 1145<sup>a</sup> | Camphene hydrate |       |       |       | 0.1   | 0.1   | 0.1   | 0.1   |       |       |       |       |       |
| 1161  | 1165<sup>b</sup> | Hydrocinnamaldehyde |       |       |       |       | 0.9   |       | 1.5   | 0.5   |       |       |       |       |
| 1166  | 1165<sup>a</sup> | Borneol          |       |       |       | 0.2   | 0.1   | 0.2   | 0.1   |       |       |       |       | 0.3   |
| 1177  | 1174<sup>a</sup> | Terpinen-4-ol    |       |       |       | 0.1   | 0.1   | 0.2   | 0.1   |       |       |       |       | 0.1   |
| 1186  | 1187<sup>a</sup> | trans-p-Mentha-1(7),8-dien-2-ol |       |       |       | 0.1   |       |       |       | 0.4   | 0.2   |       |       |
| 1187  | 1189<sup>a</sup> | trans-Isocarveol |       |       |       |       |       |       |       |       |       |       |       | 0.4   |
| 1191  | 1186<sup>a</sup> | α-Terpineol      |       |       |       |       |       |       |       |       |       |       |       | 0.1   |
| 1218  | 1215<sup>a</sup> | trans-Canveol    |       |       |       |       |       |       |       |       |       |       |       |       |
| 1221  | 1218<sup>a</sup> | endo-Fenchyl acetate | 0.7   | 0.2   | 0.4   | 0.3   | 0.4   | 0.4   | 0.7   |       |       |       |       |       |
| RI<sub>(C)</sub> | RI<sub>(L)</sub> | Constituents (%) | PG-01 | PG-02 | PG-03 | PG-04 | PG-05 | PG-06 | PG-07 | PG-08 | PG-09 | PG-10 | PG-11 | PG-12 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1226 | 1227<sup>a</sup> | *cis*-p-Mentha-1(7),8-dien-2-ol | 0.4 | 0.2 | 0.1 | 0.3 | 0.1 |
| 1243 | 1239<sup>a</sup> | Carvone | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| 1267 | 1261<sup>a</sup> | *cis*-Chrysanthenyl acetate | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| 1286 | 1287<sup>a</sup> | Bornyl acetate | 1.5 | 0.6 | 0.7 | 0.5 | 0.9 | 1.5 | 0.1 |
| 1300 | 1298<sup>a</sup> | *trans*-Pinocarvyl acetate | 1.5 | 0.3 | 0.5 | 0.1 | 2.4 | 16.0 |
| 1324 | 1322<sup>a</sup> | Methyl geranate | 0.2 | 0.6 | 0.6 | 0.4 | 0.3 | 0.3 | 0.9 | 20.0 | 0.3 |
| 1326 | 1324<sup>a</sup> | Myrtenyl acetate | 0.1 | 0.1 | 0.1 |
| 1336 | 1335<sup>a</sup> | α-Bemene | 0.2 | 0.1 | 0.1 | 0.1 | 0.1 | 23 |
| 1338 | 1339<sup>a</sup> | *trans*-Carvyl acetate | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| 1364 | 1359<sup>a</sup> | Neryl acetate | 0.1 | 0.1 | 0.1 |
| 1367 | 1369<sup>a</sup> | Cyclosativene | 0.1 | 0.1 | 0.1 |
| 1378 | 1374<sup>a</sup> | α-Copaene | 8.1 | 6.2 | 8.1 | 2.0 | 3.0 | 3.7 | 4.2 | 4.7 | 2.5 | 1.1 | 0.3 |
| 1383 | 1379<sup>a</sup> | Geranyl acetate | 0.1 | 1.1 | 1.0 | 1.7 | 0.6 | 0.8 | 0.2 | 0.2 | 1.9 | 0.5 | 0.8 |
| 1401 | 1401<sup>a</sup> | *iso*-Italicene | 0.5 | 0.6 | 0.6 | 0.2 | 0.1 |
| 1406 | 1405<sup>a</sup> | Sesquithujene | 0.0 | 0.1 | 0.1 |
| 1416 | 1410<sup>a</sup> | α-Cedrene | 0.0 | 0.8 | 0.8 | 1.0 | 0.4 | 0.5 |
| 1417 | 1407<sup>a</sup> | Acora-3,7(14)-diene | 0.9 | 0.6 | 1.0 | 0.5 |
| 1426 | 1419<sup>a</sup> | β-Cedrene | 0.1 | 0.3 | 0.1 | 0.1 |
| 1431 | 1430<sup>a</sup> | β-Copaene | 0.0 | 0.2 | 0.2 |
| 1435 | 1434<sup>a</sup> | γ-Elemene | 0.1 | 0.1 | 0.1 |
| 1433 | 1432<sup>a</sup> | *trans*-α-Bergamotene | 0.3 | 0.3 | 0.3 | 0.2 |
| 1436 | 1435<sup>a</sup> | Perillyl acetate | 0.1 | 0.1 | 0.1 | 0.2 | 0.2 | 0.2 |
| 1440 | 1439<sup>a</sup> | Aromadendrene | 0.2 | 0.1 | 0.1 | 0.2 | 0.2 | 0.2 | 0.4 |
| 1441 | 1439<sup>a</sup> | Phenylethyl but-2-anoate | 0.3 | 0.3 | 0.3 | 0.2 | 0.3 |
| 1444 | 1440<sup>a</sup> | (Z)-β-Farnesene | 0.2 |
| 1444 | 1442<sup>a</sup> | Guai-6,9-diene | 0.1 |
| 1447 | 1445<sup>a</sup> | εp-β-Santalene | 0.1 | 0.1 | 0.1 |
| 1452 | 1446<sup>a</sup> | Amorpha-4,11-diene | 0.3 |
| 1452 | 1454<sup>a</sup> | Germanol | 0.2 |
| 1455 | 1452<sup>a</sup> | α-Humulene | 0.9 | 0.7 | 0.3 | 0.5 | 0.1 | 0.9 | 0.4 | 0.1 | 0.2 | 2.8 |
| 1458 | 1454<sup>a</sup> | β-β-Farnesene | 1.0 | 0.1 | 0.5 | 0.2 | 0.3 | 0.1 |
| 1461 | 1457<sup>a</sup> | β-Santalene | 1.2 | 1.1 | 0.5 | 0.5 |
| 1464 | 1460<sup>a</sup> | allo-Aromadendrene | 0.2 | 0.2 | 0.3 | 0.3 | 0.1 | 0.1 |
| 1467 | 1464<sup>a</sup> | α-Acoradiene | 1.3 | 1.1 | 1.3 | 0.6 | 0.7 |
| 1467 | 1469<sup>a</sup> | β-Acoradiene | 0.4 | 0.3 | 0.4 | 0.2 | 0.2 |
Table 2 continued

| RI(C) | RI(L) | Constituents (%) | PG-01 | PG-02 | PG-03 | PG-04 | PG-05 | PG-06 | PG-07 | PG-08 | PG-09 | PG-10 | PG-11 | PG-12 |
|-------|-------|------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1471  | 1471a | 4,5-di-epi-Aristolochene | 0.1   | 0.1   | 0.1   | 0.1   |       |       |       |       |       |       |       |       |
| 1474  | 1474a | 10-epi-β-Acoradiene   |       |       |       |       |       |       |       |       |       |       |       |       |
| 1477  | 1475a | γ-Gurjunene         | 0.3   |       |       |       |       |       |       |       |       |       |       |       |
| 1477  | 1476a | β-Chamigrene        |       |       |       |       |       |       |       |       |       |       |       |       |
| 1478  | 1478a | γ-Murolene          | 0.4   | 0.8   | 0.1   | 0.3   | 0.5   | 0.2   | 0.1   |       |       |       |       |       |
| 1479  | 1475a | γ-Curcumene         | 0.4   |       |       |       |       |       |       |       |       |       |       |       |
| 1481  | 1479a | ar-Curcumene        | 5.0   | 4.6   | 2.5   | 0.6   | 1.6   | 0.1   |       |       |       |       |       |       |
| 1482  | 1481a | γ-Himachalene       | 1.0   | 0.9   |       |       |       |       |       |       |       |       |       |       |
| 1483  | 1488a | β-Selinene          | 0.7   | 0.8   | 1.0   | 3.8   | 0.5   | 3.2   | 3.0   | 3.7   | 0.1   |       |       |       |
| 1495  | 1493a | α-Zingiberene       |       |       |       |       |       |       |       |       |       |       |       |       |
| 1497  | 1498a | α-Selinene          | 0.9   | 3.7   | 0.3   | 2.7   | 4.3   | 2.4   |       |       |       |       |       |       |
| 1502  | 1500a | α-Murolene          | 0.4   | 0.3   | 0.5   | 0.5   | 0.1   | 0.2   | 0.3   | 0.4   | 0.2   | 0.1   | 0.2   |       |
| 1502  | 1506a | (Z)-α-Bisabolene    | 0.1   |       |       |       |       |       |       |       |       |       |       |       |
| 1509  | 1505a | (E,E)-α-Farnesene   | 0.8   | 0.3   | 1.0   | 0.7   | 0.6   | 0.1   |       |       |       |       |       |       |
| 1515  | 1511a | 6-Astragalin        |       |       |       |       |       |       |       |       |       |       |       |       |
| 1521  | 1529a | (E)-γ-Bisabolene    |       |       |       |       |       |       |       |       |       |       |       |       |
| 1538  | 1533a | trans-Cadin-1,4-diene| 0.1   | 0.1   | 0.1   | 0.1   |       |       |       |       |       |       |       |       |
| 1534  | 1536a | Italicene ether     | 0.2   | 0.5   | 0.2   | 0.5   |       |       |       |       |       |       |       |       |
| 1539  | 1540a | 10-epi-cis-Dracunculifolol | 0.1   | 0.4   | 0.1   |       |       |       |       |       |       |       |       |       |
| 1543  | 1540a | (E)-α-Bisabolene    | 0.8   | 0.6   | 0.4   | 0.4   |       |       |       |       |       |       |       |       |
| 1543  | 1545a | Selina-3,7(11)-diene| 0.2   |       |       |       |       |       |       |       |       |       |       |       |
| 1544  | 1544a | α-Calacorene        | 0.2   | 0.3   | 0.1   | 0.3   | 0.3   | 0.7   |       |       |       |       |       |       |
| 1559  | 1559a | Germacrene B        | 0.1   | 0.1   |       |       |       |       |       |       |       |       |       |       |
| 1565  | 1561a | E-Nerolidol         | 0.3   | 0.1   | 0.4   | 0.2   | 0.1   | 0.1   | 1.0   | 1.3   | 0.9   | 2.2   | 0.2   | 0.4   |
| 1570  | 1571a | Caryolan-8-ol       | 0.3   | 0.2   |       |       |       |       |       |       |       |       |       |       |
| 1572  | 1570a | Caryophyllenyl alcohol | 0.3   |       |       |       |       |       |       |       |       |       |       |       |
| 1579  | 1578a | ar-Tumerol          | 0.3   | 0.6   | 0.1   |       |       |       |       |       |       |       |       |       |
| 1580  | 1577a | Spathulenol         | 0.7   | 0.4   | 0.6   |       |       |       |       |       |       |       |       |       |
| 1584  | 1590a | Globulol            | 0.1   | 0.4   |       |       |       |       |       |       |       |       |       |       |
| RI(C) | RI(L) | Constituents (%) | PG-01 | PG-02 | PG-03 | PG-04 | PG-05 | PG-06 | PG-07 | PG-08 | PG-09 | PG-10 | PG-11 | PG-12 |
|-------|-------|------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1585  | 1586a | Gleenol          | 0.3   |       |       |       |       |       |       |       |       |       |       |       |
| 1586  | 1582a | Caryophyllene oxide | 2.5  | 0.7   |       | 0.6   | 2.7   | 1.0   | 0.3   | 1.2   | 14.1  |       |       |       |
| 1589  | 1590a | β-Copaen-4-α-ol  |       |       | 0.5   | 0.1   | 0.2   | 0.3   | 0.2   | 0.8   |       |       |       |       |
| 1594  | 1592a | Viridiflorol     | 0.2   | 0.9   | 0.2   | 0.1   | 0.1   | 0.2   | 0.3   |       | 0.2   | 0.3   |       |       |
| 1596  | 1595a | Cubeban-11-ol    |       |       |       |       | 0.1   | 0.2   |       |       |       |       |       |       |
| 1599  | 1600a | Guaiol           |       |       |       |       |       |       |       |       |       |       |       | 0.5   |
| 1601  | 1600a | Cedrol           |       |       |       |       |       |       |       | 0.4   | 0.4   | 0.5   | 0.8   |       |
| 1609  | 1619a | (Z)-8-hydroxy-Linalool | 0.9 | 0.7   | 0.1   |       |       |       |       |       |       |       |       |       |
| 1611  | 1613b | Humulene Epoxide | 0.4   | 0.1   | 0.1   | 0.1   |       |       |       |       |       |       |       | 1.0   |
| 1615  | 1613a | Copaborneol      |       |       |       |       |       |       |       |       |       |       |       |       |
| 1617  | 1618a | 1,10-di-epi-Cubenol | 0.2  |       |       |       |       |       |       |       |       |       |       | 1.7   |
| 1625  | 1622b | 10-epi-γ-Eudesmol |       |       |       |       |       |       |       |       |       |       |       | 2.1   |
| 1630  | 1627b | epi-Cubenol      |       |       |       |       |       |       |       |       |       |       |       | 0.5   |
| 1631  | 1632a | α-Acorenol       |       |       |       |       |       |       |       |       |       |       |       |       |
| 1632  | 1630a | Muurola-4,10(14)-dien-1-β-ol | 5.8 | 2.4   | 3.6   | 2.3   | 1.6   | 2.6   |       |       |       |       |       |       |
| 1635  | 1636a | β-Acorenol       |       |       |       |       | 0.4   | 0.5   | 0.3   | 0.8   |       |       |       |       |
| 1637  | 1638a | Gossanorol       |       |       |       |       | 1.0   | 1.6   | 0.5   | 0.3   | 1.1   |       |       |       |
| 1639  | 1638a | Caryophylla-4(12),8(13)-dien-5β-ol | 1.3 | 0.3   | 0.3   | 2.1   |       |       |       |       |       |       |       |       |
| 1641  | 1640a | epi-α-Cadinol    | 1.9   | 1.8   | 1.7   | 1.7   | 0.6   | 1.3   | 1.1   | 1.6   | 0.4   | 0.8   | 1.4   |       |
| 1644  | 1640a | epi-α-Muurolo1   | 1.1   | 0.9   | 1.2   | 0.3   |       |       |       |       |       |       |       | 2.6   |
| 1649  | 1644a | α-Muurolo1       |       |       | 0.6   | 1.8   | 0.7   | 0.4   | 1.1   | 1.0   | 1.6   | 3.1   |       |       |
| 1653  | 1649a | β-Eudesmol       |       |       | 1.2   | 1.1   | 0.4   | 0.8   | 1.1   | 1.0   | 1.6   | 3.1   |       |       |
| 1654  | 1652a | α-Cadinol        | 1.8   | 2.0   | 1.8   |       |       |       | 0.5   | 0.4   | 2.4   |       |       |       |
| 1655  | 1651a | Pogostol         |       |       |       |       |       |       | 3.8   | 4.8   | 0.1   |       |       |       |
| 1659  | 1658b | Selin-11-en-4α-ol |       | 4.2   | 3.7   |       |       |       |       |       |       |       |       | 4.4   |
| 1659  | 1668b | Intermedeol      |       |       |       |       |       |       |       |       |       |       |       | 0.5   |
| 1660  | 1666a | α-Bisabolol Oxide B |       |       |       |       |       |       |       |       |       |       |       | 2.3   |
| 1671  | 1670a | epi-β-Bisabolol  |       |       | 8.1   | 6.5   | 9.5   | 8.2   | 18.1  |       |       |       |       |       |
| 1674  | 1674b | β-Bisabolol      |       |       | 2.9   | 1.9   | 3.6   | 39.6  | 56.1  |       |       |       |       |       |
| 1675  | 1675a | 14-hydroxy-9-epi-β-Caryophyllene | 1.4 | 0.7   |       |       |       |       |       |       |       |       |       |       |
| 1677  | 1675a | Cadalene         |       |       | 0.1   | 0.6   |       |       |       |       |       |       |       |       |
| 1678  | 1674a | Helifolenol A    |       |       | 0.6   | 0.2   |       |       |       |       |       |       |       |       |
| 1680  | 1679a | Khusinol         |       |       | 0.3   | 0.2   |       |       |       |       |       |       |       |       |
| 1685  | 1683a | epi-α-Bisabolol  |       |       | 1.0   | 0.8   | 1.3   | 12.2  | 2.5   |       |       |       |       |       |
| RI(C) | RI(L) | Constituents (%) | PG-01 | PG-02 | PG-03 | PG-04 | PG-05 | PG-06 | PG-07 | PG-08 | PG-09 | PG-10 | PG-11 | PG-12 |
|-------|-------|------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| 1687  | 1685a | α-Bisabolol       | 2.8   | 4.0   | 2.6   | 2.2   | 3.4   |       |       |       |       |       |       |       |
| 1692  | 1692a | Acorenone         |       |       |       |       |       | 0.2   |       |       |       |       |       |       |
| 1696  | 1696d | Juniper camphor   |       |       |       |       |       | 0.8   |       |       |       |       |       |       |
| 1698  | 1700a | Eudesm-7(11)-en-4-ol | 0.1 |       |       |       |       |       |       |       |       |       |       |
| 1714  | 1713a | (2E,6Z)-Farnesal   | 0.2   | 1.3   | 1.5   | 2.7   | 0.2   |       | 1.0   | 0.4   | 2.8   |       |       |
| 1721  | 1722a | (2Z,6E)-Farnesol   |       |       |       |       | 3.7   | 4.6   |       | 0.2   |       |       |       |
| 1722  | 1724a | (2E,6E)-Farnesol   | 0.4   | 2.2   |       |       | 1.1   | 0.2   | 0.9   | 0.3   | 4.9   |       |       |
| 1741  | 1740a | (2E,6E)-Farnesal   | 0.3   | 1.9   | 2.1   | 3.6   | 0.4   |       | 0.7   | 1.4   | 0.6   | 3.8   |       |       |
| 1751  | 1751a | Xanthorrhizol      |       |       |       |       |       |       |       |       |       |       | 0.1   | 0.1   |
| 1757  | 1753a | Isobaeckeol        |       |       |       |       |       |       |       |       |       |       | 0.2   |       |
| 1767  | 1768a | α-Bisabolol        | 0.1   | 0.2   | 0.2   |       |       |       |       |       |       |       |       |
| 1841  | 1832d | Farnesyl acetate   | 0.1   | 0.3   | 0.2   |       |       |       |       |       |       |       |       | 0.1   |
| 1843  | 1845a | (2E,6E)-Farnesyl acetate | 0.1 |       |       |       |       | 0.7   | 0.1   | 0.1   | 0.1   | 0.1   |       |
| 1962  | 1958a | Geranyl benzoate   | 0.1   | 0.1   | 0.2   |       |       |       |       |       |       |       |       | 0.1   |

**Italic:** main constituents above 5%

RI(C): retention time calculated; RI(L): retention time of literature

a Adams [20]
b Mondello [18]
composed by the specimens PG-01 to PG-06, collected in Curuçá (PG-01 to PG-05) and Santarém (PG-06), Pará state, Brazil, with 49.2% similarity between the samples.

*Group II* Characterized by the presence of the sesquiterpenes β-bisabolene (4.0-8.9%) and epi-β-bisabolol (6.5-18.1%), consisting by PG-07 to PG-10 specimens

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**Fig. 2** Dendrogram representing the similarity relation in the oils composition of *P. guineense*

**Fig. 3** Biplot (PCA) resulting from the analysis of the oils of *P. guineense*
collected in Monte Alegre (PG-07 and PG-08) and Santarém (PG-09 and PG-10), Pará State, Brazil, with 50.3% similarity between samples.

**Group III** Characterized by the presence of a significant content of β-caryophyllene (24.0%) and caryophyllene oxide (14.1%), constituted by the PG-12 specimen, collected in the city of Ponta de Pedras, Pará state, Brazil, which presented zero% similarity with the other groups.

Thus, based on the study of these essential oils, the multivariate analysis (PCA and HCA) has suggested the existence of three chemical types among the twelve specimens of P. guineense collected in different locations of the Brazilian Amazon. It would then be the chemical types α-pinene/limonene (Group I), β-bisabolene/epi-β-bisabolol (Group II) and β-caryophyllene/caryophyllene oxide (Group III). Taking into account that two essential oils with a predominance of α-pinene/limonene and β-bisabolene/epi-β-bisabolol, respectively, were previously described [14, 15], it is understood that adding these two chemical types to that one rich in β-caryophyllene + caryophyllene oxide, which was a product of this study, besides the other chemical type with a high value of sathulenol, before reported by Nascimento and colleagues (2018) [16], will be now, at least, four chemical types known for the P. guineense essential oils.

Several studies have demonstrated the anti-inflammatory activities of limonene, α-pinene and β-caryophyllene, the primary constituents found in the oils of P. guineense presented in this paper. Limonene showed significant anti-inflammatory effects both in vivo and in vitro, suggesting a beneficial role as a diet supplement in reducing inflammation [21]; limonene decreased the infiltration of peritoneal exudate leukocytes and reduced the number of polymorphonuclear leukocytes, in the induced peritonitis [22]. α-Pinene presented anti-inflammatory effects in human chondrocytes, exhibiting potential anti-osteoarthritic activity [23], and in mouse peritoneal macrophages induced by lipopolysaccharides [24], being, therefore, a potential source for the pharmaceutical industry. The anti-arthritic and the in vivo anti-inflammatory activities of β-caryophyllene were evaluated by molecular imaging [25].

**Conclusion**

In addition to the great use of the fruits of P. guineense, which are rich in minerals and functional elements, it is understood that the knowledge of the chemical composition of the essential oils of leaves of their different chemical types may contribute to the selection of varieties with more significant biological activity. The study intended to address this gap.

**Abbreviations**

HCA: Hierarchical Cluster Analysis; PCA: Principal Component Analysis; GC: Gas chromatography; GC-MS: Gas chromatography-Mass spectrometry; IAN: Herbarium of Embrapa Amazônia Oriental; HSTH: Herbarium of Santarém.

**Authors’ contributions**

PLBF participated in the collection and preparation the plants to the herbaria, run the laboratory work, analyzed the data and contributed to the drafted paper. RCS helped with lab work. JKR guided the lab work and data analysis. CS identified the plants and managed their introduction in herbaria. RHVM helped with lab work and data analysis. JGSM proposed the work plan, guided the laboratory work and drafted the manuscript. All authors read and approved the final manuscript.

**Author details**

1 Programa de pós-graduação em Química, Universidade Federal do Pará, 66075-900 Belém, PA, Brazil. 2 Faculdade de Química, Universidade Federal do Pará, Belém, PA, Brazil. 3 Programa de Pós-Graduação em Biotecnologia, Universidade Federal do Pará, Belém, PA, Brazil. 4 Laboratório de Botânica, Universidade Federal do Oeste do Pará, Santarém, PA, Brazil. 5 Laboratório de Bioprospecção e Biologia Experimental, Universidade Federal do Oeste do Pará, Santarém, PA, Brazil.

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**Competing interests**

The authors declare that they have no competing interests.

**Ethics approval and consent to participate**

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