

New Essential Oils from Ecuadorian *Gynoxys cuicochensis* Cuatrec. and *Gynoxys sancti-antonii* Cuatrec. Chemical Compositions and Enantioselective Analyses

Yessenia E. Maldonado, Evelin A. Betancourt, Erika S. León, Omar Malagón, Nixon Cumbicus, and Gianluca Gilardoni*



Cite This: *ACS Omega* 2024, 9, 25902–25913



Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: The present study belonged to an unfunded project, dealing on the systematic description of unprecedented essential oils (EOs), distilled from 12 species of genus *Gynoxys* Cuatrec. In this very case, the aim was the first chemical and enantiomeric analyses of two volatile fractions, obtained from the leaves of *Gynoxys cuicochensis* Cuatrec. and *Gynoxys sancti-antonii* Cuatrec. These EOs were analyzed by GC–MS (qualitatively) and GC–FID (quantitatively), detecting 89 and 60 components from *G. cuicochensis* and *G. sancti-antonii*, respectively. Major components for *G. cuicochensis* EO, on a nonpolar and polar stationary phase, were α -pinene (29.4–29.6%), *p*-vinylguaiaicol (3.3–3.6%), and germacrene D (20.8–19.9%). In *G. sancti-antonii* EO, the main compounds were α -pinene (3.0–2.9%), β -pinene (12.9–12.1%), γ -curcumene (19.7–18.3%), germacrene D (9.0% on the polar phase), *ar*-curcumene (5.3% on the polar phase), δ -cadinene (4.1–4.6%), α -muurolol (3.3–2.4%), α -cadinol (3.0% on both columns), and an undetermined compound, of molecular weight 220. In addition to chemical composition, the enantioselective analysis of the main chiral compounds was carried out on two different chiral selectors. In *G. cuicochensis* EO, (1*R*,5*R*)-(+)- α -pinene, (S)-(+)- β -phellandrene, (R)-(-)-piperitone, and (S)-(-)-germacrene D were enantiomerically pure, whereas β -pinene, sabinene, α -phellandrene, limonene, linalool, and terpinen-4-ol were observed as scalemic mixtures. On the other hand, in *G. sancti-antonii* EO, the pure enantiomers were (1*S*,5*S*)-(-)- α -pinene, (1*R*,5*R*)-(+)-sabinene, (R)-(-)- β -phellandrene, (S)-(-)-limonene, (1*S*,2*R*,6*R*,7*R*,8*R*)-(+)- α -copaene, (R)-(-)-terpinen-4-ol, and (S)-(-)-germacrene D, whereas β -pinene, linalool, and α -terpineol were present as scalemic mixtures. The principal component analysis demonstrated that *G. cuicochensis* volatile fraction was quite similar to many of the other EOs of the same genus, whereas *G. sancti-antonii* produced the most dissimilar EO. Furthermore, the enantioselective analyses showed the usual variable enantiomeric distribution, with a greater presence of enantiomerically pure compounds in *G. sancti-antonii* EO.



Gynoxys cuicochensis

Gynoxys sancti-antonii

Landscape of the Province of Loja, Ecuador

1. INTRODUCTION

Ecuador is a South American country, crossed by the equatorial line, and characterized by four different climatic regions, whose conditions are almost constantly maintained all year long. Therefore, a great biodiversity evolved in this region, producing an incredible number of so far unprecedented botanical species from a chemical point of view.^{1,2} This situation led the United Nations to declare Ecuador as one of the 17 “megadiverse” countries in the world.³ For these reasons, our group has been investigating natural products for about 20 years, with the purpose of enhancing and preserving the Ecuadorian flora through the knowledge of its phytochemistry and, possibly, the discovery of pharmacologically interesting metabolites.^{4,5} During the past few years, we mainly focused on the description of new essential oils (EOs), with emphasis on their chemical and enantiomeric composi-

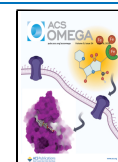
tions, olfactometric profiles, and biological activities.^{6–9} Being centered on phytochemistry and chemotaxonomy, high distillation yields, or agricultural availability are not usually leading criteria of plant selection for our research. In this perspective, the present study belonged to an unfunded project, dealing on the systematic description of new EOs from 12 plants of the genus *Gynoxys* Cuatrec. (Asteraceae) in the province of Loja, Ecuador. So far, the EOs obtained from

Received: January 11, 2024

Revised: May 19, 2024

Accepted: May 24, 2024

Published: June 5, 2024



Gynoxys miniphylla Cuatrec., *Gynoxys rugulosa* Muschl., *Gynoxys buxifolia* (Kunth) Cass., and *Gynoxys laurifolia* (Kunth) Cass. have already been studied and published.^{10–13} The composition of *Gynoxys szyszlowiczii* Hieron. volatile fraction is ready to be published, whereas *Gynoxys calyculisolvans* Hieron., *Gynoxys pulchella* (Kunth) Cass., *Gynoxys reinaldii* Cuatrec., *Gynoxys hallii* Hieron., and *Gynoxys azuayensis* Cuatrec. are currently under investigation. Finally, *Gynoxys cuicochensis* Cuatrec. and *Gynoxys sancti-antonii* Cuatrec. are the object of this report. According to botanical literature, the genus *Gynoxys* is an Andean endemism, comprising about 120 species diffused from Argentina and Bolivia to Venezuela.¹⁴ The diffusion center is Ecuador, where most of these species are endemic or native.¹⁵ In this country, *G. cuicochensis* is an endemic shrub or tree, growing between 2000 and 3500 m above the sea level, in the provinces of Azuay, Cañar, Loja, and Pichincha.¹⁶ On the other hand, *G. sancti-antonii* is a native treelet, growing between 2500 and 3500 m above the sea level in the provinces of Azuay, Cañar, Chimborazo, Loja, and Pichincha.¹⁶ No synonyms were reported for *G. cuicochensis*, whereas *G. sancti-antonii* var. *latifolia* Cuatrec. is a synonym of *G. sancti-antonii*.¹⁶ On the one hand, from the chemical point of view, *G. cuicochensis* is a completely unprecedented species. On the other hand, *G. sancti-antonii* has been previously studied about its nonvolatile metabolites.^{17,18} The aim of the present research is the chemical and enantiomeric description of two EOs obtained from *G. cuicochensis* and *G. sancti-antonii* leaves that, to the best of the authors' knowledge, are reported here for the first time. The experimental design is represented in Figure 1.

2. RESULTS AND DISCUSSION

2.1. Chemical Analysis. The dry leaves of *G. cuicochensis* produced an EO with an analytical yield of $0.08 \pm 0.003\%$ by weight. A total of eighty-nine compounds were identified and quantified on at least one of two stationary phases of different polarity. The gas chromatographic (GC) profiles of both

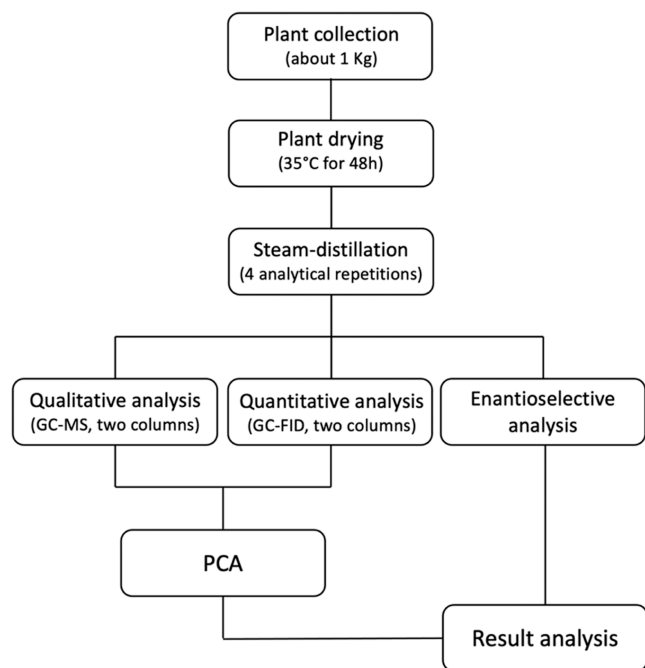


Figure 1. Experimental design of the present investigation.

essential oils on the nonpolar and polar stationary phases are represented in Figures 2 and 3, whereas the complete qualitative and quantitative analyses are detailed in Table 1. Major components ($\geq 3.0\%$ on at least one column), on the nonpolar and polar stationary phase, respectively, were as follows: α -pinene (29.4–29.6%, peak 1), *p*-vinylguaiaicol (3.3–3.6%, peak 42), and germacrene D (20.8–19.9%, peak 69). Unlike most of the other *Gynoxys* EOs, the volatile fraction of *G. cuicochensis* was not dominated by sesquiterpenes, being monoterpene and sesquiterpene fractions almost equal. In fact, monoterpenes and oxygenated monoterpenoids accounted together for 41.6–40.9%, whereas sesquiterpenes and oxygenated sesquiterpenoids corresponded to 41.2–38.7% as a sum. About *G. sancti-antonii* EO, the distillation yield was 0.08 ± 0.014 by weight. In this volatile fraction, 60 components were identified and quantified on at least one column. Main compounds were as follows: α -pinene (3.0–2.9%, peak 1), β -pinene (12.9–12.1%, peak 3), γ -curcumene (19.7–18.3%, peak 68), germacrene D (9.0% on the polar phase, peak 69), *ar*-curcumene (5.3% on the polar phase, peak 70), δ -cadinene (4.1–4.6%, peak 79), α -muurolol (3.3–2.4%, peak 92), α -cadinol (3.0% on both columns, peak 93), and an undetermined compound of molecular weight 220 (3.1–4.2%, peak 95). The volatile fraction of *G. sancti-antonii* was dominated by sesquiterpenes and oxygenated sesquiterpenoids, whose joint fractions corresponded to 64.3–59.3% on the nonpolar and polar stationary phase, respectively. On the other hand, the sum of monoterpenes and oxygenated monoterpenoids corresponded to 18.5–17.3% of the whole oil mass. Interestingly, the characteristic heavy aliphatic fraction, that we could observe in other species of this genus, were not so important in *G. cuicochensis* and *G. sancti-antonii*. In fact, despite these compounds were clearly present, their quantitative contribution did not exceed 10% of the entire oil composition in both plants.

The comparison through principal component analysis (PCA) among the main constituents of the EOs from the species *G. miniphylla*, *G. rugulosa*, *G. buxifolia*, *G. laurifolia*, *G. cuicochensis*, and *G. sancti-antonii* (see Figure 4), permitted to determine the relative closeness of the *Gynoxys* spp. so far studied for their volatile fraction compositions. In this statistical analysis, only major components were considered. On the one hand, *G. miniphylla*, *G. cuicochensis*, *G. buxifolia*, and *G. laurifolia* appeared to belong for similarity to the same group, whereas *G. szyszlowiczii* and *G. rugulosa* generated a different cluster. On the other hand, *G. sancti-antonii* was quite far from all the other plants of this family. These results were peculiarly counterintuitive since all these taxa, except *G. buxifolia*, apparently presented a quite similar chemical profile. In this sense, α -pinene and germacrene D were major components in practically all volatile fractions, whereas β -pinene, *p*-vinylguaiaicol, (*E*)- β -caryophyllene, α -humulene, δ -cadinene, and α -cadinol were constantly present in all EOs, despite not always as major constituents.^{10–13} Finally, *p*-vinylguaiaicol did not appear in *G. buxifolia* EO just because it was quantitatively dissolved in the hydrolate.¹² Occasionally, a specific metabolite was a major component of a particular EO. This was for instance the case of δ -3-carene and *trans*-myrtilan acetate for *G. miniphylla*, and γ -curcumene for *G. sancti-antonii*. Furthermore, a series of heavy aliphatic compounds (mainly long-chained aldehydes, alkenes, and alkanes) was a characteristic pattern in the final part of many GC profiles.^{10,11,13} Finally, a special consideration must be given to *G. buxifolia*

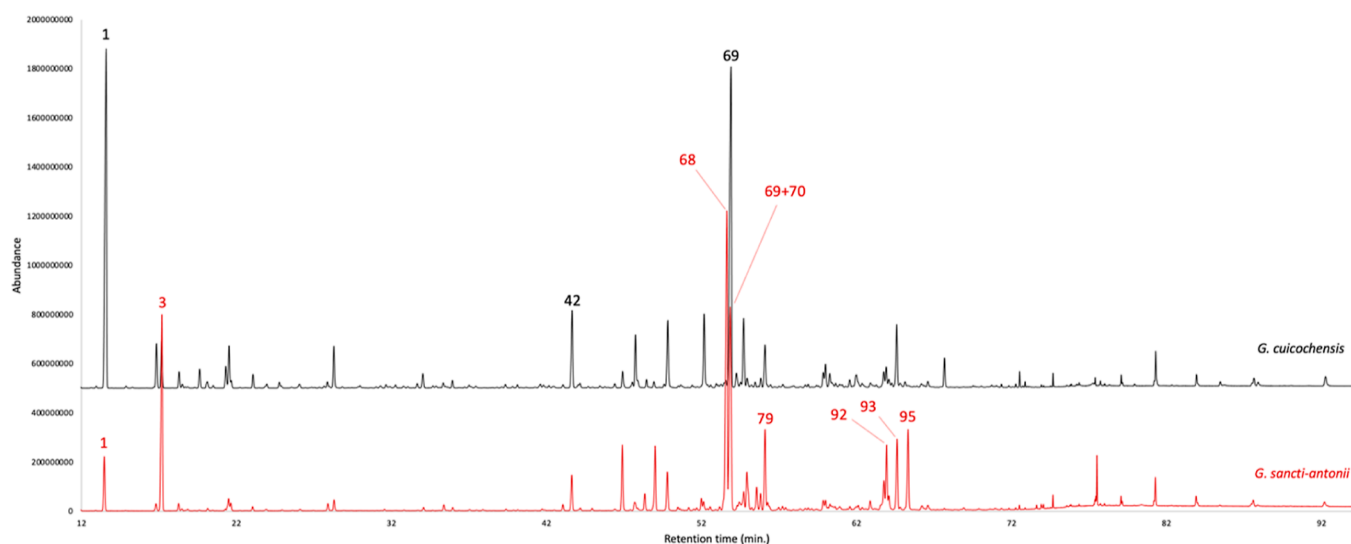


Figure 2. GC–MS profile of *G. cuicochensis* (black) and *G. sancti-antonii* (red) EOs on a 5%-phenyl-methylpolysiloxane stationary phase. The peak numbers refer to major compounds ($\geq 3.0\%$ on at least one column) in Table 1.

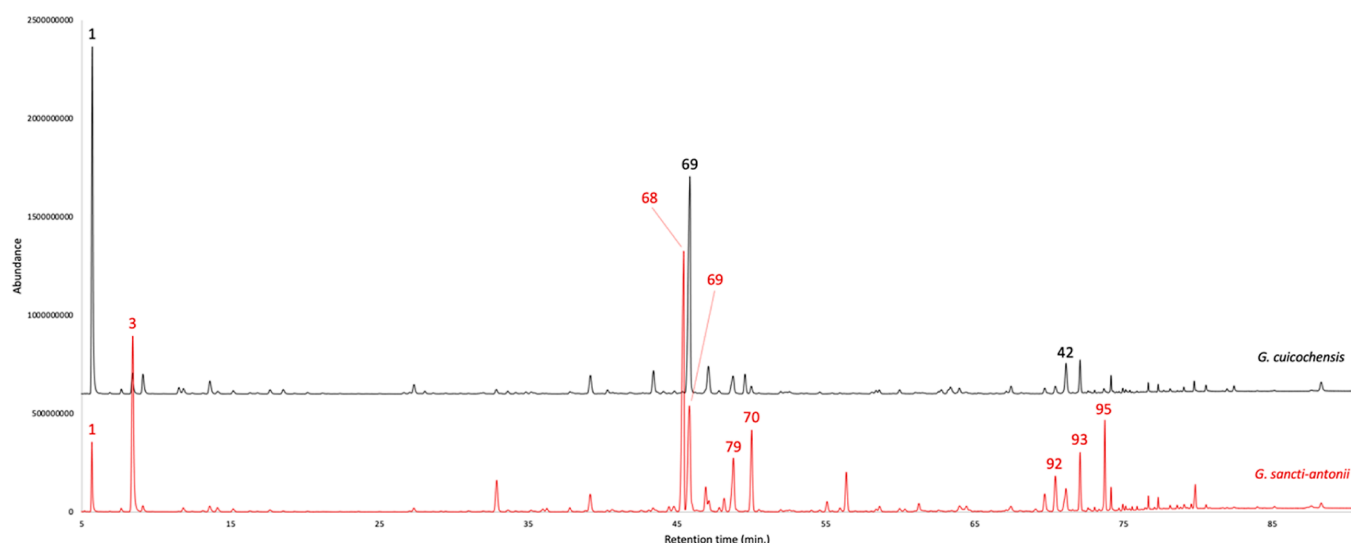


Figure 3. GC–MS profile of *G. cuicochensis* (black) and *G. sancti-antonii* (red) EOs on a polyethylene glycol stationary phase. The peak numbers refer to major compounds ($\geq 3.0\%$ on at least one column) in Table 1.

EO, whose chemical composition was completely different from all the other species, the major compounds being the very rare furanoeremophilane and bakkenolide A.¹²

2.2. Enantioselective Analysis. The enantioselective analyses permitted to identify four enantiomerically pure compounds in *G. cuicochensis* EO and seven in *G. sancti-antonii* volatile fraction. They were (1*R*,5*R*)-(+)- α -pinene, (5*S*)-(+)- β -phellandrene, (1*R*)-(-)-piperitone, and (5*S*)-(-)-germacrene D for the first plant, whereas (1*S*,5*S*)-(-)- α -pinene, (1*R*,5*R*)-(+)-sabinene, (1*R*)-(-)- β -phellandrene, (5*S*)-(-)-limonene, (1*S*,2*R*,6*R*,7*R*,8*R*)-(+)- α -copaene, (1*R*)-(-)-terpinen-4-ol, and (5*S*)-(-)-germacrene D were the ones of the second plant. All the other analyzed chiral compounds were present as scalemic mixtures in both EOs. Unlike the chemical compositions, the enantiomeric distributions of all the known *Gynoxys* EOs did not apparently present a common pattern.^{10–13} The detailed results of the enantioselective analyses on *G. sancti-antonii* and *G. cuicochensis* EOs are shown in Table 2, where two chiral selectors (2,3-diacetyl-6-*tert*-butyldimethylsilyl- β -cyclodextrin

and 2,3-diethyl-6-*tert*-butyldimethylsilyl- β -cyclodextrin) were used in order to ensure the best enantiomeric separations. As usual, the variable enantiomeric distribution of the same chiral metabolites, within a botanical genus or even the same species, is the result of different biological functions and properties, that two optical isomers can exert in a living organism.^{99,100}

3. CONCLUSIONS

The dry leaves of *G. cuicochensis* and *G. sancti-antonii* produced, by steam-distillation, two EOs with the same yield of about 0.08% by weight. The yield was therefore a little higher than the one of most of the other *Gynoxys* EOs (about 0.02%), but lower than the one of *G. buxifolia* (about 0.1%). The PCA demonstrated that *G. cuicochensis* volatile fraction was quite similar to most of the other EOs of the same genus, whereas *G. sancti-antonii* produced the most dissimilar EO. Furthermore, the heavy aliphatic fraction that characterizes many *Gynoxys* EOs was much less important in these two species. Finally, the enantioselective analyses showed the usual variable enantio-

Table 1. Qualitative (GC–MS) and Quantitative (GC–FID) Chemical Composition of *G. cuicochensis* and *G. sancti-antonii* EO on 5%-Phenyl-methylpolysiloxane and Polyethylene Glycol Stationary Phases^c

no.	compounds	5%-phenyl-methylpolysiloxane			polyethylene glycol			reference	LRI ^a	LRI ^b	LRI ^c	reference	<i>G. cuicochensis</i>		<i>G. sancti-antonii</i>		reference	
		LRI ^a	LRI ^b	%	σ	LRI ^a	LRI ^b						%	σ	LRI ^a	LRI ^b		%
1	α -pinene	933	932	29.4	4.84	3.0	0.51	19	1016	1016	1016	19	29.6	4.26	2.9	0.24	20	
2	sabinene	974	969	1.9	0.43	0.4	0.07	19	1103	1100	1100	19	1.9	0.27	0.4	0.04	21	
3	β -pinene	979	974	2.1	0.32	12.9	1.86	19	1115	1116	1116	19	2.0	0.29	12.1	1.21	22	
4	myrcene	992	988	0.7	0.08	0.2	0.02	19	1161	1161	1161	19	0.7	0.08	0.2	0.16	23	
5	pentyl furan	995	984	0.2	0.07			19	1231	1230	1230	19	0.2	0.06			24	
6	<i>n</i> -decane	1000	1000			trace			1000	1000	1000				0.2	0.02		
7	α -phellandrene	1009	1002	0.9	0.10			19	1155	1153	1153	19	0.7	0.08			25	
8	(2 <i>E</i> ,4 <i>E</i>)-heptadienal	1014	1007	0.1	0.02			19	1460	1461	1461	19	0.2	0.02			26	
9	α -terpinene	1020	1014	0.4	0.03			19	1171	1173	1173	19	0.1	0.02			27	
10	<i>p</i> -cymene	1029	1020	0.5	0.08	trace		19	1263	1264	1264	19	0.6	0.07	0.1	0.01	28	
11	limonene	1032	1024	1.5	0.18	0.6	0.08	19	1190	1190	1190	19	1.5	0.16	0.3	0.21	29	
12	β -phellandrene	1034	1025	0.2	0.04	0.4	0.06	19	1199	1198	1198	19	trace		0.4	0.04	30	
13	(<i>E</i>)- β -ocimene	1051	1044	0.5	0.05			19	1250	1251	1251	19	0.6	0.05			31	
14	benzene acetaldehyde	1061	1036	0.1	0.01			19	1677	1669	1669	19	trace				32	
15	γ -terpinene	1062	1054	0.1	0.02			19	1238	1238	1238	19	0.1	0.02			33	
16	(2 <i>E</i>)-octen-1-al	1074	1049	0.2	0.02			19	1422	1425	1425	19	0.1	0.01			34	
17	<i>trans</i> -linalool oxide (furanoid)	1082	1084	0.1	0.01			19	1466	1466	1466	19	trace				35	
18	terpinolene	1088	1086	0.1	0.01			19	1274	1274	1274	19	0.1	0.01			36	
19	linalool	1110	1113	0.3	0.03	0.5	0.04	37	1553	1556	1556	37	0.1	0.01	0.3	0.04	38	
20	nonanal	1116	1100	1.4	0.11			19	1390	1390	1390	19	1.1	0.07			39	
21	(2 <i>E</i>)-hexenyl propanoate	1116	1111			trace		40	1390	1392	1392	40			0.3	0.04	40	
22	α -campholenal	1138	1122	trace				19	1478	1485	1485	19	0.1	0.01			41	
23	(3 <i>Z</i>)-hexenyl isobutanoate	1155	1142	0.1	0.01			19	1384	1385	1385	19	0.3	0.03			42	
24	(2 <i>E</i>)-nonen-1-al	1175	1157	0.1	0.01			19	1527	1524	1524	19	0.2	0.01			35	
25	safranal	1178	1197	trace				19	1631	1622	1622	19	0.2	0.01			43	
26	<i>p</i> -mentha-1,5-dien-8-ol	1186	1166	0.2	0.02			19	1723	1723	1723	19	0.1	0.01			44	
27	terpinen-4-ol	1191	1184	0.5	0.04			45	1594	1594	1594	45	0.7	0.04	0.2	0.03	46	
28	<i>n</i> -dodecane	1200	1200	0.1	0.01				1200	1200	1200		0.3	0.04				
29	<i>p</i> -cymen-8-ol	1202	1179	trace				19	1845	1845	1845	19	0.1	0.01			31	
30	myrtenol	1209	1194	0.1	0.01			19	1784	1786	1786	19	trace				47	
31	α -terpineol	1209	1207			0.3	0.06	39	1692	1692	1692	39	0.2	0.03	0.2	0.04	23	
32	decanal	1217	1214	0.2	0.01	trace		48	1494	1494	1494	48	0.2	0.03	0.1	0.01	49	
33	β -cyclocitral	1232	1217	0.1	0.01			19	1605	1606	1606	19	0.1	0.01			50	
34	<i>trans</i> -carveol	1235	1215	0.1	0.01			19	1830	1830	1830	19	trace				35	
35	geraniol	1265	1249	trace				19	1849	1849	1849	19	0.2	0.01			51	
36	piperitone	1272	1249	0.1	0.01			19	1710	1710	1710	19	trace				52	
37	2-(<i>E</i>)-decenal	1276	1260	0.1	0.01			19	1635	1630	1630	19	0.2	0.01			39	
38	nonanoic acid	1297	1267	0.1	0.01			19										
39	<i>n</i> -tridecane	1300	1300	0.1	0.01				1300	1300	1300		0.1	0.01				

Table 1. continued

no.	compounds	5%-phenyl-methylpolysiloxane				polyethylene glycol					
		LRI ^a	LRI ^b	G. <i>caiochensis</i> %	G. <i>sancii-antonii</i> %	reference	LRI ^a	LRI ^b	G. <i>caiochensis</i> %	G. <i>sancii-antonii</i> %	reference
40	<i>cis</i> -pinocaryyl acetate	1305	1311	0.1	0.01	19	1639		0.1	0.01	§
41	undecanal	1318	1319	0.1	0.01	53	1580		0.5	0.08	54
42	<i>p</i> -vinylguaiacol	1327	1324	3.3	0.19	55	2189		3.6	0.11	56
43	(2 <i>E</i> ,4 <i>E</i>)-decadienal	1335	1315	0.3	0.01	19	1799		0.3	0.05	57
44	α -copaene	1376	1374			19	1474				58
45	α -ylangene	1377	1373	0.1	0.01	19	1474		0.6	0.05	25
46	2- <i>epi</i> - α -funebrene	1388	1380			19	1724				§
47	β -cubebene	1389	1387	0.3	0.07	19	1523		0.2	0.02	59
48	(<i>Z</i>)- β -damascenone	1390	1361	0.3	0.06	19	1806		0.1	0.02	60
49	geranyl acetate	1390	1379	1.4	0.14	19	1756		1.4	0.14	61
50	<i>n</i> -tetradecane	1400	1400	0.2	0.01		1400		0.3	0.01	
51	α -gurjunene	1407	1409	0.2	0.02	19	1511		0.3	0.01	62
52	undetermined (MW: 192)	1408					1882				
53	(<i>E</i>)- β -damascenone	1418	1416	0.4	0.03	19					
54	(<i>E</i>)- β -caryophyllene	1421	1421	2.1	0.20	19	1575		2.4	0.24	63
55	β -copaene	1432	1430	0.1	0.01	19	1570		0.1	0.01	64
56	β -gurjunene	1432	1431			19	1671				41
57	<i>cis</i> - α -bergamotene	1434	1433	0.3	0.06	19	1671		0.5	0.07	66
58	(<i>Z</i>)- β -farnesene	1443	1440	trace	trace	65	1528		0.7	0.06	67
59	myrtanyl-4(12)-ene	1447	1445	0.2	0.04	19	1633		0.2	0.03	
60	<i>trans</i> -muurola-3,5-diene	1448	1451	2.7	0.44	19			2.4	0.21	
61	(<i>E</i>)- β -farnesene	1456	1454	trace	trace	19	1611		0.1	0.02	§
62	α -humulene	1458	1452	0.6	0.13	19	1665		0.5	0.07	68
63	<i>cis</i> -cadin-1,(6),4-diene	1465	1461	0.5	0.10	19	1647		0.2	0.03	69
64	<i>cis</i> -muurola-4(14),5-diene	1466	1465	0.2	0.05	19	1689		2.6	0.23	§
65	(<i>E</i>)- β -farnesene	1472	1454	0.1	0.01	19	1523		trace		§
66	dauca-5,8-diene	1475	1471	0.3	0.05	19	1665		0.1	0.01	25
67	γ -muurolene	1480	1478	0.3	0.05	19	1642		0.2	0.04	70
68	γ -curcumene	1482	1481	0.1	0.01	19	1671		0.2	0.01	71
69	germacrene D	1486	1495	0.4	0.09	19	1682		0.3	0.10	72
70	α -curcumene	1487	1479	20.8	2.48	19	1689		19.9	2.50	73
71	(<i>E</i>)- β -ionone	1492	1487	1.2	0.15	19	1763		1.4	0.18	74
72	<i>trans</i> -muurola-4(14),5-diene	1497	1493	0.4	0.03	19	1922		trace		22
73	α -zingiberene	1500	1493	2.3	0.25	19	1695		2.2	0.22	§
74	bicyclogermacrene	1500	1500	0.8	0.18	19	1714		1.2	0.14	75
75	α -muurolene	1503	1500	3.8	1.01	19	1712		0.1	0.01	76
76	3-methyl-phenyl ethyl butanoate	1504	1495	0.1	0.01	19	1708		0.1	0.01	77
77	β -curcumene	1513	1514	1.1	0.26	78	1960				74
78	γ -cadinene	1518	1513	0.3	0.03	19	1731		1.0	0.12	79
79	δ -cadinene	1523	1522	1.5	0.15	19	1739		trace		79
				4.1	0.88	19	1742		2.2	0.19	44

Table 1. continued

no.	compounds	5%-phenyl-methylpolysiloxane				polyethylene glycol					
		LRI ^a	LRI ^b	<i>G. cuicochensis</i> %	<i>G. sancti-antonii</i> %	reference	LRI ^a	LRI ^b	<i>G. cuicochensis</i> %	<i>G. sancti-antonii</i> %	reference
80	(<i>E</i>)-nerolidol	1570	1561	0.2	0.03	19	2042	2045	0.1	0.02	80
81	germacrene D-4-ol	1586	1583	0.5	0.11	81	2034	2035	0.7	0.09	82
82	spathulenol	1589	1577	0.9	0.09	19	2106	2106	0.9	0.08	83
83	caryophyllene oxide	1588	1588	0.9	0.10	19	1967	1968	0.5	0.05	35
84	<i>n</i> -hexadecane	1600	1600	0.1	0.03	0.2	1600	1600	0.1	0.01	0.2
85	saivial-4-(14)-en-1-one	1604	1594	0.2	0.06	19	1979	1995	0.1	0.01	36
86	ledol	1616	1616	0.7	0.07	84	2005	2014	0.1	0.01	85
87	humulene epoxide II	1623	1608	0.7	0.05	19	2009	2011	0.2	0.02	44
88	1- <i>epi</i> -cubenol	1639	1638	0.1	0.01	26	2044	2035	0.3	0.03	86
89	<i>cis</i> -cadin-4-en-7-ol	1639	1635	0.2	0.04	87	2044	2044	0.3	0.03	§
90	<i>epi</i> - α -cadinol	1655	1652	0.8	0.09	19	2157	2154	0.7	0.07	88
91	<i>epi</i> - α -muurolol	1658	1640	0.8	0.10	19	2173	2176	0.9	0.11	25
92	α -muurolol	1660	1652	0.4	0.06	89	2187	2187	trace	trace	28
93	α -cadinol	1670	1670	2.4	0.34	90	2211	2212	2.5	0.31	76
94	<i>ar</i> -turmerone	1679	1668	0.4	0.04	19	2226	2226	0.1	0.01	§
95	undetermined (FW:220)	1682					2248		4.2	0.52	
96	<i>n</i> -heptadecane	1700	1700	0.2	0.03		1700	1700	0.2	0.01	
97	amorpha-4,9-dien-2-ol	1706	1700	0.3	0.04	19	2275		0.3	0.03	§
98	pentadecanal	1727	1724	0.9	0.08	19	2022	2024	1.3	0.09	91
99	(<i>Z,Z</i> ,6 <i>E</i>)-farnesol	1730	1722			19	2280	2291	0.2	0.21	92
100	<i>n</i> -octadecane	1800	1800	0.1	0.02		1800	1800	0.9	0.13	
101	hexadecanal	1833	1828	0.1	0.01	19	2129	2132	0.2	0.02	91
102	(<i>2E,6E</i>)-farnesyl acetate	1843	1845	trace		19	2233	2234	0.1	0.01	93
103	6,10,14-trimethyl-2-pentadecanone	1856	1846	0.1	0.01	19	2122	2125	0.1	0.02	80
104	heptadecanal	1932	1932	0.2	0.04	88	2238	2247	0.5	0.05	88
105	1-eicosene	1995	1993			19	2047	2047	1.0	0.08	94
106	<i>n</i> -heneicosane	2100	2100	0.1	0.02		2100	2100	0.1	0.02	
107	1-octadecanol acetate	2194	2205			95	2529	2521	0.1	0.01	96
108	<i>n</i> -docosane	2200	2200	trace			2200	2200	0.1	0.01	
109	1-tricosene	2295	2292			19	2356		2.1	0.26	§
110	<i>n</i> -tricosane	2300	2300	0.7	0.12		2300	2300	0.1	0.02	
111	1-tetracosene	2400	2402			97	2452		1.5	0.33	§
112	<i>n</i> -tetracosane	2400	2400	trace			2400	2400	0.3	0.06	
113	docosanal	2440	2434	0.1	0.03	19	2682		0.3	0.05	§
114	<i>n</i> -pentacosane	2500	2500	0.2	0.05		2500	2500	0.1	0.02	
115	1-pentacosene	2506	2496			98	2478	2488	0.1	0.01	58
116	<i>n</i> -hexacosane	2600	2600	0.3	0.07		2600	2600	0.3	0.06	
	monoterpene hydrocarbons			38.4					37.9		16.5
	oxygenated monoterpenes			3.2					3.0		0.8
	sesquiterpene hydrocarbons			31.7					31.0		49.6

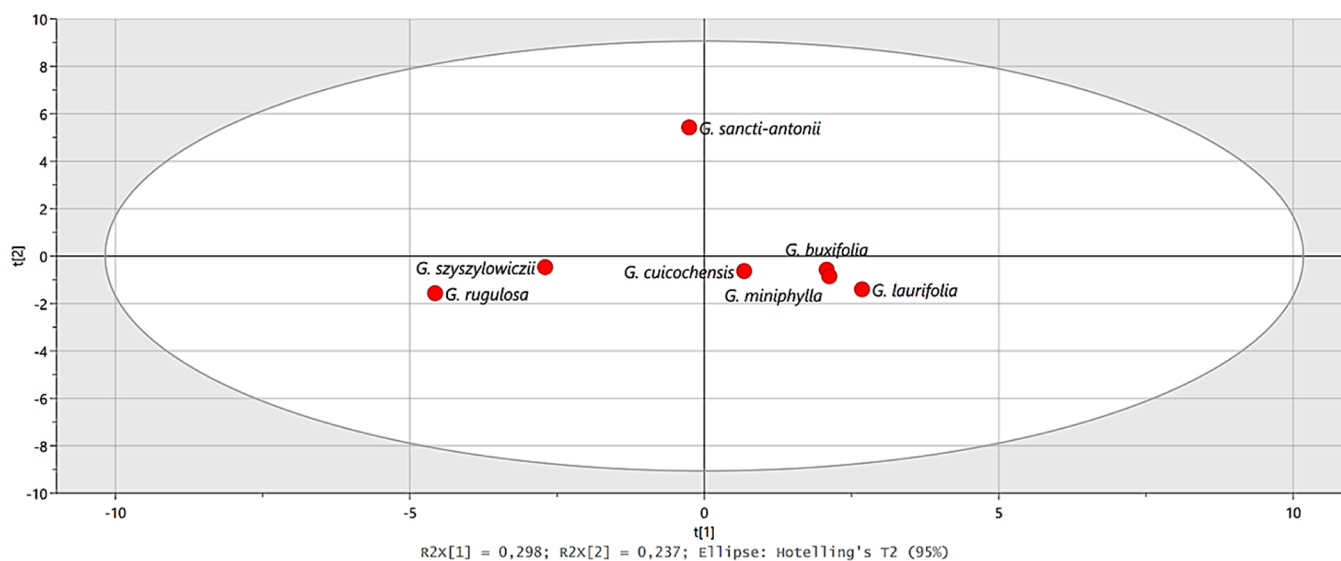


Figure 4. PCA plot of major components identified in the EOs of *G. miniphylla*, *G. rugulosa*, *G. buxifolia*, *G. laurifolia*, *G. cuicochensis*, and *G. sancti-antoni*.

Table 2. Enantioselective Analysis of Some Chiral Terpenes from *G. cuicochensis* and *G. sancti-antoni* EOs^c

enantiomers	LRI	<i>G. cuicochensis</i>		<i>G. sancti-antoni</i>	
		distribution (%)	ee (%)	distribution (%)	ee (%)
(1 <i>R</i> ,5 <i>R</i>)-(+)- α -pinene	924 ^a	100.0	100.0		
(1 <i>S</i> ,5 <i>S</i>)-(-)- α -pinene	926 ^a			100.0	100.0
(1 <i>R</i> ,5 <i>R</i>)-(+)- β -pinene	949 ^a	44.7	10.6	19.3	61.3
(1 <i>S</i> ,5 <i>S</i>)-(-)- β -pinene	959 ^a	55.3		80.7	
(1 <i>R</i> ,5 <i>R</i>)-(+)-sabinene	1008 ^b	68.2	36.4	100.0	100.0
(1 <i>S</i> ,5 <i>S</i>)-(-)-sabinene	1014 ^b	31.8			
(<i>R</i>)-(-)- α -phellandrene	1019 ^a	4.7	90.7		
(<i>S</i>)-(+)- α -phellandrene	1022 ^a	95.3			
(<i>R</i>)-(-)- β -phellandrene	1051 ^a			100.0	100.0
(<i>S</i>)-(-)-limonene	1058 ^a	97.5	95.0	100.0	100.0
(<i>R</i>)-(+)-limonene	1074 ^a	2.5			
(<i>S</i>)-(+)- β -phellandrene	1075 ^b	100.0	100.0		
(<i>R</i>)-(-)-linalool	1179 ^a	56.3	12.5	47.8	4.5
(<i>S</i>)-(+)-linalool	1189 ^a	43.7		52.2	
(<i>R</i>)-(-)-piperitone	1294 ^a	100.0	100.0		
(<i>S</i>)-(+)- α -terpineol	1300 ^a			84.7	69.5
(<i>R</i>)-(-)- α -terpineol	1313 ^a			15.3	
(1 <i>S</i> ,2 <i>R</i> ,6 <i>R</i> ,7 <i>R</i> ,8 <i>R</i>)-(+)- α -copaene	1322 ^a			100.0	100.0
(<i>R</i>)-(-)-terpinen-4-ol	1339 ^b	40.7	18.6	100.0	100.0
(<i>S</i>)-(+)-terpinen-4-ol	1376 ^b	59.3			
(<i>S</i>)-(-)-germacrene D	1465 ^a	100.0	100.0	100.0	100.0

^a2,3-diacetyl-6-*tert*-butyldimethylsilyl- β -cyclodextrin. ^b2,3-diethyl-6-*tert*-butyldimethylsilyl- β -cyclodextrin column. ^cLinear retention indice = calculated LRI; ee = enantiomeric excess.

230 °C. The MS, equipped with a single quadrupole analyzer, was operated in the SCAN mode and programmed for 40–400 *m/z* mass range. A mixture of *n*-alkane C₉–C₂₆, purchased from Sigma-Aldrich, was also injected in the same conditions as the EOs. The components of the volatile fractions were identified by comparing the linear retention indices (LRIs), calculated according to Van den Dool and Kratz,¹⁰¹ and mass spectra with data from literature (see Table 1).

4.4. Quantitative (GC–FID) Chemical Analyses. The quantitative chemical analyses were conducted on the same GC, columns, and instrument configuration, as the qualitative ones, except for the use of a flame ionization detector (FID)

instead of MS. The FID temperature was set at 230 °C, whereas the injector was operated at the split ratio of 10:1. All the EO constituents were quantified with external calibration, using *n*-nonane as internal standard and isopropyl caproate as calibration standard. The internal standard was purchased from Sigma-Aldrich, whereas the calibration standard was synthesized in one of the authors' laboratories and purified to 98.8% (GC–FID purity). A six-point calibration curve was traced for each column, as previously described in literature,¹⁰² obtaining a correlation coefficient of 0.997 in both cases. A relative response factor was calculated for each EO component versus isopropyl caproate, according to combustion enthalpy, as

described in literature.^{103,104} The percent results were obtained as a mean value and standard deviation over four repetitions, relating the amount of each compound to the whole mass of the distilled EO, analytically calculated.

4.5. PCA of Some *Gynoxys* spp. EOs. The PCA was carried out on SIMCA software, purchased from Sartorius (Göttingen, Germany). The analysis was conducted only on major constituents, accounting for at least 1% in at least one EO. The compounds included in the analysis were as follows: α -pinene, β -pinene, δ -3-carene, β -phellandrene, *trans*-myrtenol acetate, *p*-vinylguaiacol, (*E*)- β -caryophyllene, α -humulene, γ -curcumene, germacrene D, *ar*-curcumene, bicyclogermacrene, δ -cadinene, α -muurolol, α -cadinol, furanoeremophilane, bakkenolide A, *n*-heneicosane, 1-docosene, 1-tricosene, *n*-tricosane, 1-tetracosene, *n*-pentacosane, 1-hexacosene, and *n*-heptacosane. The quantitative data submitted to PCA were the mean values of each component on both nonpolar and polar columns. The analysis included data from *G. szyszylowiczii* that, despite being still unpublished, are currently partially available.

4.6. Enantioselective Analyses. The enantioselective analyses were carried out in the same GC–MS instrument as the qualitative ones. Two enantioselective capillary columns were used: one based on a 2,3-diacetyl-6-*tert*-butyldimethylsilyl- β -cyclodextrin chiral selector and the other one based on a 2,3-diethyl-6-*tert*-butyldimethylsilyl- β -cyclodextrin stationary phase. The columns were 25 m long, 250 μ m internal diameter and 0.25 μ m phase thickness, both purchased from MEGA S.r.l. (Legnano, MI, Italy). The enantiomers were identified according to mass spectra and injection of enantiomerically pure standards, that were purchased from Sigma-Aldrich. The GC oven was programmed according to the following thermal program: 50 °C for 1 min, a thermal gradient of 2 °C/min until 220 °C, finally maintained for 10 min. As usual, the enantiomer identification was limited by standard availability.

AUTHOR INFORMATION

Corresponding Author

Gianluca Gilardoni – Departamento de Química, Universidad Técnica Particular de Loja (UTPL), 110107 Loja, Ecuador;
orcid.org/0000-0003-0915-9416;
Email: gianluca.gilardoni@gmail.com

Authors

Yessenia E. Maldonado – Departamento de Química, Universidad Técnica Particular de Loja (UTPL), 110107 Loja, Ecuador
Evelin A. Betancourt – Carrera de Bioquímica y Farmacia, Universidad Técnica Particular de Loja (UTPL), 110107 Loja, Ecuador
Erika S. León – Carrera de Bioquímica y Farmacia, Universidad Técnica Particular de Loja (UTPL), 110107 Loja, Ecuador
Omar Malagón – Departamento de Química, Universidad Técnica Particular de Loja (UTPL), 110107 Loja, Ecuador
Nixon Cumbicus – Departamento de Ciencias Biológicas y Agropecuarias, Universidad Técnica Particular de Loja (UTPL), Loja 110107, Ecuador

Complete contact information is available at:
<https://pubs.acs.org/10.1021/acsomega.4c00391>

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We are grateful to the Universidad Técnica Particular de Loja (UTPL) for supporting this investigation and open access publication. We are also grateful to Prof. Carlo Bicchi (University of Turin, Italy) and Dr. Stefano Galli (MEGA S.r.l., Legnano, Italy) for their support with enantioselective columns.

REFERENCES

- (1) Malagón, O.; Ramírez, J.; Andrade, J.; Morocho, V.; Armijos, C.; Gilardoni, G. Phytochemistry and Ethnopharmacology of the Ecuadorian Flora. A Review. *Nat. Prod. Commun.* **2016**, *11*, 1934578X1601100307.
- (2) Armijos, C.; Ramírez, J.; Salinas, M.; Vidari, G.; Suárez, A. Pharmacology and Phytochemistry of Ecuadorian Medicinal Plants: An Update and Perspectives. *Pharmaceuticals* **2021**, *14*, 1145.
- (3) UNEP-WCMC. Megadiverse Countries. <https://www.biodiversitya-z.org/content/megadiverse-countries> (accessed December 11, 2023).
- (4) Chiriboga, X.; Gilardoni, G.; Magnaghi, I.; Vita Finzi, P.; Zanoni, G.; Vidari, G. New Anthracene Derivatives from *Coussarea macrophylla*. *J. Nat. Prod.* **2003**, *66*, 905–909.
- (5) Gilardoni, G.; Chiriboga, X.; Vita Finzi, P.; Vidari, G. New 3,4-Secocycloartane and 3,4-Secodammarane Triterpenes from the Ecuadorian Plant *Coussarea macrophylla*. *Chem. Biodiversity* **2015**, *12*, 946–954.
- (6) Vivanco, K.; Montesinos, J. V.; Cumbicus, N.; Malagón, O.; Gilardoni, G. The essential oil from leaves of *Mauria heterophylla* Kunth (Anacardiaceae): chemical and enantioselective analyses. *J. Essent. Oil Res.* **2023**, *35*, 563–569.
- (7) Maldonado, Y. E.; Malagón, O.; Cumbicus, N.; Gilardoni, G. A new essential oil from the native Ecuadorian species *Steiractinia sodiroi* (Hieron.) S.F. Blake (Asteraceae): chemical and enantioselective analyses. *Sci. Rep.* **2023**, *13*, 17180.
- (8) Gilardoni, G.; Enríquez, A. A.; Maldonado, Y. E.; Cumbicus, N.; Malagón, O. A New Essential Oil from the Native Andean Species *Nectandra laurel* Klotzsch ex Nees of Southern Ecuador: Chemical and Enantioselective Analyses. *Plants* **2023**, *12*, 3331.
- (9) Espinosa, S.; Bec, N.; Larroque, C.; Ramírez, J.; Sgorbini, B.; Bicchi, C.; Gilardoni, G. Chemical Enantioselective, and Sensory Analysis of a Cholinesterase Inhibitor Essential Oil from *Coreopsis triloba* S.F. Blake (Asteraceae). *Plants* **2019**, *8*, 448.
- (10) Malagón, O.; Cartuche, P.; Montaña, A.; Cumbicus, N.; Gilardoni, G. A new essential oil from the leaves of the endemic Andean species *Gynoxys miniphylla* Cuatrec. (Asteraceae): chemical and enantioselective analyses. *Plants* **2022**, *11*, 398.
- (11) Maldonado, Y. E.; Malagón, O.; Cumbicus, N.; Gilardoni, G. A New Essential Oil from the Leaves of *Gynoxys rugulosa* Muschl. (Asteraceae) Growing in Southern Ecuador: Chemical and Enantioselective Analyses. *Plants* **2023**, *12*, 849.
- (12) Cumbicus, C.; Malagón, O.; Cumbicus, N.; Gilardoni, G. The leaf essential oil of *Gynoxys buxifolia* (Kunth) Cass. (Asteraceae): a good source of furanoeremophilane and bakkenolide A. *Plants* **2023**, *12*, 1323.
- (13) Gilardoni, G.; Lara, L. R.; Cumbicus, N.; Malagón, O. A New Leaf Essential Oil from Endemic *Gynoxys laurifolia* (Kunth) Cass. of Southern Ecuador: Chemical and Enantioselective Analyses. *Plants* **2023**, *12*, 2878.
- (14) Kadereit, J. W.; Jeffrey, C. *Flowering Plants Eudicots. Asterales*; Kubitzki, K., Ed.; *The Families and Genera of Vascular Plants*; Springer-Verlag: Berlin, Heidelberg, 2007; Vol. VIII.
- (15) Tropicos.Org. Missouri Botanical Garden. <https://www.tropicos.org> (accessed December 11, 2023).
- (16) Jorgensen, P.; León-Yanez, S. *Catalogue of the Vascular Plants of Ecuador*; Missouri Botanical Garden Press: St. Louis, 1999.
- (17) Bohlmann, F.; Grenz, M.; Suwita, A. Inhaltsstoffe aus *Gynoxys*- und *Pseudogynoxys*-arten. *Phytochemistry* **1977**, *16*, 774–776.

- (18) Jakupovic, J.; Zdero, C.; King, R. M. Furanoeremophilanes from *Gynoxys* Species. *Phytochemistry* **1995**, *40*, 1677–1679.
- (19) Adams, R. P. *Identification of Essential Oil Components by Gas Chromatography/Mass Spectrometry*, 4th ed.; Allured Publishing Corporation: Carol Stream, 2007.
- (20) Shellie, R.; Marriott, P.; Zappia, G.; Mondello, L.; Dugo, G. Interactive use of linear retention indices on polar and apolar columns with an MS-Library for reliable characterization of Australian tea tree and other *Melaleuca* sp. Oils. *J. Essent. Oil Res.* **2003**, *15*, 305–312.
- (21) Loayza, I.; de Groot, W.; Lorenzo, D.; Dellacassa, E.; Mondello, L.; Dugo, G. Composition of the essential oil of *Porophyllum ruderale* (Jacq.) Cass. from Bolivia. *Flavour Fragrance J.* **1999**, *14*, 393–398.
- (22) Cavaleiro, C.; Salgueiro, L. R.; Miguel, M. G.; Proença da Cunha, A. Analysis by gas chromatography-mass spectrometry of the volatile components of *Teucrium lusitanicum* and *Teucrium algarbiensis*. *J. Chromatogr. A* **2004**, *1033*, 187–190.
- (23) Pinto, E.; Pina-Vaz, C.; Salgueiro, L.; Gonçalves, M. J.; Costa-de-Oliveira, S.; Cavaleiro, C.; Palmeira, A.; Rodrigues, A.; Martinez-de-Oliveira, J. Antifungal activity of the essential oil *Thymus pulegioides* on *Candida*, *Aspergillus* and dermatophyte species. *J. Med. Microbiol.* **2006**, *55*, 1367–1373.
- (24) Pozo-Bayon, M. A.; Ruiz-Rodríguez, A.; Pernin, K.; Cayot, N. Influence of eggs on the aroma composition of a sponge cake and on the aroma release in model studies on flavored sponge cakes. *J. Agric. Food Chem.* **2007**, *55*, 1418–1426.
- (25) Fanciullino, A.-L.; Gancel, A.-L.; Froelicher, Y.; Luro, F.; Ollitrault, P.; Brillouet, J.-M. Effects of Nucleo-cytoplasmic Interactions on Leaf Volatile Compounds from *Citrus* Somatic Diploid Hybrids. *J. Agric. Food Chem.* **2005**, *53*, 4517–4523.
- (26) Shellie, R.; Mondello, L.; Marriott, P.; Dugo, G. Characterisation of lavender essential oils by using gas chromatography-mass spectrometry with correlation of linear retention indices and comparison with comprehensive two-dimensional gas chromatography. *J. Chromatogr. A* **2002**, *970*, 225–234.
- (27) Möllenbeck, S.; König, T.; Schreier, P.; Schwab, W.; Rajaoarivony, J.; Ranarivelo, L. Chemical composition and analyses of enantiomers of essential oils from Madagascar. *Flavour Fragrance J.* **1997**, *12*, 63–69.
- (28) Brophy, J. J.; Goldsack, R. J.; Forster, P. I. Essential oils of the genus *Lophostemon* (Myrtaceae). *Flavour Fragrance J.* **2000**, *15*, 17–20.
- (29) Boido, E.; Lloret, A.; Medina, K.; Fariña, L.; Carrau, F.; Versini, G.; Dellacassa, E. Aroma composition of *Vitis vinifera* Cv. tannat: the typical red wine from Uruguay. *J. Agric. Food Chem.* **2003**, *51*, 5408–5413.
- (30) Bianchi, F.; Cantoni, C.; Careri, M.; Chiesa, L.; Musci, M.; Pinna, A. Characterization of the aromatic profile for the authentication and differentiation of typical Italian dry-sausages. *Talanta* **2007**, *72*, 1552–1563.
- (31) Flamini, G.; Cioni, P. L.; Morelli, I.; Maccioni, S.; Baldini, R. Phytochemical typologies in some populations of *Myrtus communis* L. on Caprione Promontory (East Liguria, Italy). *Food Chem.* **2004**, *85*, 599–604.
- (32) Bianchi, F.; Careri, M.; Mangia, A.; Musci, M. Retention indices in the analysis of food aroma volatile compounds in temperature-programmed gas chromatography: Database creation and evaluation of precision and robustness. *J. Sep. Sci.* **2007**, *30*, 563–572.
- (33) Bassole, I. H. N.; Ouattara, A. S.; Nebie, R.; Ouattara, C. A. T.; Kabore, Z. I.; Traore, S. A. Chemical composition and antibacterial activities of the essential oils of *Lippia chevalieri* and *Lippia multiflora* from Burkina Faso. *Phytochemistry* **2003**, *62*, 209–212.
- (34) Hallier, A.; Prost, C.; Serot, T. Influence in rearing conditions on the volatile compounds of cooked fillets of *Silurus glanis* (European catfish). *J. Agric. Food Chem.* **2005**, *53*, 7204–7211.
- (35) Salgueiro, L. R.; Pinto, E.; Gonçalves, M. J.; Costa, I.; Palmeira, A.; Cavaleiro, C.; Pina-Vaz, C.; Rodrigues, A. G.; Martinez-De-Oliveira, J. Antifungal activity of the essential oil of *Thymus capitellatus* against *Candida*, *Aspergillus* and dermatophyte strains. *Flavour Fragrance J.* **2006**, *21*, 749–753.
- (36) Stashenko, E. E.; Cervantes, M.; Combariza, Y.; Fuentes, H.; Martínez, J. R. HRGC/FID and HRGC/MSD analysis of the secondary metabolites obtained by different extraction methods from *Lepechinia schiedeana*, an in vitro evaluation of its antioxidant activity. *J. High Resolut. Chromatogr.* **1999**, *22*, 343–349.
- (37) Mahattanatawee, K.; Perez-Cacho, P. R.; Davenport, T.; Rouseff, R. Comparison of three lychee cultivar odor profiles using gas chromatography-olfactometry and gas chromatography-sulfur detection. *J. Agric. Food Chem.* **2007**, *55*, 1939–1944.
- (38) Kundakovic, T.; Fokialakis, N.; Kovacevic, N.; Chinou, I. Essential oil composition of *Achillea lingulata* and *A. umbellata*. *Flavour Fragrance J.* **2007**, *22*, 184–187.
- (39) Cho, I. H.; Namgung, H.-J.; Choi, H.-K.; Kim, Y.-S. Volatiles and key odorants in the pileus and stipe of pine-mushroom (*Tricholoma matsutake* Sing.). *Food Chem.* **2008**, *106*, 71–76.
- (40) Ruther, J. Retention index database for identification of general green leaf volatiles in plants by coupled capillary gas chromatography-mass spectrometry. *J. Chromatogr. A* **2000**, *890*, 313–319.
- (41) Couladis, M.; Chinou, I. B.; Tzakou, O.; Loukis, A. Composition and antimicrobial activity of the essential oil of *Ballota pseudodictamnus* L. Benth. *Phytother. Res.* **2002**, *16*, 723–726.
- (42) Umamo, K.; Hagi, Y.; Nakahara, K.; Shoji, A.; Shibamoto, T. Volatile chemicals identified in extracts from leaves of Japanese mugwort (*Artemisia princeps* Pamp.). *J. Agric. Food Chem.* **2000**, *48*, 3463–3469.
- (43) Cozzani, S.; Muselli, A.; Desjobert, J.-M.; Bernardini, A.-F.; Tomi, F.; Casanova, J. Chemical composition of essential oil of *Teucrium polium* subsp. *capitatum* (L.) from Corsica. *Flavour Fragrance J.* **2005**, *20*, 436–441.
- (44) Riu-Aumatell, M.; Lopez-Tamames, E.; Buxaderas, S. Assessment of the Volatile Composition of Juices of Apricot, Peach, and Pear According to Two Pectolytic Treatments. *J. Agric. Food Chem.* **2005**, *53*, 7837–7843.
- (45) Sabulal, B.; Dan, M.; John, A.; Kurup, R.; Chandrika, S. P.; George, V. Phenylbutanoid-rich rhizome oil of *Zingiber neesatum* from Western Ghats, southern India. *Flavour Fragrance J.* **2007**, *22*, 521–524.
- (46) Saroglou, V.; Marin, P. D.; Rancic, A.; Veljic, M.; Skaltsa, H. Composition and antimicrobial activity of the essential oil of six *Hypericum* species from Serbia. *Biochem. Syst. Ecol.* **2007**, *35*, 146–152.
- (47) Werkhoff, P.; Güntert, M.; Krammer, G.; Sommer, H.; Kaulen, J. Vacuum headspace method in aroma research: flavor chemistry of yellow passion fruits. *J. Agric. Food Chem.* **1998**, *46*, 1076–1093.
- (48) Lozano, P. R.; Miracle, E. R.; Krause, A. J.; Drake, M.; Cadwallader, K. R. Effect of cold storage and packaging material on the major aroma components of sweet cream butter. *J. Agric. Food Chem.* **2007**, *55*, 7840–7846.
- (49) Mahadevan, K.; Farmer, L. Key Odor Impact Compounds in Three Yeast Extract Pastes. *J. Agric. Food Chem.* **2006**, *54*, 7242–7250.
- (50) Pinto, E.; Salgueiro, L. R.; Cavaleiro, C.; Palmeira, A.; Gonçalves, M. J. In vitro susceptibility of some species of yeasts and filamentous fungi to essential oils of *Salvia officinalis*. *Ind. Crops Prod.* **2007**, *26*, 135–141.
- (51) Lin, J.; Rouseff, R. L. Characterization of aroma-impact compounds in cold-pressed grapefruit oil using time-intensity GC-olfactometry and GC-MS. *Flavour Fragrance J.* **2001**, *16*, 457–463.
- (52) Ledauphin, J.; Saint-Clair, J.-F.; Lablanquie, O.; Guichard, H.; Fournier, N.; Guichard, E.; Barillier, D. Identification of trace volatile compounds in freshly distilled calvados and cognac using preparative separations coupled with gas chromatography-mass spectrometry. *J. Agric. Food Chem.* **2004**, *52*, 5124–5134.
- (53) Varlet, V.; Knockaert, C.; Prost, C.; Serot, T. Comparison of odor-active volatile compounds of fresh and smoked salmon. *J. Agric. Food Chem.* **2006**, *54*, 3391–3401.
- (54) Verzera, A.; Trozzi, A.; Zappala, M.; Condruso, C.; Cotroneo, A. Essential Oil Composition of *Citrus meyerii* Y. Tan. and *Citrus medica* L. cv. Diamante and Their Lemon Hybrids. *J. Agric. Food Chem.* **2005**, *53*, 4890–4894.

- (55) Klesk, K.; Qian, M. Aroma extract dilution analysis of Cv. Marion (*Rubus spp. hyb*) and Cv. Evergreen (*R. iaciniatus* L.) blackberries. *J. Agric. Food Chem.* **2003**, *51*, 3436–3441.
- (56) Vichi, S.; Romero, A.; Tous, J.; Tamames, E. L.; Buxaderas, S. Determination of volatile phenols in virgin olive oils and their sensory significance. *J. Chromatogr. A* **2008**, *1211*, 1–7.
- (57) Brophy, J. J.; Goldsack, R. J.; Punruckvong, A.; Bean, A. R.; Forster, P. I.; Lepschi, B. J.; Doran, J. C.; Rozefelds, A. C. Leaf essential oils of the genus *Leptospermum* (Myrtaceae) in eastern Australia. Part 7. *Leptospermum petersonii*, *L. liversidgei* and allies. *Flavour Fragrance J.* **2000**, *15*, 342–351.
- (58) Flamini, G.; Tebano, M.; Cioni, P. L.; Bagci, Y.; Dural, H.; Ertugrul, K.; Uysal, T.; Savran, A. A multivariate statistical approach to *Centaurea* classification using essential oil composition data of some species from Turkey. *Plant Syst. Evol.* **2006**, *261*, 217–228.
- (59) Bortolomeazzi, R.; Berno, P.; Pizzale, L.; Conte, L. S. Sesquiterpene, Alkene, and Alkane Hydrocarbons in Virgin Olive Oils of Different Varieties and Geographical Origins. *J. Agric. Quimica Alimentaria.* **2001**, *49*, 3278–3283.
- (60) Jirovetz, L.; Buchbauer, G.; Stoyanova, A.; Balinova, A.; Guangjiun, Z.; Xihan, M. Solid phase microextraction/gas chromatographic and olfactory analysis of the scent and fixative properties of the essential oil of *Rosa damascena* L. from China. *Flavour Fragrance J.* **2005**, *20*, 7–12.
- (61) Chisholm, M. G.; Jell, J. A.; Cass, D. M., Jr. Characterization of the major odorants found in the peel oil of *Citrus reticulata* Blanco cv. Clementine using gas chromatography-olfactometry. *Flavour Fragrance J.* **2003**, *18*, 275–281.
- (62) Ollé, D.; Baumes, R. L.; Bayonove, C. L.; Lozano, Y. F.; Sznaper, C.; Brillouet, J.-M. Comparison of free and glycosidically linked volatile components from polyembryonic and monoembryonic mango (*Mangifera indica* L.) cultivars. *J. Agric. Food Chem.* **1998**, *46*, 1094–1100.
- (63) Kim, T. H.; Thuy, N. T.; Shin, J. H.; Baek, H. H.; Lee, H. J. Aroma-active compounds of miniature beefsteak plant (*Mosla dianthera* Maxim.). *J. Agric. Food Chem.* **2000**, *48*, 2877–2881.
- (64) Mahajan, S. S.; Goddik, L.; Qian, M. C. Aroma Compounds in Sweet Whey Powder. *J. Dairy Sci.* **2004**, *87*, 4057–4063.
- (65) Ebrahim Sajjadi, S.; Eskandari, B. Chemical constituents of the essential oil of *Nepeta oxyodonta*. *Chem. Nat. Compd.* **2005**, *41*, 175–177.
- (66) Gauvin, A.; Ravaomanarivo, H.; Smadja, J. Comparative analysis by gas chromatography-mass spectrometry of the essential oils from bark and leaves of *Cedrelopsis grevei* Baill, an aromatic and medicinal plant from Madagascar. *J. Chromatogr. A* **2004**, *1029*, 279–282.
- (67) Kjeldsen, F.; Christensen, L. P.; Edelenbos, M. Changes in volatile compounds of carrots (*Daucus carota* L.) during refrigerated and frozen storage. *J. Agric. Food Chem.* **2003**, *51*, 5400–5407.
- (68) Gancel, A.-L.; Ollitrault, P.; Froelicher, Y.; Tomi, F.; Jacquemond, C.; Luro, F.; Brillouet, J.-M. Leaf volatile compounds of six citrus somatic allotetraploid hybrids originating from various combinations of lime, lemon, citron, sweet orange, and grapefruit. *J. Agric. Food Chem.* **2005**, *53*, 2224–2230.
- (69) Maric, S.; Jukic, M.; Katalinic, V.; Milos, M. Comparison of chemical composition and free radical scavenging ability of glycosidically bound and free volatiles from Bosnian pine (*Pinus heldreichii* Christ. var. *leucodermis*). *Molecules* **2007**, *12*, 283–289.
- (70) Mazzoni, V.; Tomi, F.; Casanova, J. A daucane-type sesquiterpene from *Faucus carota* seed oil. *Flavour Fragrance J.* **1999**, *14*, 268–272.
- (71) Le Quere, J.-L.; Latrasse, A. Composition of the Essential Oils of Blackcurrant Buds (*Ribes nigrum* L.). *J. Agric. Food Chem.* **1990**, *38*, 3–10.
- (72) Paolini, J.; Muselli, A.; Bernardini, A.-F.; Bighelli, A.; Casanova, J.; Costa, J. Thymol derivatives from essential oil of *Doronicum corsicum* L. *Flavour Fragrance J.* **2007**, *22*, 479–487.
- (73) Stevanovic, T.; Garneau, F.-X.; Jean, F.-L.; Gagnon, H.; Vilotic, D.; Petrovic, S.; Ruzic, N.; Pichette, A. The essential oil composition of *Pinus mugo* Turra from Serbia. *Flavour Fragrance J.* **2005**, *20*, 96–97.
- (74) Paolini, J.; Costa, J.; Bernardini, A. F. Analysis of the essential oil from the roots of *Eupatorium cannabinum* subsp. *corsicum* (L.) by GC, GC-MS and ¹³C-NMR. *Phytochem. Anal.* **2007**, *18*, 235–244.
- (75) Stashenko, E. E.; Prada, N. Q.; Martínez, J. R. HRGC/FID/NP and HRGC/MSD study of Colombian Ylang-Ylang (*Cananga odorata*) oils obtained by different extraction techniques. *J. High Resolut. Chromatogr.* **1996**, *19*, 353–358.
- (76) Bendiabdallah, A.; El Amine Dib, M.; Djabou, N.; Allali, H.; Tabti, B.; Muselli, A.; Costa, J. Biological activities and volatile constituents of *Daucus muricatus* L. from Algeria. *Chem. Cent. J.* **2012**, *6*, 48.
- (77) Kabouss, A. E.; Charrouf, Z.; Faid, M.; Garneau, F.-X.; Collin, G. Composición química y actividad antimicrobiana del aceite esencial de hoja de *Argania spinosa* L. Skeels. *J. Essent. Oil Res.* **2002**, *14*, 147–149.
- (78) Petrakis, P. V.; Tsitsimpikou, C.; Tzakou, O.; Couladis, M.; Vagias, C.; Roussis, V. Needle volatiles from five *Pinus* species growing in Greece. *Flavour Fragrance J.* **2001**, *16*, 249–252.
- (79) Cavalli, J.-F.; Tomi, F.; Bernardini, A.-F.; Casanova, J. Composition and chemical variability of the bark oil of *Cedrelopsis grevei* H. Baillon from Madagascar. *Flavour Fragrance J.* **2003**, *18*, 532–538.
- (80) Yu, E. J.; Kim, T. H.; Kim, K. H.; Lee, H. J. Aroma-active compounds of *Pinus densiflora* (red pine) needles. *Flavour Fragrance J.* **2004**, *19*, 532–537.
- (81) Mondello, L.; Zappia, G.; Cotroneo, A.; Bonaccorsi, I.; Chowdhury, J. U.; Yusuf, M.; Dugo, G. Studies on the essential oil-bearing plants of Bangladesh. Part VIII. Composition of some *Ocimum* oils *O. basilicum* L. var. *purpurascens*; *O. sanctum* L. green; *O. sanctum* L. purple; *O. americanum* L., citral type; *O. americanum* L., camphor type. *Flavour Fragrance J.* **2002**, *17*, 335–340.
- (82) Paolini, J.; Tomi, P.; Bernardini, A.-F.; Bradesi, P.; Casanova, J.; Kaloustian, J. Detailed analysis of the essential oil from *Cistus albidus* L. by combination of GC/RI, GC/MS and ¹³C-NMR spectroscopy. *J. Agric. Res.* **2008**, *22*, 1270–1278.
- (83) Takeoka, G.; Butter, R. G. Volatile constituents of pineapple (*Ananas comosus* [L.] Merr.). *Flavor Chemistry Trends and Developments*; Teranishi, R., Buttery, R. G., Shahidi, F., Eds.; American Chemical Society: Washington, DC, 1989; pp 223–237.
- (84) Zouari, N.; Ayadi, I.; Fakhfakh, N.; Rebai, A.; Zouari, S. Variations of chemical composition of essential oils in wild populations of *Thymus algeriensis* Boiss. et Reut., a North African endemic species. *Lipids Health Dis.* **2012**, *11*, 28.
- (85) Chagonda, L. S.; Makanda, C. D.; Chalchat, J.-C. The essential oils of *Ocimum canum* Sims (basilic camphor) and *Ocimum urticifolia* Roth from Zimbabwe. *Flavour Fragrance J.* **2000**, *15*, 23–26.
- (86) Singh, B.; Kumar, R.; Bhandari, S.; Pathania, S.; Lal, B. Volatile constituents of natural *Boswellia serrata* oleo-gum-resin and commercial samples. *Flavour Fragrance J.* **2007**, *22*, 145–147.
- (87) Mardarowicz, M.; Wianowska, D.; Dawidowicz, A. L.; Sawicki, R. Comparison of terpene composition in Engelmann Spruce (*Picea engelmannii*) using hydrodistillation, SPME and PLE. *Zeitschrift für Naturforschung C* **2004**, *59*, 641–648.
- (88) Choi, H.-S. Headspace analyses of fresh leaves and stems of *Angelica gigas* Nakai, a Korean medicinal herb. *Flavour Fragrance J.* **2006**, *21*, 604–608.
- (89) Miyazawa, M.; Kawauchi, Y.; Utsumi, Y.; Takahashi, T. Character impact odorants of wild edible plant - *Cacalia hastata* L. var. *orientalis* - used in Japanese traditional food. *J. Oleo Sci.* **2010**, *59*, 527–533.
- (90) Sabulal, B.; Dan, M.; Anil, J. J.; Kurup, R.; Pradeep, N. S.; Valsamma, R. K.; George, V. Caryophyllene-rich rhizome oil of *Zingiber nimmonii* from South India: Chemical characterization and antimicrobial activity. *Phytochemistry* **2006**, *67*, 2469–2473.
- (91) Flamini, G.; Cioni, P. L.; Morelli, I. Essential oils of *Galeopsis pubescens* and *G. tetrahit* from Tuscany (Italy). *Flavour Fragrance J.* **2004**, *19*, 327–329.

- (92) Minh Tu, N. T.; Thanh, L. X.; Une, A.; Ukeda, H.; Sawamura, M. Volatile constituents of Vietnamese pummelo, orange, tangerine and lime peel oils. *Flavour Fragrance J.* **2002**, *17*, 169–174.
- (93) Stashenko, E. E.; Torres, W.; Morales, J. R. M. A study of the compositional variation of the essential oil of ylang-ylang (*Cananga odorata* Hook Fil. et Thomson, forma genuina) during flower development. *J. High Resolut. Chromatogr.* **1995**, *18*, 101–104.
- (94) Shimoda, M.; Yoshimura, Y.; Yoshimura, T.; Noda, K.; Osajima, Y. Volatile flavor compounds of sweetened condensed milk. *J. Food Sci.* **2001**, *66*, 804–807.
- (95) Vedernikov, D. N.; Roshchin, V. I. Extractive compounds of Birch Buds (*Betula pendula* Roth.): I. Composition of fatty acids, hydrocarbons, and esters. *Russ. J. Bioorg. Chem.* **2010**, *36*, 894–898.
- (96) Iscan, G.; Kirimer, N.; Kurkcuoglu, M.; Arabaci, T.; Küpelı, E.; Can Başer, K. H. Biological Activity and Composition of the Essential Oils of *Achillea schischkinii* Sosn. and *Achillea aleppica* DC. subsp. *aleppica*. *J. Agric. Food Chem.* **2006**, *54*, 170–173.
- (97) Zheng, Y.; White, E. *Retention Data; NIST Mass Spectrometry Data Center*, 2008.
- (98) Zaikin, V. G.; Borisov, R. S. Chromatographic-mass spectrometric analysis of Fischer–Tropsch synthesis products. *J. Anal. Chem.* **2002**, *57*, 544–551.
- (99) Brenna, E.; Fuganti, C.; Serra, S. Enantioselective Perception of Chiral Odorants. *Tetrahedron: Asymmetry* **2003**, *14*, 1–42.
- (100) Lis-Balcin, M.; Ochocka, R. J.; Deans, S. G.; Asztemborska, M.; Hart, S. Differences in bioactivity between the enantiomers of α -pinene. *J. Essent. Oil Res.* **1999**, *11*, 393–397.
- (101) Van den Dool, H.; Kratz, P. D. A Generalization of the Retention Index System Including Linear Temperature Programmed Gas–Liquid Partition Chromatography. *J. Chromatogr.* **1963**, *11*, 463–471.
- (102) Gilardoni, G.; Matute, Y.; Ramírez, J. Chemical and Enantioselective Analysis of the Leaf Essential Oil from *Piper coruscans* Kunth (Piperaceae), a Costal and Amazonian Native Species of Ecuador. *Plants* **2020**, *9*, 791.
- (103) De Saint Laumer, J. Y.; Cicchetti, E.; Merle, P.; Egger, J.; Chaintreau, A. Quantification in Gas Chromatography: Prediction of Flame Ionization Detector Response Factors from Combustion Enthalpies and Molecular Structures. *Anal. Chem.* **2010**, *82*, 6457–6462.
- (104) Tissot, E.; Rochat, S.; Debonneville, C.; Chaintreau, A. Rapid GC–FID quantification technique without authentic samples using predicted response factors. *Flavour Fragrance J.* **2012**, *27*, 290–296.