ORIGINAL ARTICLE

A C G publications

Rec. Nat. Prod. 13:4 (2019) 324-332

records of natural products

Chemical Compositions of Essential Oil of *Piper* Species from Atlantic Forest of Amazonia, Brazil

Carolina A. de Araujo [1], Claudio A.G. da Camara [1*], Marcilio M. de Moraes [1], Geraldo José Nascimento de Vasconcelos [2], Marta R. Pereira [3] and Charles E. Zartman [3]

[1] *Department of Chemistry, Rural Federal University of Pernambuco, Street Dom Manoel de Medeiros s/n, 52.171-030 Recife, PE, Brazil*

[2] *Federal University of Amazonas – Campus ICET. Street Nossa Senhora do Rosário, 3863, Tiradentes - CEP: 69103-128, Itacoatiara, Amazonas, Brazil*

[3] *National Institute for Amazonian Research, Department of Biodiversity Av. André Araújo, 2936, Petrópolis, CEP 69060-001, Manaus, Amazonas, Brazil*

(*Received September 13, 2018; Revised November 06, 2018; Accepted November 07, 2018*)

Abstract: Essential oils from the leaves of *Piper japurense* (Miq.) C. DC., *P. coariense* Yunk., *P. auriculifolium* Yunk., *P. curtistilum* C.DC., *P. alatipetiolatum* Yunk. and *P. brevesanum* Yunk. from the Amazon Forest (Brazil) were obtained through hydrodistillation. The chemical composition of the oils was determined using gas chromatography and mass spectrometry, which revealed the presence of 108 compounds representing 95.14%, 95.64%, 95.57%, 92.05%, 96.24% and 91.316% of the oils, respectively. All oils had an abundance of sesquiterpenes, except the oil from *P. alatipetiolatum*, which had a higher percentage of monoterpenes. The major components were α-eudesmol in the *P. japurense* (22.05%) and *P. coariense* (27.33%) oils, premnaspirodiene (32.26%) in the *P. auriculifolium* oil, caryophyllene oxide (28.69%) in the *P. curtistilum* oil, linalool (43.88%) in the *P. alatipetiolatum* oil and β-elemene (12.75%) in the *P. brevesanum* oil. Although the oils were composed of terpenes, the chemical analysis revealed qualitative and quantitative differences. This is the first report of the chemical composition of these six species of *Piper* that occur in the Amazonia biome in Brazil.

Keywords: *Piper* spp; essential oil; α-eudesmol; premnaspirodiene; caryophyllene oxide; linalool.

1. Introduction

The family Piperacea is considered one of the most basal clades among angiosperms [1]. There are approximately 290 species of this family distributed throughout Brazil, with a greater concentration in equatorial northern region of the county. One hundred thirty-seven species have been recorded for the state of Amazonas [2], which is located in the center of the Amazon Forest. The leaves of many species of the genus *Piper* are used in the form of infusions as folk remedies for the treatment of fever and inflammation [3].

The investigation of the biological properties of essential oils from plants of this genus has reveled antimicrobial [4], antioxidant [5], acaricidal [6] and insecticidal [7] activities. These oils are

* Corresponding author: E-Mail: claudio_agc@hotmail.com ; Phone:086-592-2184180 Fax:086-592-2181722

The article was published by ACG Publications
http://www.acgpubs.org/journal/records-of-natural-products © July-August 2019 EISSN:1307-6167
DOI: http://doi.org/10.25135/rnp.110.18.09.904

basically composed of phenylpropanoids, such as safrole, dillapiole and myristicin, or terpenes, such as limonene, *β*-caryophyllene, spathulenol, (*E*)-nerolidol, bicyclogermacrene and *α*-cadinol [8].

The species *Piper japurense* (Miq.) C. DC., *P. coariense* Yunk., *P. auriculifolium* Yunk., *P. curtistilum* C.DC., *P. alatipetiolatum* Yunk. and *P. brevesanum* Yunk. occur in the state of Amazonas, Brazil. Due to the shape of their inflorescences, these plants are known locally as “long pepper” or “monkey pepper”. The six species selected for the present study are bushes with considerable morphological similarity. As part of a larger investigation of the aromatic flora of the Amazonia biome, this paper offers the first description and comparation study of the chemical composition of essential oils from the leaves of *P. japurense*, *P. coariense*, *P. auriculifolium*, *P. curtistilum*, *P. alatipetiolatum* and *P. brevesanum* that occur in the state of Amazonas, Brazil.

2. Materials and Methods

2.1. Collection of Plant Material

The fresh leaves of *P. japurense* (Miq.) C. DC. (S 04° 05' 26"; W 63° 18' 51"), *P. coariense* Yunk. (S 04° 05' 26"; W 63° 19' 50") and *P. auriculifolium* Yunk. (S 04° 07' 18"; W 63° 04' 30") were collected in Coari, in the interior of the state of Amazonas. *P. curtistilum* C.DC. (S 03° 46' 32"; W 60° 18' 22") were collected in Careiro da Várzea, metropolitan region of the state of Amazonas. *P. alatipetiolatum* Yunk (S 02° 39' 04"; W 60° 02' 29") and *P. brevesanum* Yunk. (S 02° 39' 04"; W 60° 02' 29") were collected in Manaus, capital of the state of Amazonas. The plants were identified by botanist Pereira M.R. (National Institute for Amazonian Research). Voucher of both samples were mounted and deposited in the Herbário do Instituto Nacional de Pesquisas da Amazônia (INPA), under numbers: (681) *P. japurense*, (682) *P. coariense*, (684) *P. auriculifolium*, (698) *P. curtistilum*, (701) *P. alatipetiolatum* and (703) *P. brevesanum*.

2.2. Chemicals

All monoterpenes (*α*-pinene, limonene, linalool e *α*-terpineol), sesquiterpenes (*α*-copaene, *β*-caryophyllene, aromadendrene, *α*-humulene, *allo*-aromadendrene, bicyclogermarcrene, (*E*)-nerolidol and caryophyllene oxide were purchased from Sigma-Aldrich - Brazil.

2.3. Essential Oils Extraction and GC-FID Analysis

The essential oils from fresh leaves (100 g) were separately isolated using a modified Clevenger-type apparatus and hydrodistillation for 2h. The oil layers were separated and dried over anhydrous sodium sulfate, stored in hermetically sealed glass containers, and kept at low temperature (-5ºC) until analysis. Total oil yields were expressed as percentages (g/100 g of fresh plant material). All experiments were carried out in triplicate. Quantitative GC analysis were carried out using a PerkinElmer Clarus 500 GC apparatus equipped with a flame ionization detector (FID) and a non-polar DB-5 fused silica capillary column (30 m x 0.25 mm x 0.25 μm) (J & W Scientific). The oven temperature was programmed from 60 to 240°C at a rate 3°C min^{-1}. Injector and detector temperatures were 260°C. Hydrogen was used as the carrier gas at a flow rate of 1 mL min^{-1} in split mode (1:30). The injection volume was 0.5 µL of diluted solution (1/100) of oil in *n*-hexane. The amount of each compound was calculated from GC-FID peak areas in the order of DB-5 column elution and expressed as a relative percentage of the total area of the chromatograms. Analyses were carried out in triplicate.

2.4. GC-MS Analysis

The qualitative Gas Chromatography-Mass Spectrometry (GC-MS) analysis were carried out using a Varian 220-MS IT GC system with a mass selective detector, mass spectrometer in EI 70 eV with a scan interval of 0.5 s and fragments from 40 to 550 Da. fitted with the same column and temperature program as that for the GC-FID experiments, with the following parameters: carrier gas = helium; flow rate = 1 mL min^{-1}; split mode (1:30); injected volume = 1 µL of diluted solution (1/100) of oil in *n*-hexane.

2.5. Identification of Components

Identification of the components was based on GC-MS retention indices with reference to a homologous series of C8-C40 n-alkanes calculated using the Van der Dool and Kratz equation [9] and by computer matching against the mass spectral library of the GC-MS data system (NIST and WILEY 11th) and co-injection with authentic standards as well as other published mass spectra [10-12]. Area percentages were obtained from the GC-FID response without the use of an internal standard or correction factors.

3. Results and Discussion

Hydrodistillation of the leaves of the six species of *Piper* furnished yellowish oils with citric aromas. The highest yield was obtained with *P. auriculifolium* (0.25%), followed by *P. coariense* (0.10%), *P. alatipetiolatum* (0.10%), *P. japurense* (0.05%), *P. brevesanum* (0.05%) and *P. curtistilum* (0.03%) (Table 1). These results are in agreement with data described for other species of *Piper*. Santana *et al*., (2016) report a 0.2% yield for *P. longispicum*, which is close to the yield found for *P. auriculifolium* [13]. Rameshkumar *et al*., (2011) found the same yield for the leaf oil from *P. longum* as that obtained for *P. japurense* and *P. brevesanum* [14] (Table 1). Andrade and Zoghbi (2007) report the same yield for the leaf oil from *P. glandulosissimum* (0.03%) as that found for *P. curtistilum* [15]. Besides the genetic variability of each species investigated, biotic and abiotic factors can also affect the yield of essential oils [16].

Table 1. Percentage composition, yield of essential oils from leaves of *Piper* species.

Compounds	**RI[a]**	**RI[b]**	**Pja**	**Pco**	**Pau**	**Pcu**	**Pal**	**Pbr**	**MI**
			(%±SD[a])						
Yield (w/w)			0.05	0.10	0.25	0.03	0.10	0.05	
α-Pinene	932	935	-	-	-	-	2.56	-	RI, MS, CI
Limonene	1024	1022	-	-	-	0.61	1.88	-	RI, MS, CI
Sylvestrene	1025	1028	-	-	-	-	-	0.29	RI, MS
Benzene acetaldehyde	1036	1040	-	-	0.48	-	-	-	RI, MS
Linalool	1095	1100	0.36	-	-	0.72	43.88	-	RI, MS, CI
Phenyl ethyl alcohol	1106	1110	-	-	0.64	-	-	-	RI, MS
Coahuilensol	1166	1165	-	-	5.00	-	-	-	RI, MS
α-Terpineol	1186	1190	0.24	-	-	-	2.23	-	RI, MS, CI
δ-Elemene	1335	1335	-	-	-	0.70	-	0.38	RI, MS
α-Cubebene	1345	1350	-	-	4.10	0.99	-	0.34	RI, MS
α-Ylangene	1373	1374	0.80	-	-	1.47	-	-	RI, MS
α-Copaene	1374	1375	-	0.74	-	2.57	0.90	5.71	RI, MS, CI
Isoledene	1374	1378	-	-	1.04	-	-	-	RI, MS
β-Bourbonene	1387	1382	-	-		0.70	-	-	RI, MS
β-Elemene	1389	1388	0.73	-	0.89	4.71	-	12.75	RI, MS
Longifolene	1407	1405	0.25	-	-	-	-	-	RI, MS
α-Gurjunene	1409	1405	-	0.43	-	-	-	-	RI, MS
β-Caryophyllene	1417	1412	5.71	10.30	-	2.55	16.11	7.26	RI, MS, CI
β-Copaene	1430	1428	1.11	0.51	0.43	1.61	-	0.47	RI, MS
β-Gurjunene	1431	1429	-	-	0.44	-	-	-	RI, MS
α-*trans*-Bergamotene	1432	1433	-	-	0.37	-	-	-	RI, MS
Aromadendrene	1439	1436	-	0.38	-	-	-	-	RI, MS, CI
α-Himachalene	1449	1452	-	-	0.93	-	-	-	RI, MS
α-Humulene	1452	1453	0.78	0.98	-	-	2.99	1.86	RI, MS, CI
allo-Aromadendrene	1458	1457	-	0.48	-	-	-	0.72	RI, MS, CI
cis-Muurola-4(14),5-diene	1465	1470	2.17	-	-	-	-	-	RI, MS
4,5-*di-epi*-Aristolochene	1471	1472	-	-	0.41	-	-	-	RI, MS

Table 1 Continued..	**RI[a]**	**RI[b]**	**Pja**	**Pco**	**Pau**	**Pcu**	**Pal**	**Pbr**	**MI**
γ-Gurjunene			-	0.76	-	-	-	-	RI, MS
β-Chamigrene	1476	1477	-	-	-	-	0.49	1.08	RI, MS
γ-Muurolene	1478	1478	1.86	-	3.91	6.30	0.95	0.50	RI, MS
Widdra-2,4(14)-diene	1481	1484	1.86	-	-	-	-	-	RI, MS
Germacrene D	1484	1488	0.38	-	-	-	5.79	7.05	RI, MS
β-Selimene	1489	1489	-	-	-	1.74	2.62	3.19	RI, MS
cis-β-Guaiene	1492	1490	-	0.57	-	-	-	-	RI, MS
epi-Cubebol	1493	1491	-	-	-	2.44	-	-	RI, MS
Viridiflorene	1496	1492	-	1.22	-	-	3.40	-	RI, MS
Valencene	1496	1494	-	-	-	-	-	6.23	RI, MS
Curzerene	1499	1496	3.81	-	-	-	-	-	RI, MS
4-*epi*-*cis*-Dihydroagarofuran	1499	1496	-	4.26	-	-	-	-	RI, MS
Bicyclogermacrene	1500	1498	1.38	-	-	-	-	11.61	RI, MS, CI
α-Muurolene	1500	1500	1.12	-	-	1.81	-	-	RI, MS
β-Dihydro agarofuran	1503	1502	3.81	15.35	-	-	-	-	RI, MS
(*E*,*E*)-*α*-Farnesene	1505	1504	0.30	-	-	-	-	-	RI, MS
Premnaspirodiene	1505	1502	-	-	32.26	-	-	-	RI, MS
α-Bulnesene	1509	1507	-	-	10.01	-	-	-	RI, MS
δ-Amorphene	1511	1511	-	0.41	-	-	-	-	RI, MS
γ-Cadinene	1513	1512	5.83	1.23	-	3.15	0.59	8.25	RI, MS
Cubebol	1514	1513	-	-	-	1.62	-	-	RI, MS
trans-Calamenene	1521	1515	0.88	0.41	-	3.19	-	-	RI, MS
β-Sesquiphellandiene	1521	1517	-	-	0.39	-	-	-	RI, MS
δ-Cadinene	1522	1520	-	-	0.62	-	-	-	RI, MS
cis-Calamenene	1528	1525	-	-	2.70	-	-	-	RI, MS
α-Cadinene	1537	1534	0.67	-	-	1.98	-	-	RI, MS
α-Calacorene	1544	1541	0.80	-	0.63	-	-	-	RI, MS
Hedycaryol	1546	1546	1.71	0.68	-	-	-	0.35	RI, MS
Germacrene B	1559	1555	3.26	0.33	-	-	-	2.81	RI, MS
(*E*)-Nerolidol	1561	1560	0.65	-	2.98	0.60	2.71	1.07	RI, MS, CI
Palustrol	1567	1567	-	0.44	-	-	-	-	RI, MS
1*α*,10*α*-epoxy Amorph-4-ene	1570	1570	-	-	0.36	-	-	-	RI, MS
Caryolan-8-ol	1571	1572	-	-	-	0.63	-	-	RI, MS
Spathulenol	1577	1573	0.91	0.36	-	-	0.64	1.21	RI, MS
Caryophyllene oxide	1582	1578	2.24	2.52	1.41	28.69	2.73	1.07	RI, MS, CI
Gleenol	1586	1587	-	-	0.53	-	-	-	RI, MS
β-Copaen-4-*α*-ol	1590	1590	-	-	0.40	-	-	-	RI, MS
Viridiflorol	1592	1593	1.07	-	-	-	-	-	RI, MS
Salvial-4(14)-em-1-one	1594	1594	0.24	-	-	-	-	-	RI, MS
Carotol	1594	1594	0.73	-	-	-	-	-	RI, MS
Cubeban-11-ol	1595	1597	0.58	0.67	-	-	-	-	RI, MS
Widdrol	1599	1603	-	-	0.73	-	-	-	RI, MS
Rosifoliol	1600	1603	0.98	0.89	-	-	-	-	RI, MS
Guaiol	1600	1603	-	1.22	-	0.60	-	-	RI, MS
Humelene epoxide II	1608	1606	-	-	-	2.22	-	-	RI, MS
β-Athantol	1608	1613	-	-	-	-	-	2.09	RI, MS
1,10-*di*-*epi*-Cubenol	1618	1616	1.36	-	-	0.69	-	-	RI, MS
Junenol	1618	1620	-	-	-	0.61	-	-	RI, MS
10-*epi*-*γ*-Eudesmol	1622	1623	6.01	13.32	1.12	-	-	-	RI, MS
1-*epi*-Cubenol	1627	1625	1.72	-	1.79	3.27	-	-	RI, MS
Eremoligenol	1629	1627	0.63	1.55	-	-	-	-	RI, MS
γ-Eudesmol	1630	1630	3.67	2.43	-	0.73	-	-	RI, MS
Hinesol	1640	1637	0.39	0.49	-	-	-	-	RI, MS
epi-*α*-Muurolol	1640	1632	-	-	0.90	2.22	-	1.40	RI, MS

Table 1 Continued..	**RI[a]**	**RI[b]**	**Pja**	**Pco**	**Pau**	**Pcu**	**Pal**	**Pbr**	**MI**
α-Muurolol	1644	1640	4.33	0.35	0.91	1.09	-	-	RI, MS
Cubenol	1645	1645	2.23	-	-	-	-	-	RI, MS
Agarospirol	1646	1646	-	1.74	-	-	-	-	RI, MS
β-Eudesmol	1649	1652	-	-	2.94	-	-	-	RI, MS
Pogostol	1651	1655	-	-	-	-	-	6.59	RI, MS
α-Eudesmol	1652	1656	22.05	27.33	-	-	-	-	RI, MS
α-Cadinol	1652	1646	-	-	0.69	5.77	2.40	-	RI, MS
Valerianol	1656	1657	-	-	0.49	-	-	-	RI, MS
Selin-11-en-4-*α*-ol	1658	1658	1.82	-	-	-	1.38	2.46	RI, MS
neo-Intermedeol	1658	1662	-	-	0.98	-	-	-	RI, MS
Allo-himachalol	1661	1660	-	-	2.36	-	-	-	RI, MS
7-*epi*-*α*-Eudesmol	1662	1661	0.57	1.13	-	-	-	-	RI, MS
Intermedeol	1665	1664	-	-	-	-	-	1.17	RI, MS
trans-Calamenen-10-ol	1668	1667	0.29	-	0.71	0.89	-	-	RI, MS
14-*hydroxy*-9-*epi*-(*E*)-Caryophyllene	1668	1669	-	0.59	-	-	-	-	RI, MS
epi-Zizanone	1668	1670	0.37	-	-	-	-	-	RI, MS
8-*hydroxy*-Isobornyl isobutanoate	1674	1671	2.48	0.40	-	-	-	-	RI, MS
Cadalene	1675	1676	-	-	-	3.22	-	-	RI, MS
Helifolenol C	1681	1679	-	-	2.49	-	-	-	RI, MS
8-Cedren-13-ol	1688	1685	-	-	1.24	-	-	-	RI, MS
Eudesmol-7(11)-en-4-ol	1700	1694	-	0.41	-	-	-	-	RI, MS
Mayurone	1709	1711	-	-	0.43	-	-	-	RI, MS
Isobicyclogermacrenal	1733	1726	-	-	0.48	-	-	-	RI, MS
7,14-anydro-Amorpha-4,9-diene	1755	1749	-	-	2.01	-	-	-	RI, MS
Benzyl benzoate	1759	1761	-	0.76	-	-	-	-	RI, MS
2-*α*-*hydroxy*-Amorpha-4,7(11)-diene	1775	1771	-	-	-	1.96	-	-	RI, MS
(*3E*)-Cembrene A	1947	1951	-	-	-	-	-	3.40	RI, MS
(6*E*,10*Z*)-Pseudo phytol	2018	2025	-	-	0.90	-	-	-	RI, MS
Total			95.14	95.64	95.57	92.05	96.24	91.31	
Monoterpenes			0.60	-	6.12	1.33	50.55	0.29	
Sesquiterpenes			94.54	95.64	89.45	90.72	45.69	91.02	

RI[a] = Retention indices from the literature [10,11,12]. RI[b] = Retention indices calculated from retention times in relation to those of a series C_8–C_{40} of n-alkanes on a 30m DB-5 capillary column. Pja = *P. japurense*, Pco = *P. coariense*, *Pau = P. auriculifolium*, Pcu = *P. curtistilum*, Pal = *P. alatipetiolatum* and Pbr = *P. brevesanum*. **[a]** Standard deviation were insignificant and were excluded from the Table except where stated. RI = retention index; MS = mass spectroscopy; CI: Co-injection with authentic compounds.

Species of *Piper* are known for the production of essential oils, which are responsible for different biological properties. These properties can be attributed to wide varieties of metabolites belonging to the chemical classes of monoterpenes, sesquiterpenes and phenylpropanoids (17). The following major constituents stood out in the *Piper* oils investigated in the present study: linalool, caryophyllene oxide, *α*-eudesmol, *β*-elemene, bicyclogermacrene, 10-*epi*-*γ*-eudesmol, *β*-dihydroagarofuran and *β*-caryophyllene. Moreover, this is the first report of the occurrence of the sesquiterpene premnaspirodiene in the essential oil from a species of the genus *Piper*. In contrast, the other major constituents identified in the present study have also been reported for other species of *Piper* collected in different regions of Brazil and the world. For instance, the percentage of linalool in found in the oil from *P. alatipetiolatum* (43.88%) was greater than that reported for leaf oils from *P. aduncum* (31.7%) collected in the state of São Paulo, Brazil [18], *P. jacquemontianum* (14.5%) collected in the Republic of Panama [13] and *P. augustum* (10.3%) collected in Costa Rica [19]. In contrast, this oxygenated monoterpene has been found at higher percentages in the oil from *P.*

claussenianum (53.5%) collected in the state of Espírito Santo, Brazil [20] and *P. jacquemontianum* (69.4%) collected in Guatemala [21].

Caryophyllene oxide was characterized as the major constituent of the oil from *P. curtistilum* (28.69%) and has been found in lower quantities in the leaf oil from other species of *Piper*, such as *P. amapense* (17.0%) and *P. duckei* (18.4%) collected in the state of Amazonas, Brazil [22], *P. carniconnectivum* (21.3%) in the state of Rondonia, Brazil [23], *P. miniatum* (20.3%) in Malaysia [24] and *P. brachypodom* (10.8%) in Colombia [25].

α-Eudesmol was the main component in the oils from *P. japurense* (22.05%) and *P. coariense* (27.33%) and has been found at lower percentages in *P. duckei* (9.1%) and *P. arboreum* (12.21%) in the Brazilian states of Amazonas and Rio de Janeiro, respectively [22, 26].

In the present investigation, *β*-elemene was found in a significant quantity in the oil from *P. brevesanum* (12.75%). This compound has been identified at higher percentages in the leaf oil from *P. demerararum* (33.1%) in the state of Amazonas, Brazil [27] and *P. reticulatum* (16.1%) in the Republic of Panama [13].

Bicyclogermacrene was found in the oils from *P. japurense* (1.38%) and was a major component of the oil from *P. brevesanum* (11.61%). This sesquiterpene has also been found at higher percentages in oils from *P. arboreum* (21.40%) and *P. amalago* (16.4%) collected from the Brazilian states of Rondônia [7] and Minas Gerais [28], respectively.

10-*epi*-*γ*-Eudesmol (13.32%) and *β*-dihydro agarofuran (15.35%) were major constituents of the oil from *P. coariense* and have also been reported as major components of oils from other species of *Piper* that occur in different regions of Brazil. Previous studies report percentages of 10-*epi*-*γ*-eudesmol close to that found in the present study in the leaf oil from *P. cernuum* (16.8%) collected in the state of Minas Gerais [28] and *P. arboreum* (11.6%) collected in the Federal District of the country [29]. In contrast, *β*-dihydro agarofuran was identified in higher quantities than that reported herein in two samples of *P. cernuum* collected in the states of Santa Catarina (36.7%) [30] and Minas Gerais (22.4%) [28].

β-Caryophyllene was found in significant quantities in the leaf oils from *P. coariense* (10.30%) and *P. alatipetiolatum* (16.11%) and has been reported as a major constituent in the oil from other species of *Piper* in different regions of Brazil and the world. Similar quantities to that found in the oil from *P. alatipetiolatum* have been reported for leaf oils from *P. diospyrifolium* (16.76%) and *P. gaudichaudianum* (17.4%) collected in southern Brazil [31, 32]. Oliveira *et al*., (2016) found a similar percentage to that reported here for *P. coariense* in the oil from *P. ilheusense* (11.8%), which occurs in the northeastern region of the country [4]. Similar percentages of *β*-caryophyllene are reported for *P. pseudolanceifolium* (11.6%) collected in Colombia [33] and *P. officinarum* (11.2%) collected in Malaysia [34]. Higher percentages (> 20%) of *β*-caryophyllene have been reported in the leaf oil of other species of *Piper* in different locations, such as *P. duckei* (27.1%) and *P. cyrtopodon* (34.6%) in northern Brazil [27,35], *P. dilatatum* (25.03%) in northeastern Brazil [36] as well as *P. arboreum* (25.1%) and *P. truncatum* (24.2%) in southeastern Brazil [18,37]. Outside Brazil, this sesquiterpene is reported as a major constituent of oils from *P. majusculum* (20.7%) collected in Vietnam [38], *P. longispicum* (45.2%) in the Republic of Panama [7], *P. umbellatum* (28.2%) in Cameroon [39] and *P. chaba* (28.6%) in India [14].

Other compounds belonging to the chemical classes of monoterpenes (*β*-pinene, 1,8-cineole and limonene) and phenylpropanoids (safrole, apiole and dillapiole) have been reported in oils from other species of *Piper* that occur in Brazil and specifically in the state of Amazonas, but were not found in the present analyses [6, 7, 16, 18,40-42].

As a conlusion, this study offers the first description of the chemical profile of the essential oils from the leaves of the species *P. japurense, P. coariense, P. auriculifolium, P. curtistilum, P. alatipetiolatum* and *P. brevesanum,* which occur in the Amazonia Biome in northern Brazil. With the exception of *P. alatipetiolatum,* the oils from the other plants exhibited a predominance of sesquiterpenes. However, qualitative and quantitative differences were found in the chemical composition of the six species. Among the 108 constituents identified in the oils, premnaspirodiene (32.26%), which was the major constituent of the leaf oil from *P. auriculifolium*, is reported for the first time for the genus *Piper*.

Acknowledgments

The authors are grateful to the Fundação de Amparo à Ciência e Tecnologia do Estado de Pernambuco (FACEPE), Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior for awarding a grant (CAPES – Proc. # IBPG-0984-5.01/10; a productivity scholarship (CNPq, # 312277/2013-0) and research funding for this study (CNPq # 403162/203-0; FACEPE # APQ-1008-1.06/15; APQ-0476-1.06/14; APQ-08601.06/16; IBPG-0715-1.06/18; BCT-0185-1.06/17).

Supporting Information

Supporting information accompanies this paper on http://www.acgpubs.org/journal/records-of-natural-products

ORCID
Carolina Alves de Araujo: 0000-0002-4293-1255
Claudio Augusto Gomes da Camara: 0000-0001-8508-1230
Marcílio Martins de Moraes: 0000-0002-7597-6775
Geraldo José Nascimento de Vasconcelos: 0000-0002-2581-9931
Marta Regina Pereira: 0000-0001-7236-2383
Charles Eugene Zartman: 0000-0001-8481-9782

References

[1] D.G. Frodin (2004). History and concepts of big plant genera, *Taxon*. **53**, 753-776.
[2] Piperaceae. In: Lista de espécies da flora do Brasil. Jardim Botânico do Rio de Janeiro. (2017). Available from: http://floradobrasil.jbrj.gov.br/jabot/floradobrasil/FB12735
[3] M. Pio-Corrêa (1984). Dicionário de plantas úteis do Brasil e das exóticas cultivadas. Imprensa Nacional. Rio de Janeiro.
[4] R.A. Oliveira, A.M.A.D. Assis, L.A.M. Silva, J.L. Andrioli and F.F. Oliveira (2016). Chemical profile and antimicrobial activity of essential oil of *Piper ilheusense*, *Chem. Nat. Compd.* **52**, 331-333.
[5] V. Woguem, F. Maggi, H.P. Fogang, L.A. Tapondjoua, H.M. Womeni, Q. Luana, M. Bramuccici, L.A. Vitali, D. Petrelli, G. Lupidi, F. Papa, S. Vittori and L. Barboni (2013). Antioxidant, antiproliferative and antimicrobial activities of the volatile oil from the wild pepper *Piper capense* used in Cameroon as a culinary spice, *Nat. Prod. Commun.* **8**, 1791-1796.
[6] M.J.C. Araújo, C.A.G. Da Camara, F.S. Born, M.M. Moraes and C. A. Badji (2012). Acaricidal activity and repellency of essential oil from *Piper aduncum* and its components against *Tetranychus urticae*, *Exp. Appl. Acarol.* **57**, 139-155.
[7] H.T. Santana, F.T.T. Trindade, R.G. Stabeli, A.A.E. Silva, J.S.L.T. Militão and V.A. Facundo (2015). Essential oils of leaves of *Piper* species display larvicidal activity against the dengue vector, *Aedes aegypti* (Diptera: Culicidae), *Rev. Bras. Pl. Med.* **17**, 105-111.
[8] J.G.S. Maia and E.H.A. Andrade (2009). Database of the Amazon aromatic plants and their essential oils, *Quím. Nova*. **32**, 595-622.
[9] H. Van Den Dool and P.D. Kratz (1963). A generalization of the retention index system including linear temperature programmed gas-liquid partition chromatography, *J. Chromatogr. A.* **11**, 463-471.
[10] R.P. Adams (2007). Identification of Essential Oil Components by Gas Chromatography/Quadrupole Mass Espectroscopy, 4th ed. Allured publishing Co. Carol Stream, Illinois.
[11] P.J. Linstrom and W.G. Mallard (2014). NIST Chemistry WebBook, NIST Standard Reference Database Number 69. (http://webbook.nist.gov).
[12] V.I. Babushok, P.J. Linstrom and I.G. Zenkevich (2011). Retention indices for frequently reported compounds of plant essential oils, *J Phys Chem Ref Data*. **40**, 1-47.
[13] A.I. Santana, R. Vila, S. Cañigueral and M.P. Gupta (2016). Chemical composition and biological activity of essential oils from different species of *Piper* from Panama, *Planta Med*. **82**, 986-991.
[14] K.B. Rameshkumar, A.P. Anu Aravind and P.J. Mathew (2011). Comparative phytochemical evaluation and antioxidant assay of *Piper longum* L. and *Piper chaba* Hunter used in Indian traditional systems of medicine, *J. Herbs Spices Med. Plants.* **17**, 351-360.

[15] E.H.A. Andrade and M.G.B. Zoghbi (2007). Volatile constituents of the leaves and stems of *Piper glandulosissimum* Yunck, *J. Essent. Oil Res*. **19**, 401-402.

[16] F.V. Pacheco, R.P. Avelar, I.C.A. Alvarenga, S.K.V. Bertolucci, A.A. Alvarenga and J.E.B.P. Pinto (2016). Essential oil of monkey-pepper (*Piper aduncum* L.) cultivated under different light environments, *Ind. Crop. Prod.* **85**, 251–257.

[17] R.Takeara, R. Gonçalves, V.F.S. Ayres and A.C. Guimarães (2017). Biological properties of essential oils from the *Piper* species of Brazil: A review. In: Aromatic and Medicinal Plants-Back to Nature. *Ed*: InTechOpen, Croatia, pp. 81–93.

[18] H.M.D. Navickiene, A.A. Morandim, A.C. Alécio, L.O. Regasini, D.C.B. Bergamo, M. Telascrea, A.J. Cavalheiro, M.N. Lopes, V.S. Bolzani, M. Furlan, M.O.M. Marques, M.C.M. Young and M.J. Kato (2006). Composition and antifungal activity of essential oils from *Piper aduncum*, *Piper arboreum* and *Piper tuberculatum*, *Quím. Nova*. **29**, 467-470.

[19] J.F. Cicció (2005) Essential oil from the leaves of *Piper augustum* from "Alberto M. Brenes" biological preserve, Costa Rica, *J. Essent. Oil Res*. **17**, 251-253.

[20] A.M. Marques, C.E. Fingolo and M.A.C. Kaplan (2017). HSCCC separation and enantiomeric distribution of key volatile constituents of *Piper claussenianum* (Miq.) C. DC. (Piperaceae), *Food Chem Toxicol.* **109**, 1111-1117.

[21] S.M. Cruz, A. Cáceres, L. Álvarez, J. Morales, M.A. Apel, A.T. Henriques, E. Salamanca, A. Giménez, Y. Vásquez and M.P. Gupta (2011). Chemical composition of essential oils of *Piper jacquemontianum* and *Piper* variabile from Guatemala and bioactivity of the dichloromethane and methanol extracts, *Rev. Bras. Farmacogn.* **21**, 587-593.

[22] A.S. Santos, E.H.A. Andrade, M.D.G.A. B. Zoghbi, A.I.R. Luz and J.G.S. Maia (1998). Sesquiterpenes of Amazonian *Piper* species, *Acta Amaz*. **28**, 127-127.

[23] V.A. Facundo, C.M. Rezende, A.C. Pinto (2006). Essential oil of *Piper carniconnectivum* C.CD. Leaves and Stems, *J. Essent. Oil Res*. **18** 296-297.

[24] W.M. Salleh, M.F. Kammil, F. Ahmad and H.M. Sirat (2015). Antioxidant and anti-inflammatory activities of essential oil and extracts of *Piper miniatumi*, *Nat. Prod. Commun*. **10**, 2005-2008.

[25] S.M. Leal, N. Pino, E.E. Stashenko, J.R. Martínez and P. Escobar (2013). Antiprotozoal activity of essential oils derived from *Piper* spp. grown in Colombia, *J. Essent. Oil Res*. **25**, 512-519.

[26] P.R.D. Santos, D.L. Moreira, E.F. Guimarães and M.A.C. Kaplan (2001). Essential oil analysis of 10 Piperaceae species from the Brazilian Atlantic forest, *Phytochemistry* **58**, 547–551.

[27] D.F.M. Carmo, A.C.F. Amaral, G.M.C. Machado, L.L. Leon and J.R.A. Silva (2012). Chemical and biological analyses of the essential oils and main constituents of *Piper* species, *Molecules* **17**, 1819-1829.

[28] J.M.O. Mesquita, C. Cavaleiro, A.P. Cunha, J.A. Lombardi and A.B. Oliveira (2005). Estudo comparativo dos óleos voláteis de algumas espécies de Piperaceae, *Rev. Bras. Farmacogn.* **15**, 6-12.

[29] M.C.L. Potzernheim, H.R. Bizzo and R.F. Vieira (2006). Análise dos óleos essenciais de três espécies de *Piper* coletadas na região do Distrito Federal (Cerrado) e comparação com óleos de plantas procedentes da região de Paraty, RJ (Mata Atlântica), *Rev. Bras. Farmacogn.* **16**, 246-251.

[30] A. Gasparetto, A.B. Cruz, T.M. Wagner, T.J. Bonomini, R. Correa and A. Malheiros (2017). Seasonal variation in the chemical composition, antimicrobial and mutagenic potential of essential oils from *Piper cernuum*, *Ind. Crop. Prod.* **95**, 256-263.

[31] S.C.H. Vieira, L.F. Paulo, T.I.E. Svidzinski, B.P.D. Filho, C.V. Nakamura, A. Souza, M.C.M. Young and D.A.G. Cortez (2011). Antifungal activity of *Piper diospyrifolium* Kunth (Piperaceae) essential oil, *Braz. J. Microbiol*. **42**, 1001-1006.

[32] G.L. von Poser, L.R. Rörig, A.T. Henriques, G. Lamaty, C. Menut and J.M. Bessière (1994). Aromatic plants from Brazil. III. The chemical composition of *Piper gaudichaudianum* Kunth and *P. mikanianum* (Kunth) Steudel essential oils, *J. Essent. Oil Res.* **6**, 337-340.

[33] K. Caballero-Gallardo, N. Pino-Benitez, N. Pajaro-Castro, E. Stashenko and J. Olivero-Verbel (2014). Plants cultivated in Choco, Colombia, as source of repellents against *Tribolium castaneum* (Herbst), *J. Asia-Pac. Entomol*. **17**, 753-759.

[34] W.M.N.H.W. Salleh, F. Ahmad, H.M. Sirat and K.H. Yen (2012). Chemical compositions, antioxidant and antimicrobial activity of the essential oils of *Piper officinarum* (Piperaceae), *Nat. Prod. Commun*. **7**, 1659-1662.

[35] E.H.A Andrade, E.F. Guimarães, M.H.L. Silva and R.A. Pereira (2006). Essential oil composition of *Piper cyrtopodon* (Miq.) C. DC., *J. Essent. Oil. Bear. Plant*. **9**, 53-59.

[36] J.B. Cysne, K.M. Canuto, O.D.L. Pessoa, E.P. Nunes and E.R. Silveira (2005). Leaf essential oils of four *Piper* species from the State of Ceará - Northeast of Brazil, *J. Brazil. Chem. Soc*. **16**, 1378-1381.

[37] A.P.F. Trindade, L.S.M. Velozo, E.F. Guimarães and M.A.C. Kaplan (2010). Essential oil from organs of *Piper truncatum* Vell, *J. essent. oil Res.* **22**, 200-202.

[38] L.D. Hieu, T.D. Thang, T.M. Hoi and I.A. Ogunwande (2014). Chemical composition of essential oils from four Vietnamese species of *Piper* (Piperaceae), *J. Oleo Sci.* **63**, 211-217.

[39] T. Francois, J.D.P. Michel, S.M. Lambert, F. Ndifor, W.N.A. Vyry, A.Z.P. Henri and M. Chantal (2009). Comparative essential oils composition and insecticidal effect of different tissues of *Piper capense* L., *Piper guineense* Schum. et Thonn., *Piper nigrum* L. and *Piper umbellatum* L. grown in Cameroon, *Afr. J. Biotechnol*. **8**, 424-431.

[40] J.K. Silva, R. Trindade, N.S. Alves, P.L. Figueiredo, J.G.S. Maia and W.N. Setzer (2017). Essential oils from neotropical *Piper* species and their biological activities, *Int. J. Mol. Sci.* **18**, 1-42.

[41] R.N.P Souto, A. Y. Harada , E. H. A. Andrade and J. G. S. Maia (2012). Insecticidal activity of *Piper* essential oils from the Amazon against the fire ant *Solenopsis saevissima* (Smith) (Hymenoptera: Formicidae), *Neotrop. Entomol.* **41**, 510-517.

[42] A.I.R. Luz, J. D. da Silva, M.G.B. Zoghbi, E.H.A. Andrade, M.H.L. da Silva and J.G.S. Maia (2000). Volatile constituents of Brazilian Piperaceae. Part 4. Essential oil composition of *Piper dactylostigmum*, *P. plurinervosum* and *P. Vitaceum*, *J. Essent. Oil Res.* **12**, 94-96.