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HS-SPME-GC/MS analysis of the volatile components of the resins of different *Commiphora* Jacq. Species collected in Socotra Island

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ABSTRACT

In this paper, the volatile phytochemical pattern of the resins of five *Commiphora* Jacq. species collected in Socotra Island was reported. Different populations were studied, some of which for the first time, by using head space-solid phase microextraction (HS-SPME) sampling technique to collect the volatiles emitted from these species. All the captured volatile compounds in the accessions were identified and quantified by means of Gas-Chromatography/Mass Spectrometry (GC/MS). The obtained results highlighted the presence of terpene compounds, mainly monoterpenes and sesquiterpenes, which followed a different trend among the studied species in accordance with the ecology of the collection areas of the species. Sesquiterpenes were predominant in *C. bunifons* and *C. parvifolia*, whereas oxygenated monoterpenes were predominant in *C. socotrana*. A high number of the so-called other volatile compounds were found in *C. planifrons*. The dominant compounds were γ -cadinene in both accessions of *C. kua*, β -eudesmol in the first accession of *C. parvifolia*, terpinen-4-ol in both accessions of *C. socotrana*. The meaning of the data was considered under the chemophenetic, ecological and ethnobotanical aspects.

1. Introduction

Commiphora Jacq. is a genus of dicotyledon Angiosperm plants included in the Bursearaceae family and comprising around 200 species (www.worldfloraonlie.org. Lastly consulted in May 2024). They are shrubs or trees which are mainly distributed in sub-tropical Africa, India, Arabian Peninsula and South America and are characterized by pinnately compound leaves, an exfoliating bark, succulent stems, dioecious flowers, and drupes (Gillett et al., 1991). Many species of the genus can exude an aromatic resin from the stems when cut and this dried resin, generally called myrrh, has an important economic value since it is widely employed for fragrances due to its pleasant smell and for medicinal purposes due to its antiseptic, wound healing, emmenagogue, hypolipidemic, analgesic, antitumoral, antioxidant, antidiabetic, cardioprotective, hepatoprotective, antiulcer and anti-inflammatory properties (Shen et al., 2012; El et al., 2003; La et al., 2023). There are several

works in the literature on the analysis of the chemical components of these species reporting the presence of essential oil compounds, aliphatic acid derivatives, diterpenoids, triterpenoids, lignans, flavonoids and carbohydrates (Shen et al., 2012). There are also several works on the phytochemical analysis of the resins derived from Commiphora species evidencing essential oil components, triterpenoids, diterpenoids, lignans, and carbohydrates as well (Dekebo et al., 2021). To date, several authors investigated the volatilome of Commiphora sp. collected in Socotra Island, but essential oils obtained by hydro-distillation or different solvent extracts were analyzed (Madera et al., 2017; Ali et al., 2008; Ulrich et al., 2022; Mothana et al., 2010). For instance, Madêra et al. (Maděra et al., 2017), studied, by means of GC-MS, the volatile components of the methanol extracts of five different species of the genus namely Commiphora kua (R.Br. ex Royle) Vollesen, C. ornifolia (Balf.f.) J.B.Gillett, C. planifrons Engl., C. parvifolia Engl. and C. socotrana Engl. collected in the Socotra Island. In this work,

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the same species collected in Socotra Island were also studied for their resin volatile compositions, but two populations for each species were considered, thus pointing out the possible differences on their contents. In addition, unlike the past, head space-solid phase microextraction (HS-SPME) technique was used as extraction method whereas GC-MS was employed as separation and identification methodology, again. Although distillation and solvent extraction are frequently used, they are time-consuming and can cause thermal degradation of some components (Mame-Marietou et al., 2021). Therefore, HS-SPME has increased its use being a solvent-free sample preparation technology; in fact, it allows the execution of sampling, pre-concentration of the analyte and extraction in a single phase, with zero solvent consumption, minimal invasiveness and without using high amounts of plant to achieve small amounts of final extract. It is well known how the extraction procedure can deeply affect the qualitative and quantitative results of any phytochemical analysis (Rostagno and Prado, 2013) and, therefore, it is extremely important to use different extraction techniques to provide more exhaustive and complete data on the phytochemistry of any plant species. To the best of our knowledge, SPME-GC/MS was applied to Commiphora resins for the first time. A comparison of these results with the previous ones was also performed.

2. Materials and methods

2.1. Plant material

Two accessions of each species *i.e., C. kua* (R.Br. ex Royle) Vollesen, *C. ornifolia* (Balf.f.) J.B.Gillett, *C. planifrons* Engl., *C. parvifolia* Engl. and *C. socotrana* Engl. were considered for this work. These accessions were collected in Socotra Island in April 2023 with geographical coordinates and altitudes taken with a GPS, as reported in Table 1. The botanical identification of the plant species was performed by Dr. Dario La Montagna by comparing their morphological features with those reported in the literature (Gillett et al., 1991; Miller and Morris, 2004a).

2.2. Resin recovery

For each sample, the resin was recovered in glass vials by directly tapping with a knife the tree individuals. The vials were then closed with Teflon caps and sealed with Parafilm until further analysis in order to prevent degradation and loss of volatile compounds. The collection and exportation were approved by the Environment Protection Authority (EPA) of the Republic of Yemen responsible for the Socotra Archipelago.

2.3. HS-SPME extraction

The extraction of the volatile components of the resins was achieved by means of SPME technique followed by GC/MS analysis. Each sample (ca. 0.1 g) was placed individually inside a 7 mL glass vial with PTFEcoated silicone septum and a SPME device from Supelco (Bellefonte, PA) with 1 cm fiber coated with 50/30 μ m DVB/CAR/PDMS (divinylbenzene/carboxen/polydimethylsiloxane), was used to adsorb the

Species	Number of samples	Geographical coordinates	Altitude (a.s.l.)
C. kua	CKA1	12°54′53″ N 53°71′48″ E	57 m
	CKA2	12°53'71" N 53°71'04" E	48 m
C. ornifolia	COA1	12°49'58" N 54°29'49" E	211 m
	COA2	12°61'60" N 53°95'69" E	96 m
C. planifrons	CPS1	12°56'99" N 54°04'39" E	939 m
	CPS2	12°56'93" N 54°04'39" E	926 m
C. parvifolia	CPA1	12°60'18" N 54°16'67" E	100 m
	CPA2	12°60'96" N 54°15'24" E	127 m
C. socotrana	CSA1	12°39'97" N 53°63'78" E	140 m
	CSA2	12°67'08" N 53°62'22" E	291 m

volatiles. After conditioning the fiber, it was exposed to the headspace of the sample for 50 min at 45 °C. Then, for the desorption of the components, the fiber was inserted in the GC injector maintained at 250 °C in spitless mode. Before moving on to the next sample, the fiber was reconditioned to avoid contamination resulting from the previous sampling.

2.4. GC-MS analysis of Commiphora samples

A Clarus 500 model PerkinElmer (Waltham, MA, USA) gas chromatograph equipped with FID (flame detector ionization) and coupled with a single quadrupole mass spectrometer (Clarus 500 model PerkinElmer), was used to carry out the analyses. A capillary column (Varian Factor Four VF-1; 60 m \times 0.32 mm ID, DF = 1.0 μ m) was housed in the GC oven whose programmed temperature was set initially at 50 °C then a gradient of 6 °C/min to 220 °C for 15 min. The injector GC was set at 250 °C. Helium was used as carrier gas at a constant rate of 1 mL/min. MS detection was performed with electron ionization (EI) at 70 eV operating in the full-scan acquisition mode in the m/z range 35-550 amu. To identify the volatile compounds, the MS-fragmentation pattern obtained was compared with those of pure components stored in the NIST11 mass spectra library database. Further, the Linear Retention Indices (LRIs) were calculated using a mixture of n-alkanes (C₈-C₃₀) aliphatic hydrocarbons), injected into both polar (Restex Stabilwax) and apolar columns under the same operating conditions. GC-FID (flameionization detector) analysis was performed using the apolar column as described for the GC-MS measurements. The relative amounts of the components were expressed as percent peak area relative to total peak area without the use of an internal standard and any factor correction. The analysis was carried out in triplicate.

2.5. Statistical analysis

All results were expressed as means \pm standard deviation (SD) and the Anova test (One-way analysis of variance test) followed by Tukey's HSD test was used to analyze significant differences among means (p < 0.01).

3. Results and discussion

By HS-SPME/GC-MS chemical analyses the volatile chemical profile of *Commiphora* resin samples according to the accessions, was described (Table 2).

The volatile compounds composition of the resins resulted to be quite similar between the two studied accessions but quite different among the studied species. No compound was evidenced in all the species whereas the same compounds were generally reported in the different accessions of the same species. The dominant compounds were γ -cadinene in both accessions of C. kua, β -eudesmol in the first accession of C. ornifolia and δ -cadinene in its second accession, limonene in both accessions of both C. planifrons and C. parvifolia, terpinen-4-ol in both accessions of C. socotrana. On the other hand, the least abundant compounds were germacrene D in the first accession of C. kua and α-pinene in its second accession; 3,4-dimethyl-1,5-hexadiene-3,4-diol, along with δ -cadinol in the first accession of *C. ornifolia* and lilac aldehyde A along with γ -cadinene in its second accession, six compounds in traces (2,4dimethyl-heptane, trans-p-mentha-2,8-diene-1-ol, terpinen-4-ol, a-gurjunene, γ -muurolene, α -selinene) in the first accession of *C. planifrons* and humulene along with humulene epoxide in its second accession, γ -cadinene in the first accession of C. parvifolia and α -farnesene in its second accession, α -cubebene along with (-)- β -bourbonene and β -curcumene in the first accession of *C. socotrana* and (-)- β -bourbonene along with β -caryophyllene and β -curcumene in its second accession. A higher similarity between the specific accessions was observed for the dominant compounds rather than the least abundant ones but this is normal from a statistical point of view. No new compound in absolute was

Table 2

Chemical composition (percentages mean values \pm standard deviation) of *Commiphora* samples.

Components	LRI ^a	LRI ^b	LRI ^c	LRI ^d	Commiphora kua		ua Commiphora ornifolia		Commiphora planifrons		Commiphora parvifolia		Commiphora socotro	
					CKA1	CKA2	COA1	COA2	CPS1	CPS2	CPA1	CPA2	CSA1	CSA2
n-heptane	712	700	720	717	$0.9 \pm 0.03^{\rm a}$	-	-	-	$28.4 \pm 0.0223^{ m b}$	$25.4 \pm 0.121^{\circ}$	-	-	-	-
n-octane	805	800		nd	-	-	-	-	0.1 ± 0.02	-	-	-	-	-
neo-pentyl acetate	814	816		nd	-	-	-	-	-	-	$\begin{array}{c} 0.8 \pm \\ 0.03 \end{array}$	-	-	-
2,4-dimethyl- heptane	832	837		nd	-	-	-	-	Tr	-	-	-	-	-
3-methyl- cyclopentyl acetate	900	904		nd	-	-	$\begin{array}{c} 3.6 \pm \\ 0.022^a \end{array}$	$\begin{array}{l} \textbf{4.1} \pm \\ \textbf{0.022}^{b} \end{array}$	-	-	-	-	-	-
nonane	911	916		nd	-	-	-	-	$\frac{11.6 \ \pm}{0.0711^{\rm a}}$	$\begin{array}{c} 10.5 \pm \\ 0.0722^b \end{array}$	-	-	-	-
α-thujene	921	923	1020	1015	-	-	-	-	$\begin{array}{c} \textbf{0.4} \pm \\ \textbf{0.02^a} \end{array}$	$\begin{array}{c} 0.2 \ \pm \\ 0.01^{b} \end{array}$	-	-	$0.3 \pm 0.02^{\mathrm{a}}$	$0.4 \pm 0.02^{\mathrm{a}}$
α-pinene	938	942	1025	1021	-	$\begin{array}{c} 1.2 \pm \\ 0.021^{a} \end{array}$	-	-	$\begin{array}{c} 0.3 \pm \\ 0.02^{b} \end{array}$	$\begin{array}{c} 0.5 \ \pm \\ 0.02^{\rm c} \end{array}$	-	-	-	-
β -thujene	965	968	1115	1110	-	-	$\begin{array}{c} 1.5 \pm \\ 0.023^{a} \end{array}$	-	$\begin{array}{c} 13.2 \pm \\ 0.063^{b} \end{array}$	${\begin{array}{c} 11.6 \pm \\ 0.0812^{c} \end{array}}$	-	$\begin{array}{c} 1.6 \ \pm \\ 0.041^a \end{array}$	-	$0.2 \pm 0.01^{ m d}$
β -myrcene	984	987	1156	1150	-	-	-	-	$\begin{array}{c} 0.8 \pm \\ 0.02^{\rm a} \end{array}$	$\begin{array}{c} 0.4 \ \pm \\ 0.02^{b} \end{array}$	-	-	-	$\begin{array}{c} 0.2 \pm \\ 0.02^{\rm c} \end{array}$
limonene	1020	1023	1191	1187	$\begin{array}{c} 0.7 \ \pm \\ 0.02^a \end{array}$	$\begin{array}{c} 2.9 \ \pm \\ 0.034^b \end{array}$	$13.7 \pm 0.0911^{\circ}$	${\begin{array}{c} 9.1 \ \pm \\ 0.081^{d} \end{array}}$	36.4 ± 1.21^{e}	$\begin{array}{c} \textbf{45.7} \pm \\ \textbf{2.51}^{\mathrm{f}} \end{array}$	93.8 ±	$\begin{array}{c} 92.2 \pm \\ 9.23^{hg} \end{array}$	-	-
1.9 gipcolo	1020	1022	1010	1206					01		8.12 ^g		47	FOL
1,8-спіебіе	1026	1035	1210	1200	-	-	-	-	0.1 ± 0.02^{a}	-	-	-	4.7 ± 0.032^{b}	0.02 ^c
γ -terpinene	1055	1057	1241	1236	-	-	-	-	$\begin{array}{c} 0.2 \pm \\ 0.02^{a} \end{array}$	-	-	-	$\begin{array}{c} 14.1 \pm \\ 0.104^{\mathrm{b}} \end{array}$	${14.2} \pm \\ 0.0611^{\rm cb}$
terpinolene	1075	1076	1280	1273	-	-	-	-	$0.1~\pm$ $0.02^{ m a}$	-	-	-	$\begin{array}{c} \textbf{2.4} \pm \\ \textbf{0.022^b} \end{array}$	$\begin{array}{c} \textbf{2.4} \pm \\ \textbf{0.021}^{cb} \end{array}$
linalool	1078	1082	1530	1536	-	-	-	-	-	-	-	-	$\begin{array}{c} 11.4 \pm \\ 0.0442^{\mathrm{a}} \end{array}$	$\begin{array}{c} 10.4 \pm \\ 0.0442^{\mathrm{b}} \end{array}$
<i>trans-p</i> -mentha- 2,8-diene-1-ol	1100	1103		nd	-	-	-	-	Tr	-	-	-	-	-
undecane	1110	1115		nd	-	-	-	-	$\begin{array}{c} \textbf{0.2} \pm \\ \textbf{0.02} \end{array}$	-	-	-	-	-
1,3,8-p- menthatriene	1116	1118	1410	1401	-	-	-	-	-	-	-	-	$\begin{array}{c} \textbf{2.9} \pm \\ \textbf{0.031^a} \end{array}$	$\begin{array}{c} 3.4 \pm \\ 0.031^{b} \end{array}$
<i>trans</i> -limonene oxide	1120	1125	1450	1445	-	-	-	-	$\begin{array}{c} 0.1 \ \pm \\ 0.01 \end{array}$	-	-	-	-	-
camphor	1124	1126	1490	1485	-	-	-	-	-	-	-	-	$0.5 \pm 0.02^{\mathrm{a}}$	$0.4 \pm 0.02^{\mathrm{a}}$
1-menthone	1140	1142	1505	1500	-	-	-	-	-	-	-	-	$\begin{array}{c} 13.7 \ \pm \\ 0.06122^{a} \end{array}$	$\begin{array}{c} 14.4 \pm \\ 0.0705^{b} \end{array}$
levo-menthol	1149	1150	1620	1618	-	-	-	-	-	-	-	-	11.4 ± 0.0512^{a}	$\begin{array}{c} 13.3 \pm \\ 0.0834^{b} \end{array}$
lilac aldehyde A	1151	1154		nd	-	-	${3.1}\pm {0.053}^{a}$	$\begin{array}{c} 0.7 \pm \\ 0.03^{\mathrm{b}} \end{array}$	-	-	-	-	-	-
terpinen-4-ol	1178	1182	1585	1590	-	-	-	-	Tr	-	-	-	32.01 ± 2.011^{a}	$22.8 \pm 1.101^{\mathrm{b}}$
β -citral	1220	1225	1692	1689	-	-	-	-	-	-	-	-	-	$\begin{array}{c} 3.0 \ \pm \\ 0.02 \end{array}$
a-citral	1282	1287	1731	1725	-	-	-	-	-	-	-	-	-	$\begin{array}{c} \textbf{3.9} \pm \\ \textbf{0.033} \end{array}$
menthol acetate	1292	1294		nd	-	-	-	-	-	-	-	-	$\begin{array}{c} 3.2 \pm \\ 0.042^{\mathrm{a}} \end{array}$	$\begin{array}{c} \textbf{3.6} \pm \\ \textbf{0.044}^{\text{a}} \end{array}$
a-cubebene	1442	1345	1470	1465	-	-	-	-	-	-	$\begin{array}{c} \textbf{0.7} \pm \\ \textbf{0.02} \end{array}$	-	-	-
δ -elemene	1346	1347	1482	1478	$\begin{array}{c} 0.3 \pm \\ 0.02 \end{array}$	-	-	-	-	-	-	-	-	-
α -cubebene	1351	1356		nd	-	-	-	-	-	-	-	-	0.1 ± 0.01^{a}	$0.2 \pm 0.02^{\mathrm{a}}$
iso-ledene	1370	1373		nd	$\begin{array}{c} 0.3 \ \pm \\ 0.02 \end{array}$	-	-	-	-	-	-	-	-	-
a-copaene	1382	1385	1495	1490	1.2 ± 0.032^{a}	-	$3.2 \pm 0.021^{ m b}$	$3.3 \pm 0.064^{\mathrm{b}}$	-	-	-	-	-	-
(–)- β -bourbonene	1388	1390	1515	1510	0.8 ± 0.02^{a}	-	-	-	-	-	1.4 ± 0.051^{b}	-	$0.1 \pm 0.001^{\circ}$	0.1 ± 0.01^{cd}
β -elemene	1410	1406		nd	0.02 0.8 ±	-	-	-	-	-	-	-	-	-
α-gurjunene	1416	1420		nd	0.02 0.4 ± 0.02	-	-	-	Tr	-	-	-	-	-

(continued on next page)

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Table 2 (continued)

Components	LRI ^a	LRI ^b	LRI ^c	LRI ^d	Commiphora kua		Commiphora ornifolia		Commiphora planifrons		Commiphora parvifolia		Commiphora socotrana	
					CKA1	CKA2	COA1	COA2	CPS1	CPS2	CPA1	CPA2	CSA1	CSA2
β -caryophyllene	1418	1421	1591	1585	${\begin{array}{c} 13.6 \ \pm \\ 0.0612^{a} \end{array}}$	$\begin{array}{c} 11.2 \pm \\ 0.054^{b} \end{array}$	${\begin{array}{c} 10.3 \pm \\ 0.0812^{c} \end{array}}$	$\begin{array}{c} 5.0 \ \pm \\ 0.03^d \end{array}$	$3.4 \pm 0.042^{\rm e}$	$\begin{array}{c} 1.9 \ \pm \\ 0.042^{\rm f} \end{array}$	-	-	$\begin{array}{c} \textbf{2.9} \pm \\ \textbf{0.033}^{g} \end{array}$	$\begin{array}{c} 0.1 \ \pm \\ 0.002^{h} \end{array}$
β -cubebebene	1422	1426		nd	$\begin{array}{c} 0.5 \pm \\ 0.02 \end{array}$	_	-	-	-	-	$\begin{array}{c} \textbf{0.4} \pm \\ \textbf{0.02} \end{array}$	-	-	_
humulene	1452	1454	1663	1660	$\begin{array}{c} 3.3 \pm \\ 0.042^a \end{array}$	$\begin{array}{c} 5.4 \pm \\ 0.063^{b} \end{array}$	1.5 ± 0.033^{c}	$\begin{array}{c} 1.3 \pm \\ 0.022^{dc} \end{array}$	$\begin{array}{c} 0.3 \pm \\ 0.02^{\rm e} \end{array}$	$\begin{array}{c} 0.1 \ \pm \\ 0.01^{\rm fd} \end{array}$	$\begin{array}{c} 0.7 \ \pm \\ 0.04^{g} \end{array}$	$\begin{array}{c} 1.5 \pm \\ 0.031^{hc} \end{array}$	-	-
α -guaiene	1456	1458		nd	$\begin{array}{c} 1.9 \pm \\ 0.033 \end{array}$	-	-	-	-	-	-	-	-	-
aromadendrene	1465	1460	1595	1590	$\begin{array}{c} \textbf{2.8} \pm \\ \textbf{0.032}^{a} \end{array}$	$\begin{array}{c} \textbf{4.1} \pm \\ \textbf{0.042}^{b} \end{array}$	$\begin{array}{c} 1.5 \pm \\ 0.022^c \end{array}$	$\begin{array}{c} 1.3 \pm \\ 0.031^{dc} \end{array}$	-	-	-	-	$\begin{array}{c} 0.2 \pm \\ 0.02^{e} \end{array}$	$\begin{array}{c} 1.9 \ \pm \\ 0.033^{f} \end{array}$
germacrene D	1477	1479	1672	1670	$\begin{array}{c} 0.2 \pm \\ 0.02^a \end{array}$	$\begin{array}{c} \textbf{2.2} \pm \\ \textbf{0.023}^{b} \end{array}$	-	$\begin{array}{c} 0.8 \pm \\ 0.02^c \end{array}$	-	-	-	-	-	-
α-muurolene	1479	1480	1691	1695	$\begin{array}{c} \textbf{2.2} \pm \\ \textbf{0.031}^{a} \end{array}$	-	$\begin{array}{c} 1.4 \pm \\ 0.032^{b} \end{array}$	8.9 ± 0.063^{c}	-	-	-	-	-	-
β -eudesmene	1482	1481		nd	-	-	-	-	$0.1 \pm 0.01^{\mathrm{a}}$	-	-	$\begin{array}{c} \textbf{2.7} \pm \\ \textbf{0.032}^{\mathrm{b}} \end{array}$	-	-
γ-muurolene	1487	1486	1683	1679	$\begin{array}{c} \textbf{2.8} \pm \\ \textbf{0.021}^{a} \end{array}$	$3.5 \pm 0.031^{ m b}$	-	-	Tr	-	1.7 ± 0.033^{c}	-	-	-
α -selinene	1490	1489		nd	-	-	-	-	Tr	-	-	-	-	-
α-farnesene	1494	1496		nd	-	-	$0.9 \pm 0.02^{ m a}$	-	-	-	$\begin{array}{c} 0.4 \pm \\ 0.02^{\mathrm{b}} \end{array}$	$\begin{array}{c} 0.9 \ \pm \\ 0.02^{\rm a} \end{array}$	-	-
β-curcumene	1500	1503		nd	-	-	-	-	-	-	-	-	0.1 ± 0.01^{a}	$0.1 \pm 0.001^{\rm a}$
δ-cadinene	1510	1509	1751	1746	-	-	3.3 ± 0.044^{a}	49.1 ± 2.25^{b}	-	-	-	-	-	-
7-epi- α -selinene	1525	1526		nd	-	-	-	1.8 ± 0.031	-	-	-	-	-	-
α-calacorene	1528	1530		nd	-	-	$1.0 \pm 0.02^{ m a}$	$1.5 \pm 0.032^{\mathrm{b}}$	-	-	-	-	-	-
elemol	1531	1535		nd	-	-	-	-	$\begin{array}{c} 0.2 \pm \\ 0.02 \end{array}$	-	-	-	-	-
γ-cadinene	1538	1536	1758	1755	46.7 ± 6.20 ^a	57.0 ± 7.50^{b}	-	0.7 ± 0.04 ^c	-	-	0.1 ± 0.01^{d}	1.1 ± 0.031^{e}	-	-
α-cadinene	1545	1542		nd	3.0 ± 0.02	-	-	-	-	-	-	-	-	_
nerolidol	1563	1565	1000	nd	-	-	1.7 ± 0.033 ^a	$0.9 \pm 0.02^{\mathrm{b}}$	-	-	-	-	-	_
oxide	1578	1580	1980	1975	1.0 ± 0.01^{a}	12.5 ± 0.0821^{b}	6.2 ± 0.041 ^c	1.6 ± 0.041^{d}	0.9 ± 0.03^{a}	0.5 ± 0.03^{e}	-	-	-	_
numulene epoxide	1690	1593		na	-	-	-	-	0.1 ± 0.001^{a}	0.1 ± 0.001^{a}	-	-	-	-
epicubenoi	1620	1618	0100	na	2.4 ± 0.022	-	-	-	-	-	-	-	-	-
τ-cadinol	1622	1625	2193	2191 nd	14.2 ± 0.0412	-	-	-	-	-	-	-	-	-
o-cadilloi	1620	1620		nd	-	-	0.8 ± 0.02^{a}	1.4 ± 0.031^{b}	-	-	-	-	-	-
γ-eudesmor	1631	1630		na	-	-	-	-	0.1 ± 0.01	-	-	-	-	-
	1045	1652	0102	2179	-	-	-	-	0.2 ± 0.02	-	-	-	-	-
	1651	1650	2105	2176	-	-	9.2 ± 0.053^{a}	0.072 ^b	0.02 ^c	0.02 ^{dc}	-	-	-	-
p-eudesmoi	1051	1059	2208	2200	-	-	19.0 ± 0.101^{a}	2.4 ± 0.022^{b}	1.9 ± 0.032^{c}	$2.5 \pm 0.042^{\rm db}$	-	-	-	-
α -terpinene	2005	2001	2225	2220	-	-	11.3 ± 0.0511^{a}	0.9 ± 0.02^{b}	-	-	-	-	-	-
andrographolide	2031	e	2035	2630	-	-	5.4 ± 0.043^{a}	1.4 ± 0.023^{b}	$0.1 \pm 0.02^{\circ}$	-	-	-	-	-
Monoterpenes					100.0 0.7	100.0 4.1	100.0 15.2	9.1	99.9 51.4	100.0 58.4	93.8	100.0 93.8	100.0 19.7	20.8
Monoterpenes					-	-	-	-	0.2	-	0.7	-	76.9	76.8
Sesquiterpenes Oxygenated					80.8 17.6	83.4 12.5	23.1 37.5	73.7 10.1	3.8 4.1	2.0 3.7	4.7 -	6.2 -	3.4 -	2.4
Sesquiterpenes Diterpenes					_	_	5.4	1.4	0.1	-	-	_	-	_
Others					0.9	-	18.8	5.7	40.3	35.9	0.8	-	-	-

^a Linear Retention indices were measured on apolar column.
 ^b Linear Retention indices from literature for apolar column.
 ^c Linear Retention indices were measured on polar column.
 ^d Linear Retention indices from literature for polar column.

^e Linear Retention Index not available; -: not detected; tr: percentage mean values < 0.1%. Data are means \pm standard deviation of three (n = 3) replicates. Means with different letters, between the columns, are significant different (at a p < 0.01 significance level).

evidenced during this study. Even better, the reported compounds are quite common in nature, having been reported in several species belonging to different families like Lamiaceae, Araucariaceae, Apiaceae and Asteraceae (Frezza et al., 2019, 2020; Spinozzi et al., 2021; Benvenuti et al., 2017). For what concerns the classes of volatile compounds, sesquiterpenes were predominant in C. kua and in part in C. ornifolia, whereas monoterpenes were predominant in C. planifrons and C. parvifolia and oxygenated monoterpenes were predominant in C. socotrana. A high number of the so-called other volatile components were found in C. planifrons. These results are perfectly in accordance with the ecology of the collection areas of the species. In fact, Socotra is an island which is deeply hit by summer and winter monsoons that bear extremely strong and dry winds along with intense but short-lived precipitations, creating an arid environment in the lowland areas and a fresher environment in the mountainous regions where the aridity is mitigated by light rainfall, drizzle, and humidity. These conditions significantly affect the type of plants that can grow on this island as well as the surrounding environment of their growth areas under different aspects and, as a consequence, the phytochemical patterns of these plants as already demonstrated (Li et al., 2020; Moore et al., 2014). This is because plants must develop physiological and biochemical adaptation strategies to cope with any stress condition to survive. In the context of Socotra Island, intense sunlight, high temperatures, and limited water availability represent the stress conditions as already reported and the plants biochemically react to this by modifying the normal biosynthesis and accumulation of classes of natural compounds like phenolics including flavonoids and terpenoids including monoterpenes, sesquiterpenes, diterpenes, and their oxygenated derivatives (Yang et al., 2018). Phenolics are non-volatile compounds and are not considered in this paper. Indeed, for what concerns the terpenes, the presence of major amounts of sesquiterpenes in C. kua and the second accession of C. ornifolia collected at lower altitudes may be simply explained by the need for the two accessions to biosynthesize compounds which can provide a higher defense against thermal stress, herbivores and pathogens (Ibrahim et al., 2010; Schaub et al., 2010). The latter ones are the targets for which these species are also ethnobotanically employed, especially to treat eczema (Miller and Morris, 2004b). On the other hand, the first accession of C. ornifolia does not extremely need this accumulation and, in fact, the amount of this kind of compounds is sensibly lower. In this case, oxygenated sesquiterpenes were predominant but these compounds are also important since they are well known to exert antimicrobial and anti-inflammatory effects which are very useful to prevent infections in plant wounds, a significant risk in arid conditions (Ogundajo et al., 2021). This thing is also reflected in the ethnobotanical uses of this species by local populations who use its bark and resin to also heal infected wounds and toothache (Miller and Morris, 2004b; Gostel et al., 2016). The three species C. parvifolia, C. planifrons and C. socotrana are related from a morphological standpoint. In fact, they exhibit similar characteristics and likely belong to the same infrageneric clade "Spinescens" (Zuo et al., 2017) even though further phylogenetic analyses are needed to confirm this. Indeed, under the biochemical standpoint, they show high levels of monoterpenes and oxygenated monoterpenes which are helpful to facilitate cooling and to lower the leaf temperature (Abdelgaleil et al., 2021). This is extremely reasonable for C. parvifolia and C. socotrana which were collected at low altitudes, but this is apparently not for C. planifrons since its accessions were collected at high altitudes. Actually, also this high accumulation of monoterpenes in this species is reasonable but that may be explained by the increased solar radiation that hits it. In addition, both accessions of this species accumulated high amounts of saturated aliphatic chains which are not peculiar and have no pharmacological or ecological interest. In C. socotrana, it is worthy to note the high presence of oxygenated monoterpenes which are the predominant class here and

their accumulation clearly reflects the local uses of the plant. In fact, oxygenated monoterpenes have the function as insecticides and protect the plant from pest attacks (Ramawat et al., 2007) for which the branches of this species are locally burned to produce dense smoke to ward off pests from cattle and goats (Miller and Morris, 2004b; Ogundajo et al., 2021). On the other hand, C. parvifolia and C. planifrons resins are eaten by local people for their sweet taste during famine (Miller and Morris, 2004b) and this is perfectly associated with the high presence of monoterpenoids (Priya et al., 2011). With respect to the previous work by Madera et al. (Maděra et al., 2017), who utilized a different extraction method as already reported, some similarities from the qualitative point of view were observed but also many differences. In particular, the analyzed samples contained on average only 38% monoterpenes and 51% sesquiterpenes. No hydrocarbons were found. The compounds with the highest percentage values were β -eudesmol, α -cadinol, terpinen4-ol, limonene, α -humulene, p-cymene, phytol and α -thujene. Further, we detected some compounds not reported in the previous work; in particular, the sesquiterpene humulene present in almost all the investigated samples, L-menthone and levo-menthol present with percentage mean values higher than 10% in two of our samples and also the labdane diterpenoid andrographolide which ranged from 0.1% to 5.4%.

Most of the identified compounds in this study including all the classes of volatile compounds have not been previously evidenced in that study. On the other hand, some compounds reported in that study were not identified in this one. For what concerns the common compounds, some differences under the quantitative standpoint could also be observed. All these discrepancies can be explained by the different extraction methodologies adopted as well as by intrinsic and extrinsic factors such as the environment (Rostagno and Prado, 2013; Ramawat et al., 2007). A recent study on *Boswellia elongata*, a species from Socotra Island and a member of the same family as *Commiphora*, demonstrates that environmental factors can significantly influence resin composition (Tulková et al., 2024), supporting the role of external conditions in shaping volatile compounds. Therefore, further studies considering all these aspects are therefore necessary to precisely verify the reasons behind these different composition profiles.

4. Conclusions

The first HS-SPME-GC/MS analysis on the resins of five *Commiphora* species collected in Socotra Island evidenced the presence of several volatile compounds belonging to different classes such as, monoterpenes, sesquiterpenes and diterpenes where the monoterpene limonene, and the sesquiterpene β -caryophyllene and humulene were the components detected in almost all the investigated species. The evaluation of the phytochemical results allowed us to notice a big qualitative and quantitative difference from a previous study utilizing another extraction method as well as a strict correlation between the phytochemistry and the ecology of the species. Moreover, the presence of these volatile compounds could provide some phytochemical rationales for the ethnobotanical uses of some species. Yet, further studies are necessary to confirm these whole results under the different aspects.

CRediT authorship contribution statement

Dario La Montagna: Writing – review & editing, Writing – original draft, Resources. Daniela De Vita: Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation. Claudio Frezza: Writing – review & editing, Writing – original draft, Investigation. Stefania Garzoli: Writing – review & editing, Writing – original draft, Methodology, Investigation, Formal analysis. Fabio Attorre: Writing – review & editing, Writing – original draft, Supervision, Resources, Project administration.

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.bse.2025.104965.

Data availability

Data will be made available on request.

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