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Chemical analysis of amazonian essential oils of an Ecuadorian Shuar Community

Análisis químico de aceites esenciales amazónicos de una Comunidad Shuar Ecuatoriana

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Abstract

This research was carried out with the aim of determining the chemical composition of the essential oils of four Amazonian species from the Antuash community, Morona canton, province of Morona Santiago. These species belong to the main aromatic families of Ecuador. The essential oils (EO) of *Critoniopsis pycnantha* (Benth.) H. Rob., *Myrcia aliena* McVaugh, *Piper macrotrichum* C. DC. and *Siparuna schimpffii* Diels were obtained from the dry leaves by analytical steam distillation; a percentage yield of 0.24%, 0.80%, 0.44%, and 0.32% was achieved respectively. EO were qualitatively analyzed by gas chromatography coupled to mass spectrometry (GC-MS) and quantitatively analyzed by gas chromatography coupled to flame ionization detector (GC-FID) with a DB-5ms apolar column. The compounds were identified based on mass spectra and the Van Den Dool and Kratz retention indices. They were quantified by calculating the relative response factors based on the combustion enthalpies. *M. aliena* and *P. macrotrichum* resulted rich in monoterpenes, and *C. pycnantha* and *S. schimpffii* in sesquiterpenes. The major compounds for the essential oils of *C. pycnantha* were γ-muurolene, bicyclogermacrene, (E)-caryophyllene α-ylangene and α-humulene; *M. aliena*: α-pinene and β-pinene; *P. macrotrichum* δ-3-carene, eugenol and chavibetol acetate; and *S. schimpffii*: spathulenol, 2-undecanone, bicyclogermacrene and (E)-Isocroweacin.

Keywords: *Critoniopsis pycnantha*, *Piper macrotrichum*, *Myrcia aliena*, *Siparuna schimpffii.*

Resumen

La presente investigación se realizó con el propósito de determinar la composición química de los aceites esenciales de cuatro especies amazónicas del centro shuar Antuash en el cantón Morona, provincia de Morona Santiago; las cuales pertenecen a las principales familias aromáticas del Ecuador. Los aceites esenciales de *Critoniopsis pycnantha* (Benth.) H. Rob., *Myrcia aliena* McVaugh, *Piper macrotrichum* C. DC. y *Siparuna schimpffii* Diels, fueron obtenidos de las hojas secas mediante destilación analítica por arrastre de vapor, determinándose un rendimiento por peso con respecto a las hojas secas de 0,24 %, 0,80 %, 0,44 % y 0,32 %, respectivamente. Estos fueron analizados cualitativamente mediante cromatografía de gases acoplada a espectrometría de masas (GC-MS) y cuantitativamente mediante cromatografía de gases acoplada a detector de ionización de llama (GC-FID), con columna apolar DB-5ms. Se realizó la identificación de los compuestos en base a los espectros de masas y los índices de retención de Van Den Dool Kratz, y se cuantificó calculando los factores de respuesta relativos con base a las entalpías de combustión. Así se determinó riqueza en monoterpenos para el aceite de *M. aliena* y *P. macrotrichum* y riqueza en sesquiterpenos para el aceite de *C. pycnantha* y *S. schimpffii*. Los compuestos mayoritarios en el aceite esencial de *C. pycnantha* fueron γ-muuroleno, biciclogermacreno, (*E*)-cariofileno α-ylangeno y α-humuleno; para *M. aliena* α-pineno y β-pineno; para *P. macrotrichum* δ-3-careno, eugenol y acetato de chavibetol; y, para *S. schimpffii* espatulenol, 2-undecanona, biciclogermacreno y (*E*)-Isocroweacina.

Palabras clave: *Critoniopsis pycnantha*, *Piper macrotrichum*, *Myrcia aliena*, *Siparuna schimpffii.*

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1 Introduction

There are about 295 families of plants with medicinal use in Ecuador of which 60 to 80 families produce essential oils, such as *Asteraceae, Lamiaceae, Lauraceae, Myrtaceae, Rosaceae, Rutaceae, Apiaceae* and *Pinaceae* (Aguirre-Mendoza et al., 2017). The study of the aromatic fraction of plant species is one of the most researched approaches in relation to the great diversity of plant species distributed in the four regions of the country. Essential oils are complex mixtures of secondary metabolites mainly monoterpenes, diterpenes and sesquiterpenes produced by different parts of plants. They are widely used in the food, cosmetic and pharmaceutical industry for presenting antiseptic, antibacterial, antiviral and antifungal properties (Camus and Trujillo, 2011; Ochoa-Pumaylle et al., 2012; León-Méndez et al., 2015; Noriega-Rivera, 2009). For this reason, the aim of this research was to perform the qualitative and quantitative chemical identification of the volatile fractions of four Amazonian species *Critoniopsis pycnantha, Myrcia aliena, Piper macrotrichum* and *Siparuna schimpffii* at the center of Antuash, Morona Santiago province, from which there is very little information. The chemical analysis was performed by gas chromatography coupled to mass spectrometry and flame ionization detector.

Critoniopsis pycnantha is a native shrub or tree that grows at a height between 1500 and 3000 m.a.s.l. (Missouri Botanical Garden, 2022) and presents beekeeping utility (De la Torre et al., 2008). *Myrcia aliena* is a tree native to the Andean and Amazon region that grows at an altitude between 500 and 2500 m.a.s.l. (Missouri Botanical Garden, 2022), known locally as "awapit", its stem is timber and its fruit feeds animals (De la Torre et al., 2008). *Piper macrotrichum* is a subshrub or native shrub found in the provinces of Morona Santiago, Napo, Pastaza at an altitude between 0 and 1000 m.a.s.l. (Missouri Botanical Garden, 2022). *Siparuna schimpffii* is a native shrub or tree located at an altitude between 0 and 1500 m.a.s.l. in the provinces of Tungurahua, Napo, Pastaza, Morona Santiago and Zamora Chinchipe (Missouri Botanical Garden, 2022), known as "chiri wayusa, mal aire panka, ardillón". This species has some medicinal uses, using its leaves in infusion to combat fatigue and bark to relieve the general pain of the body produced by fever. It is also used to clean the "bad energies" and its stem is used as a pole for construction (De la Torre et al., 2008). In addition, the species of the genus Siparuna are used in traditional medicine for relieving pain, inflammation, fever and infections (Ferreira-Silva et al., 2021).

2 Materials and Methods

2.1 General data

The analysis of essential oils was performed in a Thermo Scientific (Wal-than, MA, USA) Trace 1300 gas chromatograph coupled to a simple quadrupole mass spectrometer (GC-MS) ISQ 7000 and a traditional flame ionization detector (GC-FID). A DB-5MS apolar column with a stationary phase 5 %-phenyl-methylpolysiloxane of 30 m of length, 0.25 mm in internal diameter and 0.25 μm in thickness was used.

The solvents and standards used were analytical grade with a purity greater than 99 % and acquired in Sigma Aldrich (San Luis, Missouri, USA). In the case of isopropyl caproate, it was synthesized in the laboratories of the Technical Private University of Loja with a purity of 98.8 %, determined by GC-FID.

2.2 Collection of species

The four Amazonian species *Critoniopsis pycnantha, Myrcia aliena, Piper macrotrichum* and *Siparuna schimpfii* were collected at the shuar center Antuash-Morona Santiago, with the following coordinates: 02°39'41.7348" S 77°42'44.9496" W, 02°39'44.7372" S 77°42'55.8072" W", 02°39'49.8744" S 77°43'21.2484" W and 02°39'44.5248" S 77°43'28.8588" W, respectively. The four species were found in a flowering state and were collected during the rainy period. The study was conducted according to the MAAE-ARSFC-2021-1233 research permit, under the free, prior and informed consent of access to traditional knowledge, associated with biodiversity (Biological and genetic resources), and its scope, signed freely and voluntarily between the UTPL, ProAmazonia and the community of Antuash under the legal protection of the Nagoya Protocol and Ecuadorian law. It was subscribed to the Shuar Antuash Center on April 22, 2022. The species were entered into the herbarium of the Universidad Tecnico Particular de Loja (HUTPL), with the following codes of Váucher

14684 (*C. pycnantha*), 14685 (*M. aliena*), 14691 (*P. macrotrichum*) and 14692 (*S. schimpfii*).

2.3 Obtaining and yielding essential oils

The essential oils (EO) of the aforementioned species were obtained from the dry leaves by analytical distillation by steam drag, a process that lasted three hours. The leaves were dried at a temperature of 35°C for 48 hours. The essential oil was collected on two milliliters of cyclohexane, which in turn contained nonane as an internal standard and which was placed before starting distillation. It was then recovered and stored in amber vials under refrigeration at -4°C. Yields were calculated with the quantity in volume of distilled EO in cyclohexane and nonane solution with respect to the weight of the dry leaves of *Critoniopsis pycnantha* (61.8 g), *Myrcia aliena* (81.5 g), *Piper macrotrichum* (40.6 g) and *Siparuna schimpffii* (95.5 g).

2.4 Preparation of essential oil samples

The four essential oils obtained were diluted for injection into the gas chromatograph. For the species *M. aliena* and *C. pycnantha* a 1 in 1000 dilution was performed with cyclohexane and for *P. macrotrichum*, and for the species *M. aliena* and *C. pycnantha* a 1 in 1000 dilution was performed with cyclohexane and for *P. macrotrichum* and *S. schimpffii* a 1 in 500 dilution with cyclohexane.

2.5 Qualitative analysis

2.5.1 Chromatographic method

The method used for injections of EOs in GC-MS consisted of injector temperature: 200° C; injection mode: split, with split 10 ratio, injection volume: 2 μl for *C. pycnantha, P. macrotrichum* and *S. schimpffii*, and 1 μL for *M. aliena*; DB-5ms column with a flow of He of 1 mL/min; thermal program: oven temperature 50° C for 10 minutes, with a temperature ramp of 3° C/min up to 2555° C for 5 minutes. Total running time: 81.66 minutes. A mass spectrometer transfer line temperature of 200° C and an ion source temperature of 230° C, a mass range of 40-400 m/z and two minutes waiting for the detector ignition were used.

2.5.2 Identification of compounds

With the essential oil samples and with the same chromatographic method described for mass spectrometry, a mixture of hydrocarbons of the C9 to C22 series was injected to obtain the equations that allowed to determine the Van Den Dool and Kratz indexes of each compound (Van Den Dool and Dec Kratz, 1963). The identification was based on the mass spectrum and a difference of no more than twenty units between the calculated indexes and the retention indexes described in Adams (2017).

2.6 Quantitative analysis

2.6.1 Chromatographic method

Injections in GC-FID were performed with the following conditions: injector temperature of 230° C, split injection mode, with split radius 10 for *P. macrotrichum* and 40 for *C. pycnantha, S. schimpffii* and *M. aliena*, being the injection volume 1 μL; column DB-5ms with flow of 1 mL/min; thermal program: oven temperature 50° C for 10 minutes and temperature ramp of 2° C/min to 170° C and 10° C min to 230° C for 10 minutes. The total running time was 83 minutes. The detector temperature was 230° C.

2.6.2 Quantification

The quantification of the compounds was performed with the FID detector, according to the method proposed by Tissot et al. (2012). For this, the relative response factor (RF) of each compound was calculated with respect to isopropyl caproate, which was used as the standard of quantification. The FRRs were based on combustion enthalpies and determined using the formula described by Tissot et al. (2012). Nano was used as internal standard and isopropyl caproate as calibration standard. Four replicates per sample of EO and six standards were injected under the same chromatographic conditions. These standards were prepared by weighing constant amounts of nonane (7.13 mg) and increasing amounts of isopropyl caproate (0.6, 1.4, 4.2, 8.3, 16.4 and 33.6 mg) gaging with cyclohexane. The curve presented a R^2 of 0.9998 and the obtained equation allowed us to obtain the milligrams of each compound. A detection limit of 0.1% was considered, calculating the percentages of each component in relation to the total mass of EO. The mean and standard deviation for each compound were calculated.

3 Results and discussion

3.1 *Critoniopsis pycnantha*

In the essential oil of *C. pycnantha* 63 compounds were identified, being the predominant compounds γ-muurolene in 34.45%, bicycles-germacean in 12.04%, (E)-cariophyllenein 11.05%, α-ylangen in 5.37% and α-humulene in 4.68%. These compounds are shown in the chromatogram in Figure 1 and are detailed in Table 1.

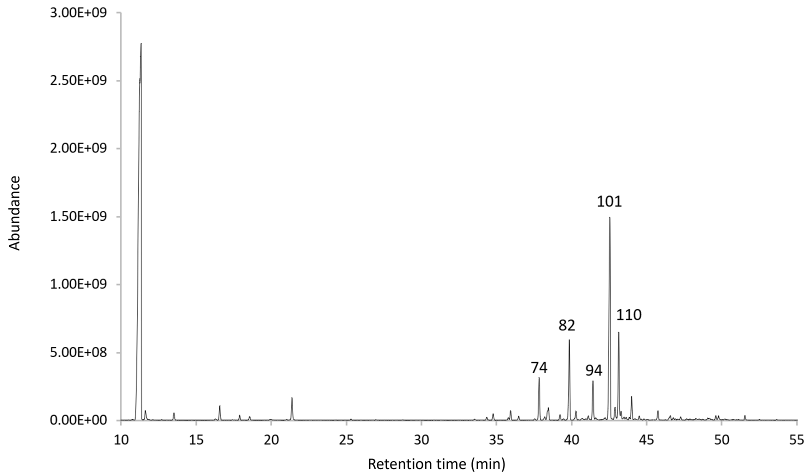

Figure 1. *C. pycnantha* essential oil chromatogram in column DB-5ms.

3.2 *Piper macrotrichum*

In the essential oil of *P. macrotrichum*, 66 compounds corresponding to 98.71% were determined. It was found that δ-3-carene (58.21%), eugenol (9.75%) and chavibetol acetate (7.81%) were major compounds, showing a greater amount of monoterpene hydrocarbons in 73.92% of the total. The identified compounds are described in Table 1 and can be observed on the chromatogram in Figure 2.

3.3 *Myrcia aliena*

In the essential oil of *M. aliena* 43 compounds were identified, representing 98.92%, being the major compounds two monoterpenes α-pinene (72.19%) and β-pinene (15.82%). The compounds can be seen on the chromatogram in Figure 3 and are detailed in Table 1.

3.4 *Siparuna Schimpffii*

In the essential oil of *S. schimpffii* 125 compounds were found, which represent 93.65% of the total. The major compounds identified were spatulenol (12.10%), 2-undecanone (10.87%), (E)-isocroweacin (6.41%) and bicyclogermacrene (5.84%), which can be seen on the chromatogram in Figure 4 and are described in Table 1.

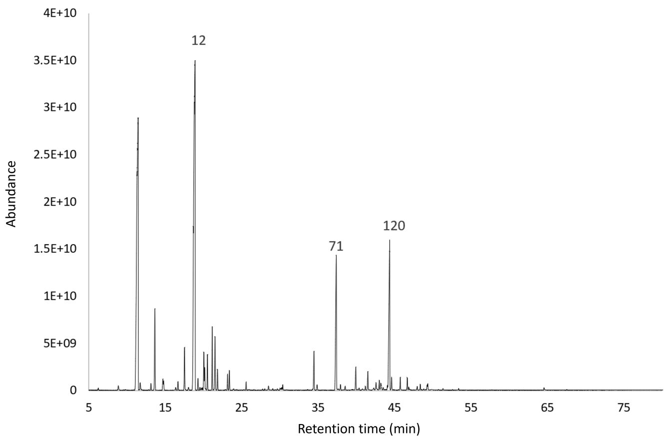

Figure 2. Essential oil chromatogram of *P. macrotrichum* in column DB-5ms.

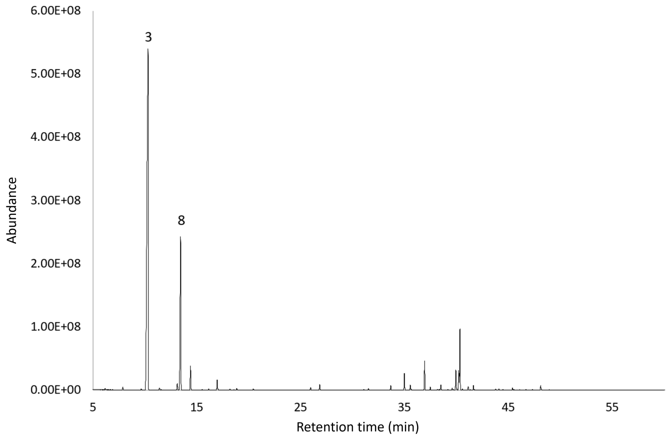

Figure 3. Essential oil chromatogram of *M. aliena* in column DB-5ms.

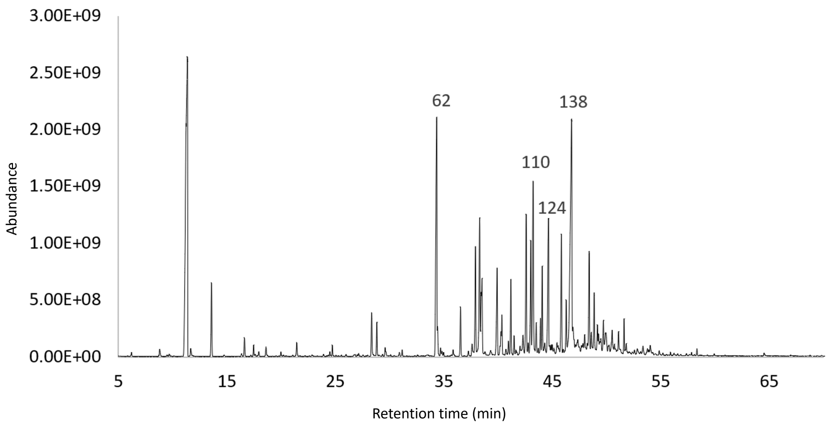

Figure 4. Essential oil chromatogram of *S. schimpffii* in column DB-5ms.

Table 1. Chemical composition of the essential oil of *Critoniopsis pycnantha, Myrcia aliena, Piper macrotrichum* and *Siparuna schimpfii* in column DB-5ms.
IRC: Calculated retention rate. **IRL**: Literature retention index. **ND**: Not determined. **PM**: Molecular weight. σ: standard deviation.

N°	Compounds	IRC	IRL	*C.pycnantha*		*M.aliena*		*P. macrotrichum*		*S.schimpffii*	
				%	σ	%	σ	%	σ	%	σ
1	(2*E*.4*E*)- hexadienol	905	912	TRAZA	0.03	-	-	TRAZA	-	TRAZA	-
2	α-Thujene	928	924	-	-	TRAZA	-	0.25	0.01	2.00	0.11
3	α-pinene	933	932	1.08	0.03	72.19	0.21	3.21	0.1	-	-
4	α-fenchene	948	945	-	-	-	-	0.44	0.02	TRAZA	-
5	Canphene	950	946	-	-	0.13	0.01	0.39	0.01	-	-
6	benzaldehyde	972	952	-	-	-	-	-	-	0.06	0.01
7	Sabineno	973	969	0.14	0.01	0.48	0.02	0.10	0.01	-	-
8	β-pinene	977	974	2.15	0.03	15.82	0.07	0.34	0.01	0.51	0.03
9	myrcene	990	988	-	-	1.60	0.03	1.60	0.05	0.32	0.01
10	2-Pentyl furan	990	984	-	-	-	-	-	-	0.10	0.01
11	δ-2-carene	1009	1001	-	-	TRAZA	-	-	-	-	-
12	δ-3-carene	1009	1008	0.04	0.02	TRAZA	-	58.21	1.72	0.22	0.01
13	α-terpinene	1017	1014	-	-	-	-	0.34	0.02	-	-
14	ρ-cymene	1023	1020	0.04	0.02	-	-	0.07	0.01	-	-
15	ND (PM 136)	1024	1025	-	-	-	-	0.14	0.01	-	-
16	o-cimene	1027	1022	-	-	0.05	0.01	TRAZA	-	TRAZA	-
17	Limonene	1029	1024	0.52	0.02	TRAZA	-	1.40	0.04	0.11	0.01
18	β-felandrene	1031	1025	0.47	0.02	0.75	0.01	0.59	0.06	TRAZA	-
19	1.8-cineol	1033	1026	-	-	-	-	TRAZA	-	TRAZA	-
20	(*Z*)-β-ocimene	1037	1032	0.12	0.03	-	-	1.15	0.04	TRAZA	-
21	*cis*-arbusculone	1045	1046	-	-	-	-	-	-	TRAZA	-
22	(*E*)-β-ocimene	1048	1044	TRAZA	-	TRAZA	-	2.74	0.27	0.05	-
23	ND (PM 120)	1052	1055	4.36	0.21	-	-	-	-	0.12	-
24	ND (PM 152)	1053	-	-	-	-	-	-	-	0.54	0.06
25	ND (PM 150)	1054	-	-	-	-	-	1.11	0.03	-	-
26	γ-terpinene	1057	1054	-	-	0.10	0.01	0.68	0.02	-	-
27	-tolualdehyde	1057	1062	-	-	0.26	0.08	-	-	-	-
28	(2*E*)-octen-1-al	1066	1049	-	-	-	-	-	-	TRAZA	-
29	linalool *trans*-oxide (furanoid)	1073	1084	-	-	-	-	-	-	TRAZA	-
30	Isoterpinolene	1082	1085	-	-	-	-	0.53	0.01	-	-
31	Terpinolene	1086	1086	-	-	0.07	0.01	0.65	0.02	TRAZA	-
32	ND (PM 154)	1094	-	-	-	-	-	0.06	0.01	-	-
33	2-nonanone	1095	1087	-	-	-	-	TRAZA	-	TRAZA	-
34	pinene α-oxide	1098	1099	-	-	-	-	TRAZA	-	-	-
35	n-nonanal	1110	1100	-	-	-	-	TRAZA	-	0.02	0.01
36	ND (PM 152)	1122	-	-	-	-	-	TRAZA	-	-	-
37	1-terpineol	1125	-	-	-	-	-	0.27	0.01	-	-
38	neo-*allo*-ocimene	1131	1140	-	-	-	-	TRAZA	-	-	-
39	α-canfolenal	1133	1122	-	-	-	-	-	-	TRAZA	-
40	*trans*-pinocarveol	1147	1135	-	-	-	-	-	-	TRAZA	-
41	Nopinone	1149	1135	-	-	-	-	-	-	0.05	0.01
42	*trans*-verbenol	1153	1140	-	-	-	-	-	-	0.12	0.01
43	Canfor	1155	1141	-	-	-	-	-	-	TRAZA	-
44	*cis*-pinocarveol	1166	1166	-	-	-	-	TRAZA	-	-	-
45	1-dodecene	1168	1187	-	-	-	-	-	-	TRAZA	-
46	Pinocarvone	1171	1160	-	-	-	-	-	-	TRAZA	-
47	α-felandren-8-ol	1172	1172	-	-	-	-	0.05	0.01	-	-
48	n-nonanol	1178	1165	-	-	-	-	-	-	0.95	0.28
49	Borneol	1179	-	-	-	TRAZA	-	-	-	-	-
50	octanoic acid	1184	1167	-	-	-	-	-	-	0.95	0.04
51	4-terpineol	1186	1174	-	-	0.17	0.01	-	-	-	-
52	ρ-cimen-8-ol	1197	1197	-	-	-	-	TRAZA	-	-	-
53	α-terpineol	1203	1186	-	-	0.33	0.01	-	-	0.22	0.09
54	ND (PM152)	1203	-	-	-	-	-	0.06	0.01	-	-
55	Safranal	1209	1197	-	-	-	-	-	-	TRAZA	-
56	ND (PM 204)	1211	-	-	-	-	-	0.08	0.01	-	-

Continued on next page

Table 1 – Continued from previous page

N°	Compounds	IRC	IRL	*C.pycnantha*		*M.aliena*		*P. macrotrichum*		*S.schimpffii*	
				%	σ	%	σ	%	σ	%	σ
57	n-decanal	1212	1201	-	-	-	-	TRAZA	-	TRAZA	-
58	octanol acetate	1215	1211	-	-	-	-	TRAZA	-	-	-
59	Verbenone	1219	1204	-	-	-	-	-	-	TRAZA	-
60	β-cyclocitral	1223	1217	-	-	-	-	0.28	0.02	0.13	0.01
61	ND (PM 164)	1234	-	-	-	-	-	-	-	0.12	0.01
62	2-undecanone	1298	1293	1.01	0.03	0.06	0.02	-	-	10.87	0.4
63	Safrol	1299	1285	-	-	-	-	TRAZA	-	0.17	0.17
64	methyl (*Z*)-cinnamate	1301	1299	-	-	-	-	1.61	0.06	-	-
65	1-tridecene	1307	1290	-	-	-	-	-	-	0.13	0.01
66	Hexenyl (3*E*)-tiglate	1310	1315	-	-	-	-	0.22	0.01	0.13	0.02
67	n-nonyl acetate	1313	1311	-	-	-	-	-	-	TRAZA	-
68	isopulegol *neo iso*-acetate	1328	1312	0.37	0.05	-	-	-	-	-	-
69	δ-element	1332	1335	0.37	0.05	-	-	-	-	TRAZA	-
70	α-cubebene	1346	1348	0.49	0.04	0.16	0.01	-	-	0.97	0.03
71	Eugenol	1363	1356	-	-	-	-	9.75	0.36	0.11	0.02
72	Cyclosativene	1368	1369	0.14	0.02	TRAZA	-	-	-	-	-
73	Isoledene	1371	1374	-	-	-	-	TRAZA	-	-	-
74	α-ylangen	1373	1373	5.37	0.09	0.58	0.01	-	-	TRAZA	-
75	α-copaene	1377	1374	-	-	-	-	0.19	0.01	3.54	0.31
76	β-borbonene	1383	1387	0.34	0.03	-	-	-	-	2.87	0.08
77	β-cubebene	1387	1387	1.33	0.03	0.18	0.04	-	-	0.46	0.46
78	β-element	1389	1389			-	-	0.10	0.01	1.01	0.43
79	α-gurjunene	1404	1409	0.71	0.02	-	-	-	-	-	-
80	ND (PM 204)	1408	-	-	-	-	-	-	-	0.09	0.01
81	*cis*-α-bergamotene	1410	1411	0.14	0.01	-	-	-	-	-	-
82	(*E*)-cariophyllene	1420	1417	11.05	0.19	1.28	0.02	-	-	-	-
83	(*Z*)-cariophyllene	1422	1408	-	-	-	-	0.85	0.03	2.59	0.06
84	(*E*)-α-ionone	1428	1428	-	-	-	-	0.06	0.01	0.93	0.12
85	ND (PM 204)	1429		0.70	0.02	-	-	-	-	-	-
86	γ-element	1431	1434	-	-	-	-	-	-	TRAZA	-
87	β-gurjunene	1432	1431	-	-	-	-	-	-	0.16	0.07
88	α-trans-bergamotene	1433	1432	-	-	0.13	0.01	-	-	-	-
89	Aromadendrene	1437	1439	0.15	0.02	-	-	-	-	0.10	0.02
90	ND (PM 204)	1438		0.09	0.03	-	-	-	-	-	-
91	ND (PM 204)	1447	1458	-	-	-	-	-	-	0.29	0.02
92	(Z)-β-farnesene	1449	1440	0.32	0.02	-	-	-	-	-	-
93	Sesquisabinene	1453	1457	-	-	TRAZA	-	-	-	1.23	0.03
94	α-humulene	1457	1452	4.68	0.07	-	-	-	-	0.38	0.01
95	Linalool isovalerate	1457	1466	-	-	0.20	0.11	-	-	-	-
96	ND (220)	1459	-	-	-	-	-	0.48	0.21	-	-
97	ND (PM 222)	1460	1458	0.11	0.03	-	-	-	-	-	-
98	*allo*-aromadendrene	1463	1458	TRAZA	-	-	-	-	-	0.08	0.03
99	*cis*-cadin 1(6).4-diene	1464	1461			-	-	-	-	TRAZA	-
100	(*E*)-9-epi-cariophyllene	1474	1464	0.34	0.03	-	-	-	-	0.14	0.02
101	γ-muurolene	1480	1478	34.45	0.6	-	-	0.22	0.24	0.36	0.06
102	*trans*-cadina1(6).4-diene	1483	1475	-	-	0.13	0.01	-	-	-	-
103	germacrene D	1485	1480	-	-	-	-	-	-	3.52	0.12
104	*trans*-muurola 4(14).5-diene	1485	1493	-	-	-	-	0.20	0.09	-	-
105	δ-selinene	1487	1492	TRAZA	-	-	-	-	-	-	-
106	ND (PM 204)	1490	-	-	-	-	-	-	-	0.09	0.03
107	β-selinene	1491	1489	1.62	0.2	0.68	0.02	-	-	-	-
108	2-tridecanone	1495	1500	-	-	TRAZA	-	-	-	-	-
109	α-selinene	1499	1498	-	-	2.89	0.09	-	-	-	-
110	Biciclogermacrene	1499	1500	12.04	0.28	-	-	0.31	0.04	5.84	0.45
111	α-murolene	1502	1500	-	-	-	-	0.33	0.02	-	-
112	(*E.E*)-α-farnesene	1502	1505	0.83	0.05	-	-	-	-	2.05	0.03
113	β-bisabolene	1506	1505	0.83	0.05	-	-	-	-	-	-
114	Myristicine	1507	1517	-	-	TRAZA	-	TRAZA	-	TRAZA	-
115	germazrene A	1509	1508	0.55	0.04	-	-	-	-	-	-
116	ND (PM 204)	1512	-	-	-	-	-	-	-	0.15	0.01
117	γ-cadinene	1517	1513	-	-	-	-	-	-	0.13	0.01

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Table 1 – Continued from previous page

N°	Compounds	IRC	IRL	*C.pycnantha*		*M.aliena*		*P. macrotrichum*		*S.schimpffii*	
				%	σ	%	σ	%	σ	%	σ
118	δ-amorfene	1518	1511	2.77	0.04	-	-	-	-	-	-
119	δ-cadinene	1521	1522	-	-	0.12	0.01	TRAZA	-	0.82	0.02
120	chavibetol acetate	1526	-	-	-	-	-	7.81	3.19	-	-
121	*cis*-calamenene	1527	1528	-	-	-	-	-	-	1.54	0.13
122	(*Z*)-carpacine	1531	1540	0.19	0.02	-	-	-	-	-	-
123	*trans*-cadin-1.4-diene	1534	1533	0.13	0.01	-	-	-	-	-	-
124	(*E*)-isocroweacin	1534	1553	-	-	0.15	0.01	0.63	0.03	6.41	1.19
125	ND (PM 222)	1538	-	-	-	-	-	-	-	0.07	0.04
126	α-cadinene	1540	1537	0.06	0.04	-	-	-	-	0.29	0.01
127	(*Z*)-nerolidol	1544	1531	-	-	-	-	-	-	0.37	0.01
128	seline 3.7(11)-diene	1546	1545	-	-	-	-	-	-	0.13	0.01
129	α-calacorene	1548	1544	-	-	-	-	-	-	TRAZA	-
130	Hedicariol	1555	1546	-	-	-	-	-	-	TRAZA	-
131	Elemycin	1558	1555	-	-	-	-	-	-	0.17	0.03
132	ND (PM 220)	1560	-	-	-	-	-	-	-	0.08	0.01
133	(*E*)-nerolidol	1563	1561	-	-	-	-	0.30	0.18	-	-
134	germazrene B	1564	1559	1.35	0.03	-	-	-	-	3.07	0.06
135	isoeugenol (*Z*)-acetate	1565	1566	-	-	-	-	0.12	0.22	-	-
136	ND (PM 218)	1573	1573	-	-	-	-	-	-	1.86	0.79
137	ND (PM 220)	1576	1576	-	-	-	-	-	-	5.57	0.48
138	Spatulenol	1585	1577	0.75	0.06	-	-	-	-	12.10	1.33
139	cariophyllene oxide	1589	1582	0.20	0.03	TRAZA	-	0.10	0.03	-	-
140	ND (PM 220)	1592	-	-	-	-	-	-	-	0.58	0.28
141	Guaiol	1600	1600	0.39	0.03	-	-	-	-	-	-
142	ND (PM 238)	1603	-	0.06	0.01	-	-	0.09	0.01	-	-
143	ND (PM 222)	1603	-	-	-	-	-	-	-	0.12	0.01
144	ND (PM 220)	1608	-	-	-	-	-	-	-	0.06	0.04
145	Ledol	1610	1602	0.14	0.03	-	-	-	-	-	-
146	β-oplopenone	1612	-	-	-	-	-	-	-	TRAZA	-
147	ND (PM 220)	1616	-	-	-	-	-	-	-	0.34	0.2
148	Humulene epoxide II	1616	1607	0.07	0.01	-	-	-	-	-	-
149	Isoeugenol (*E*)-acetate	1619	1614	-	-	-	-	TRAZA	-	-	-
150	ND (PM 220)	1621	-	-	-	-	-	-	-	0.46	0.02
151	dill apiol	1630	1620	0.23	0.03	0.11	0.01	0.20	0.01	3.21	0.05
152	1-*epi*-cubenol	1634	1627	0.15	0.03	TRAZA	-	-	-	-	-
153	ND (PM 222)	1637	-	-	-	-	-	-	-	0.12	0.04
154	epoxide *allo*-aromadendrene	1644	1639	0.12	0.02	-	-	-	-	0.80	0.16
155	ND (PM 220)	1644	-	-	-	-	-	-	-	1.58	0.02
156	ND (PM 220)	1647	-	-	-	0.05	0.01	-	-	-	-
157	β-eudesmol	1649	1649	-	-	-	-	TRAZA	-	-	-
158	Cubenol	1650	1645	-	-	TRAZA	-	-	-	-	-
159	*epi*-α-cadinol	1653	1638	-	-	-	-	-	-	TRAZA	-
160	α-muurolol (torreyol)	1648	1644	0.38	0.12	-	-	-	-	-	-
161	ND (PM 204)	1653	-	0.38	0.12	-	-	-	-	-	-
162	*epi*-α-muurolol	1655	1640	0.38	0.12	-	-	-	-	0.24	0.15
163	(*Z*)-14-*hydroxy*-cariophyllene	1656	1666	0.38	0.12	-	-	-	-	-	-
164	ND (PM 220)	1658	-	-	-	-	-	-	-	0.48	0.15
165	α-cadinol	1659	1652	0.44	0.12	TRAZA	-	0.15	0.01	0.81	0.16
166	neo-intermedeol	1668	1658	0.41	0.11	TRAZA	-	-	-	-	-
167	ND (PM 238)	1673	-	-	-	-	-	0.05	0.01	-	-
168	ND (PM 220)	1673	-	-	-	-	-	-	-	0.26	0.07
169	ND (PM 220)	1678	-	-	-	-	-	-	-	0.09	0.03
170	ND (PM 220)	1681	-	-	-	-	-	-	-	0.07	0.04
171	ND (PM 220)	1689	-	-	-	-	-	-	-	0.75	0.23
172	ND (PM 222)	1698	-	-	-	-	-	-	-	0.08	0.01
173	2-pentadecanone	1704	1697	-	-	0.20	0.01	-	-	-	-
174	ND (PM 220)	1705	-	-	-	-	-	-	-	0.47	0.06
175	ND (PM 220)	1710	-	-	-	-	-	-	-	0.22	0.08
176	tridecenol (2*E*)-acetate	1714	1703	0.45	0.01	-	-	-	-		
177	ND (PM 218)	1719	-	-	-	-	-	-	-	2.13	0.08
178	ND (PM 220)	1725	-	-	-	-	-	-	-	0.09	0.03

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Table 1 – Continued from previous page

N°	Compounds	IRC	IRL	*C.pycnantha*		*M.aliena*		*P. macrotrichum*		*S.schimpffii*	
				%	σ	%	σ	%	σ	%	σ
179	ND (PM 220)	1735	-	-	-	-	-	-	-	0.10	0.01
180	ND (PM 220)	1741	-	-	-	-	-	-	-	0.11	0.02
181	Renal isocyclothermacrene	1747	1733	-	-	-	-	-	-	0.17	0.05
182	ND (PM 220)	1753	-	-	-	-	-	-	-	0.23	0.06
183	ND (PM 220)	1760	-	-	-	-	-	-	-	0.06	0.06
184	ND (PM 220)	1762	-	-	-	-	-	-	-	0.09	0.06
185	ND (PM 220)	1768	-	-	-	-	-	-	-	0.36	0.07
186	15-al γ-curcumene	1777	1766	-	-	-	-	-	-	0.13	0.02
187	14-*hydroxy*-α-murolene	1787	1779	-	-	-	-	-	-	TRAZA	-
188	14-*hydroxy*-δ-cadinene	1810	1803	-	-	-	-	-	-	0.05	0.01
189	ND (PM 222)	1820	-	-	-	-	-	-	-	0.07	0.01
190	ND (PM 262)	1887	-	0.12	0.02	-	-	-	-	-	-
191	ND (PM 268)	1891	-	-	-	-	-	-	-	0.05	0.01
192	(*5Z.9E*)-farnesyl acetone	1912	1889	-	-	-	-	-	-	0.12	0.01
193	methyl hexadecanoate	1927	1921	-	-	-	-	TRAZA	-	-	-
194	Phytol	1942	1942	-	-	-	-	-	-	TRAZA	-
195	ND (PM 268)	1963	-	-	-	-	-	-	-	0.14	0.01
196	(*6E.10Z*)-pseudophytol	2024	2018	-	-	-	-	-	-	TRAZA	-
197	ND (PM 316)	2031	-	-	-	0.06	0.1	-	-	-	-
198	ND (PM 300)	2097	-	0.19	0.04	-	-	-	-	-	-
199	ND (PM 222)	2101	-	-	-	-	-	0.07	0.04	-	-
200	ND (PM 328)	2106	-	0.54	0.02	-	-	-	-	-	-
201	ND (PM 296)	2108	-	-	-	-	-	-	-	0.14	0.01
202	oleic acid	2125	2141	-	-	-	-	-	-	TRAZA	-
203	ND (PM 300)	2188	-	0.06	0.01	-	-	-	-	-	-
	Monoterpene hydrocarbons			4.58		91.19		73.92		3.24	
	Oxygenated monoterpenes			1.01		0.56		12.19		12.29	
	Sesquiterpene hydrocarbons			80.12		6.14		2.72		32.02	
	Oxygenated sesquiterpenes			3.68		0.45		0.76		29.32	
	Others			5.56		0.58		9.12		16.77	
	TOTAL (%)			94.94		98.92		98.71		93.65	

In this study it was shown that the essential oil of *C. pycnantha* is composed mainly of sesquiterpenes, which represent 80.12 % of its total composition. Tran and Cramer (2014) describe terpenes in general as compounds with great economic importance when used as aromas, flavors, spices and drugs, and help plant species by attracting pollinators (Xu et al., 2017).

Sesquiterpenes are compounds with antitumor, antimicrobial activity and effects on the central nervous system according to Da Silveira e Sá et al. (2015), who also mention that the major compounds are those that usually establish the biological activity of an essential oil. Among the major compounds was (E)-cariophyllene (11 %). Shan et al. (2016) mentioned it as one of the most important sesquiterpenes for possessing anticancer properties, antioxidants, antimicrobials, anti-inflammatory and local anesthetic action. (E)-cariophyllene is also used in the food and cosmetics industry as a flavor (Montanari et al., 2011).

Regarding species of the genus *Myrcia*, Barbosa de Moraes et al. (2022) and De Cerqueira et al. (2007) mention that the essential oils of the leaves of *Myrcia paivae* O.Berg and *Myrcia myrtifolia* DC are oils rich in monoterpenes with 77.0 % and 94.1 % of the total of its composition, which was observed in the essential oil of the species *Maliena*, where 91.19 % of these compounds were determined. In addition, Barbosa de Moraes et al. (2022) and De Cerqueira et al. (2007) describe α-pinene as one of the major compounds with 6.39 % in the EO of *Myrcia paivae* O.Berg and 61.5 to 90.9 % in essential oils of leaves, flowers and fruits of *Myrcia myrtifolia* DC. In our study α-pinene was found in 72.2 % and β-pinene in 15.8 %. Both compounds are also described as majority in the EO of the species *Myrcia mollis*, in which α-pinene and β-pinene were found in 29.2 % and 31.3 % (Montalván et al., 2019).

Monoterpenes protect plant species against insects, herbivores, and mammals and have allelopathic functions by blocking seed germination (Thoss et al., 2007). The monoterpenes α-pinene and β-pinene are structural isomers commonly found in essential oils. They have antiviral, antifungal, antimicrobial, anticancer, antispasmodic, antimalarial, anti-inflammatory and antioxidant activity (Zielińska-Błajet and Feder-Kubis, 2020). In addition, α-pinene and β-pinene act as bacteriostatic and fungistatic agents (Talebi-Kouyakhi et al., 2008).

Navickiene et al. (2006) mention that the essential oils of leaves, stems and fruits of the species *Piper aduncum, Piper arboreum* and *Piper tuberculatum* share certain common compounds, which are α-pinene, limonene, mircene, (E)-ocimeno, (Z)proved-ocimeno and *piper tuberculatum*. In the essential oil of *Piper macrotrichum* these compounds were also found except for linalool. The main compounds δ-3-carene (58.21 %), eugenol (9.75 %) and chavibetol acetate (7.81 %) were determined, of which eugenol was found to be the majority of the EO of *Piper divaricatum* leaves with 37.5 %, and δ-3-carene with 9.6 % and 35.3 % in the EO of *Piper aff*. Hispidum and *Piper sanctifelicis*, respectively (Jaramillo-Colorado et al., 2019). The δ-3-carene is also one of the main compounds of the EO of Piper nigrum with 14.4 %. Arunachalam et al. (2023) describe anticonvulsant activity for eugenol and linalool, while Woo et al. (2019) mentions δ-3-carene as a compound used in perfumery and cosmetics, in addition to having antifungal, anti-inflammatory and sedative activity.

Noriega-Rivera et al. (2014) report as main compounds of essential oil of *Siparuna schimpffii* to germacrene D (35.34 %), bicyclogermacrene (8.73 %), γ-muurulene (7.04 %), germacrene B (6,34 %) and cadina-1(2), 4-diene trans (5.16 %), of which only bicyclogermacrene (5.8 %) were determined as one of the majority in the analyzed essential oil of *S. schimpffii*, together with spatulenol (12.10 %), 2-undecanone(10.87 %) and (E)-isocroweacin (6.41 %). However, it can be observed that the main composition in both essential oils corresponds to sesquiterpene hydrocarbons. As described by Durán et al. (2007); Ruiz et al. (2015); Silva et al. (2021), essential oil composition differences may be due to several biotic and abiotic factors such as the presence or absence of pests, collection place, soil type, amount of moisture and light, as well as the climatic conditions in which the species develop. Spatulenol has moderate antimycobacterial action (Do Nascimento et al., 2018). Silva et al. (2007) mention antimicrobial activity for bicyclogermacrene and fungitoxic activity for germacrene B; Xu et al. (2017) detail some functions of bicyclogermacrene, including its antioxidant, fungistatic, cytotoxic, allelopathic and acetylcholinesterase inhibitor activity. Noriega-Rivera et al. (2014) also state that *S. schimpffii* is used by Shuar communities in Ecuador as an analgesic.

4 Conclusions

It was possible to determine the chemical composition of essential oils of the Amazonian species *C. pycnantha, M. aliena, P. macrotrichum* and *S. schimpffi*. A higher concentration of monoterpenes was observed in the EOs of *M. aliena* and *P. macrotrichum* and a higher content of sesquiterpenes in the EO of *C. pycnantha* and *S. schimpffii*. In addition, the main compounds of each essential oil were identified and some of its functions were described bibliographically, redirecting future studies and applications that Antuash residents can give to these species.

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