Variability of essential oil composition of wormwood (*Artemisia absinthium* L.) affected by plant organ

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Abstract

The essential oil composition of leaves and roots of twenty individuals of wormwood (*Artemisia absinthium* L.) belonging to different chemotypes has been investigated. They were obtained from two accesions coming from Hungarian and Spanish wild populations. Essential oils were extracted by hydrodistillation and analyzed by GC/MS and GC/FID.

Results showed a great individual variability of wormwood accesions. Based on leaves, three chemotypes (sabinene+myrcene, β-thujone and new sesquiterpene type accounting up to 80.8 % of sesquiterpenic fraction) were found in the Hungarian population and two chemotypes ((*Z*)-β-epoxyocimene and (*Z*)-β-epoxyocimene + (*Z*)-chrysanthemyl acetate types) were present in the Spanish one. The composition of EO of the roots from both locations was predominated by monoterpenic esters (14.5–80.2 % and 59.9-90.3 %, in Hungarian and Spanish samples respectively) but characteristic quantitative and qualitative differences were present. No relationship was found between the composition of EO of roots and leaves of the same plant.

Keywords: *Artemisia absinthium*, essential oil, chemotype, individual variation, thujone, chrysanthemyl acetate, epoxyocimene.

1. Introduction

Artemisia absinthium L. has been a valued plant species for ages because of different bioactivity aspects related to folk medicine and agricultural purposes (1). It is widely distributed in Europe and already introduced in other continents. In the early 90's it gained an adverse "reputation" due to its thujone content and mutual side effects associated with absinthism, even though they could not have been proven (2). The composition of the essential oil has been studied by several authors who highlighted that large amounts of thujones are characteristic only for one of the many chemotypes. Beside bicyclic and irregular monoterpenes mainly terpenoids of thujane skeleton and, in some cases, those of pinane skeleton are present in highest abundance in the oil (table 1). No correlation between main component and geographical distribution of the chemotype could be really established until now.

The majority of the chemotypes reported in the literature are based on four compounds: (*Z*)-β-epoxyocimene, (*Z*)-chrysanthemyl acetate, sabinyl acetate and β-thujone. Each one of them may determine a "pure" chemotype, but considering these compounds "mixed" ones have been defined as well. In the Iberian Peninsula Ariño (3) reported seven chemotypes based on three of the above mentioned main compounds: (A) (*Z*)-β-epoxyocimene; (B) (*Z*)-β- epoxyocimene + (*Z*)-chrysanthemyl acetate; (C) (*Z*)-chrysanthemyl acetate; (D) (*Z*)-β-epoxyocimene + β-thujone; (E) (Z)-β-epoxyocimene + (Z)-chrysanthemyl acetate + β-thujone; (F) (*Z*)-chrysanthemyl acetate + β-thujone and (G) β- thujone.

Table 1. Main chemotypes in *Artemisia absinthium* L. according references

Very few data are available about the essential oil composition of *Artemisia absinthium* roots. In earlier research reports (13, 14) high levels of monoterpenic hydrocarbons (α-fenchene, mainly) and monoterpenic esters have been reported. The spectrum of the oil seems to show organic differences even inside a single plant (8). Blagojevic et al. (15) reported the chemical profile of the roots in a population which - according to the aerial parts - belonged to β-thujone chemotype. The root oil, however, was characterized by a large

proportion of monoterpenic esters and hydrocarbons. Regardless of some differences related to the structure of monoterpenic esters, a similar composition was found by Llorens-Molina and Vacas (16) in a more recent study on seasonal variations in essential oil from roots belonging to the above mentioned A and B chemotypes from Spain. Nevertheless, no data are available concerning the relationships between composition of EO of roots and leaves of plants belonging to other chemotypes. In many species, a single population is practically a mixture of individuals belonging to different chemotypes (17). However, intra-population variability of wormwood accessions has only been studied in exceptional cases. Llorens-Molina et al. (18) presented the common occurrence of two well distinguishable chemotypes ((*Z*)-β-epoxyocimene (> 70% of the essential oil) and (*Z*)-β-epoxyocimene (60-70%) with (*Z*)-chrysanthemyl acetate (10-20%)) in a wild habitat in Spain. The two chemically - and presumably also genetically - distinct groups of individuals are distinguishable only by EO analysis and do not show any external marker traits.

Similarly, a recent study of a Hungarian accession revealed the wide diversity of wormwood oil composition at level of individual plants. β-thujone was the main component in 53% of the plants in this population, but in nine plants this compound had been found only in traces. The second and third most abundant components were β-myrcene and sabinene respectively, both being main compounds in 13% of the samples. Besides, in 20% of the oils, they were found in approximately equal proportions (19). It can be concluded that only individual monitoring can assure reliable results because of the obvious differences among plants of the same population.

In order to detect sources of chemodiversity in *A. absinthium* the objective of our recent investigation was focusing on the variability of the essential oil composition studying the chemical profiles of essential oils both from leaves and roots of wormwood in parallel. For this trial, individuals of two distant populations of Hungarian and Spanish origin were chosen.

2. Material and Methods

2.1. Growing conditions

The experiment was carried out in 2013 in two locations: Calamocha, Spain (40º 26’N, 6º 43’W) and Budapest (47°54’N, 19°14’E), Hungary. The territory in Calamocha has a rural vegetation, the soil is a calcareous, stony one. In Budapest, the cultivation field has a poor, sandy soil.

Two different accessions were investigated. The Spanish population is a wild growing one originating from a spontaneous habitat (Teruel). The Hungarian population is a genebank accession, collected formerly from wild habitat (Alföld) and maintained at the Department of Medicinal and Aromatic Plants (Corvinus University) in Budapest. The voucher specimens from both the Hungarian (Nr. ASTART7h) and Spanish (Nr. ASTART8h) populations are kept at the Dept. of Medicinal and Aromatic Plants of the Corvinus University, Budapest.

2.2. Plant material and sampling

In the study on compositional characteristics of different plant organs, ten perennial individuals of both accessions were marked and harvested in vegetative stage (without flowers).

For the study of leaves, uniformly developed ones were collected from the selected individuals and dried under natural conditions obtaining 20-30 g air-dried samples. Damaged and yellowish leaves were rejected.

For getting the roots, the same plants were taken from the soil carefully to avoid damage of the root system. The obtained root material (20-30 g/plant) was gently washed with distilled water, dried at room temperature and frozen at -18ºC. Before extraction, it was cut into pieces smaller than 0.5 cm.

2.3. Isolation of essential oil

The isolation of essential oil was performed by hydrodistillation method using a Clevenger apparatus. After 2 h of distillation, 2 mL of dichloromethane was added to take up the essential oil. The collected extract was dried with anhydrous sodium sulphate and stored in glass vials at -18º C in the absence of light until GC analysis.

2.4. Analysis of the essential oil composition

Analysis of the simultaneous distillation-extraction (SDE) extracts was carried out using gas chromatography coupled to flame ionization detector (GC-FID) and mass spectrometry (GC-MS). A Clarus 500 GC (PerkinElmer Inc., Wellesley, MA, USA) chromatograph equipped with a FID detector and a ZB-5 capillary column (30 m x 0.25 mm i.d. x 0.25 μm; Phenomenex Inc., Torrance, CA, USA) was used for quantitative analyses (injection volume 1 mL). The GC oven temperature program was set from 50 °C to

250 °C at a rate of 3°C min^{-1}. Helium was used as carrier gas (1.2 mL min^{-1}), and the injector and detector temperatures were set at 250 °C. The percentage composition of the essential oil was computed from the GC peak areas (without correction factors) using Total Chrom 6.2 (Perkin Elmer Inc.) software.

Analysis by GC-MS was performed using a Clarus 500 GC-MS (Perkin Elmer Inc.) with the same capillary column, mobile phase and operating conditions as described above for the GC analysis. The ionization source temperature was 200 °C, and a 70 eV electron impact mode was used. MS spectra were obtained using the total ion scan (TIC) mode (mass range m/z 45–500 uma). The total ion chromatograms and mass spectra were processed using Turbomass 5.4 (Perkin Elmer Inc.) software.

The extract components were identified based on their Kovats retention indexes relative to C7–C30 saturated alkanes (Sigma-Aldrich). The essential oil components were identified by comparison of their mass spectra with those of computer library NIST MS Search 2.0 and available data in the literature (20, 21). Identification of the following compounds was confirmed by comparison of their experimental RI with those of authentic reference standards (Sigma-Aldrich): α-pinene, β-pinene, camphene, myrcene, limonene, (Z)-β-ocimene, camphor, terpinolene, β-thujone, borneol, terpinen-4-ol, bornyl acetate, geraniol and linalool.

2.5. Statistical analysis

Student's t-test for the comparison of two means using Statgraphics 5.1 software was applied to determine significant differences in mean percentages of camphor and borneol in the EO of leaves from the Spanish population. As the raw data were expressed as % peak areas, they were subjected to arcsin[square root(%/100)] transformation to get past the homocedasticity test.

3. Results and Discussion

Representative GC/MS chromatograms from Hungarian and Spanish samples (roots and leaves) are displayed in the figures 1-4. GC/FID data for each one of the 40 processed samples are shown in table 2a (Hungarian samples) and 2b (Spanish samples).

Leaves from Hungarian samples

Based on the EO composition of the leaves, four well characterized individuals belonging to the reported two main chemotypes from Hungary could be recognized in the samples of Hungarian plants: sabinene + myrcene and β-thujone ones (19, 22). Among them, a high amount (up to 85.7.0 %) of monoterpene hydrocarbons was found in individual 2, 7 and 10, with sabinene and myrcene as major compounds (Table 2a). This composition has been reported in previous researches related to Hungarian origin although in a much lower proportion. Both compounds together (sabinene + myrcene) were also found in relatively high amounts (2.7-28.5 %) in the rest of individuals. Individual 5 was particularly rich in β-thujone (83.5 %) and can be considered as "pure" chemotype (3, 15, 22). β-thujone was also present in the essential oil of the other Hungarian plants, however, their levels did not surpass 11.1%. A unique composition with relative high levels (11.4%) of limonene, besides of the mentioned sabinene, is characteristic for individual 9.

Four other plants (individuals 1, 3, 4, 6) can be mentioned as typical sesquiterpeneic ones (sesquiterpene proportions above 50%). The most frequent sesquiterpenes in them were curcumene, caryophyllene oxide, intermedeol and nuciferyl esters (table 2a). Individual 3 and 4 showed also elevated levels of β-caryophyllene. Plants where the mono- and sesquiterpenes appeared in almost equal proportions were also found (individuals 8 and 9). This high occurrence of sesquiterpenic fraction is hardly noticeable in the literature, except for samples coming from Greece containing up to 25 % of caryophyllene oxide (5).

Leaves from Spanish samples

Two of typical chemotypes in Eastern Iberian Peninsula described previously by Ariño (3) have been clearly characterized within the six samples from Teruel (table 2b). None of them was present among the Hungarian individuals.

In chemotype A, (*Z*) + (*E*)-β-epoxyocimene accounted for 76.3-86.8 % of the essential oil, whereas (*Z*)-chrysanthemyl acetate did not surpass 2.8 % (individuals 1, 5, 6, 7, 9). In chemotype B, both epoxyocimene isomers accounted for 62.2-73.4 % of the essential oil, whereas the range of (*Z*)-chrysanthemyl acetate was 10.8-25.8 % (individuals 2, 3, 4, 8, 10). Other significant compounds were: camphor (tr.-7.1 %), chamazulene (0.6-3 %), borneol (0-2.5 %), β-caryophyllene (0.2-1.8 %), β-selinene (0.1-1.5 %) and

germacrene-D (0.2-0.5 %). These profiles agree with those reported by Ariño (3) in wild populations from the same geographical origin.

Despite the high individual variability, the chemical profiles were very similar for both chemotypes according to the proportions of the major constituents (except, obviously, for those defining chemotypes). Nevertheless, it is worth mentioning that the levels of camphor and borneol, belonging to bornane skeleton compounds, may also be characteristic for each one of both chemotypes. According to results of t-test the mean amount of camphor was higher (P=0.02) in chemotype A (5.1 ± 1.7 vs. 1.7 ± 1.8 in chemotype B), whereas the mean proportion of borneol was significantly higher (P=0.01) in chemotype B (1.2 ± 0.8 vs. 0.0 ± 0.1 detected in chemotype A).

Roots

Monoterpenic esters made up the major fraction (56.5-80.2 %) for the majority of the Hungarian samples (1, 3, 4, 5, 7, 8 and 9) and all of the Spanish individuals, but the proportion was higher and more uniform (59.9-90.3 %) in the last ones (Table 2b). In further two Hungarian individuals hydrocarbon monoterpenic fraction was the major one (individual 2: 69.8 %, individual 6: 48.5 % and individual 10: 42.1%). α-fenchene and myrcene were found the major hydrocarbon monoterpenes both in Hungarian and Spanish individuals. These compounds were particularly abundant in Hungarian individual 2 (60.8 %).

In the monoterpenic ester fraction however, Hungarian and Spanish roots showed some qualitative differences. The predominance of acyclic esters was characteristic for the Hungarian root oils (9.8-62.4 % vs. 4.7-38.8 % for cyclics), whereas cyclic esters (bornyl acetate and β-terpinyl acetate, mainly) were the most abundant ones in Spanish individuals (41.3-60.3 % vs. 10.7-40.7 %), as it has been already reported by Llorens-Molina & Vacas (16). The higher occurrence of lavandulyl and citronellol esters was characteristic for Hungarian plants while they were lower in the Spanish individuals. Blagojevic et al. (15) describe in detail the essential oil composition of roots of plants whose aerial parts represent a β-thujone (63.5 %) chemotype- a similar profile to the leaves of individual 5 from Budapest. Comparing the literature data with the profile of this individual, the fraction of monoterpenic esters showed quite similar levels (63.5 % and 68.6 % respectively). Nevertheless, the molecular structure of these esters is different. In the above

mentioned data (15), linalyl esters are the most abundant compounds, whereas geranyl, lavandulyl, bornyl and myrtanyl ones predominated in individual 5 from Budapest.

Concerning sesquiterpenic compounds, only an oxygenated sesquiterpene (azulen-2-ol, 1,4-dimethyl-7-(1-methylethyl) has been found in noticeable amounts in some Hungarian roots and Spanish ones, as well. The occurrence of this compound in *Artemisia* genus has been reported by Deng (23) in *Artemisia selengensis* Turcz. Regarding sesquiterpenic hydrocarbons, only β-caryophyllene was found in Spanish roots (0.3-1.7 %) whereas it was not detected in Hungarian roots.

The distribution of the terpenic groups in the EO of the roots did not show significant differences between the chemotypes based on the leaf composition. Thus, composition of EO seems to provide a relatively independent profile in the overground and underground organs of wormwood. Similar phenomenon was detected in related *Achillea* species as well (24, 25).

Figure 1. GC/MS chromatogram of Hungarian roots (individual 5) with the identification of the most representative compounds

Figure 2. GC/MS chromatogram of Hungarian leaves (individual 2) with the identification of the most representative compounds.

Figure 3. GC/MS chromatogram of Spanish roots (individual 3) with the identification of the most representative compounds.

Figure 4. GC/MS chromatogram of Spanish leaves (individual 2) with the identification of the most representative compounds.

Table 2a. EO composition of leaves and roots from Hungarian samples

Table 2b. EO composition of leaves and roots from Spanish samples

4. Conclusions

The results of the morphogenetic study revealed that characteristic differences exist in the EO composition of wormwood plants depending on plant organ. According to the profile of the EO of the leaves, 3 main chemotypes (sabinene+myrcene, thujon and sesquiterpene ones) were found in the Hungarian population

and 2 chemotypes were present in the Spanish one. Among them, the sesquiterpene profile - especially oxygenated sesquiterpenes - detected among the Hungarian individuals (up to 80.8 %) has not been known from literature. None of the identified chemotypes has been detected at both habitats and considered as common ones.

The composition of EO of the roots showed different profiles from those of the leaves and does not refer to the chemotype of the plant defined according to the EO spectrum of the leaves.

The root oils have been found to be more uniform and predominated by monoterpenic esters in the examined populations of both experimental locations. Nevertheless, well established qualitative and quantitative differences could be described among the individual plants and between the populations. This is similar to the findings in case of the leaf oils. However, comparing the EO composition of the examined plant organs, it can be concluded that no appreciable relationship exists between them in any of the examined individuals of *A. absinthium*.

The chemical variability of wormwood is obviously much higher in the overground parts than in the roots. The background of this diversity is not yet clear: phylogenetic processes due to environmental adaptation may be assumed, however, it should be the target of another study.

At the same time, the co-occurrence of different chemotypes inside a population has been ascertained. As previous investigations on this species have not been carried out at level of the individuals, this findings are important from both practical and theoretical points of view. It could be confirmed that the chemical profile of wormwood accessions can not be determined by collection of bulk samples but only by individual investigations. ”Mixed” samples may lead to unreproducible results. This concern may be particularly relevant when biological activity of EO is considered, given that it should be connected to a special chemical composition. For this reason, previous identification of the chemotype of each plant and introduction of the relevant species into the cultivation seems to be a prosperous alternative to assure homogenous and stable plant raw material.

5. References

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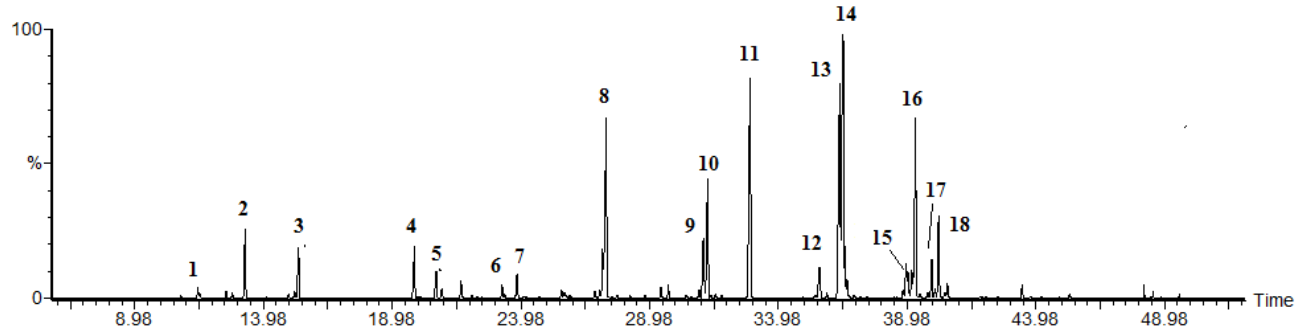

Figure 1. GC/MS chromatogram of Hungarian roots (individual 5) with the identification of the most representative compounds: (1) α-fenchene, (2) myrcene, (3) 1,8-cineole, (4) (*Z*)-*p*-menthen-2-en-1-ol, (5) (*E*)-*p*-menthen-2-en-1-ol, (6) (*Z*)- piperitol, (7) (*E*)-piperitol, (8) bornyl acetate, (9) (Z)-myrtanol acetate, (10) (*E*)-myrtanol acetate, (11) lavandulyl isobutanoate, (12) neryl isobutanoate, (13) lavandulyl 3-methylbutanoate, (14) lavandulyl 2-methylbutanoate, (15) geranyl isobutanoate, (16) neryl 2-methylbutanoate, (17) geranyl 2-methylbutanoate, (18) geranyl isovalerate.

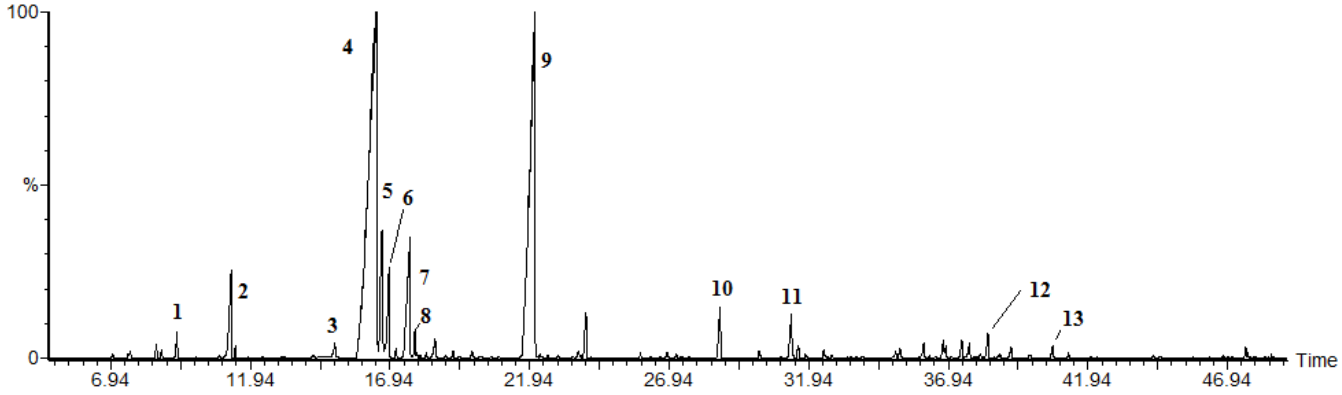

Figure 2. GC/MS chromatogram of Spanish leaves (individual 2) with the identification of the most representative compounds: (1) myrcene, (2) (*Z*)–β–ocimene, (3) linalool, (4) (*Z*)-epoxyocimene, (5) (*E*)-epoxyocimene, (6) camphor, (7) (*Z*)-chrysanthemol, (8) borneol, (9) (*Z*)-chrysanthemyl acetate, (10) β-caryophyllene, (11) β-selinene, (12) methyl jasmonate, (13) chamazulene.

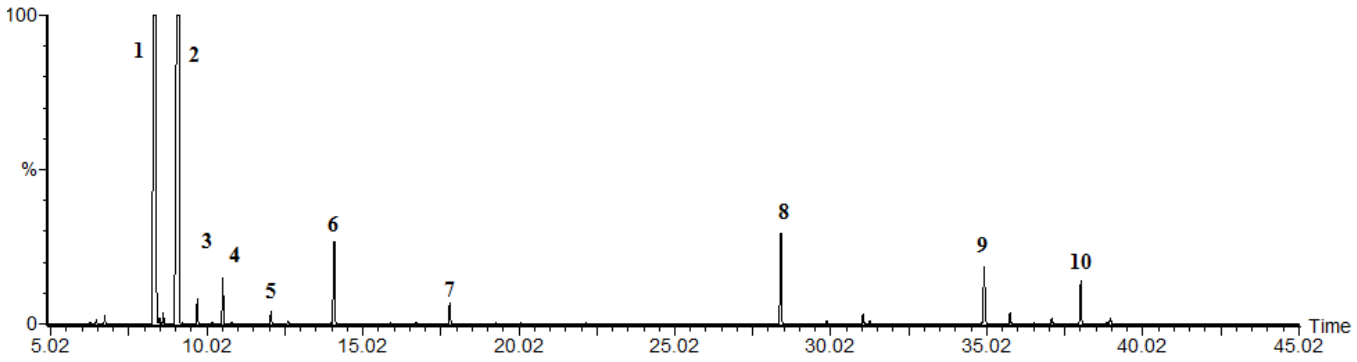

Figure 3. GC/MS chromatogram of Hungarian leaves (individual 2) with the identification of the most representative compounds: (1) sabinene (2) myrcene, (3) α-phellandrene, (4) limonene (5) γ-terpinene, (6) linalool, (7) terpinen-4-ol, (8) β-caryophyllene, (9) caryophyllene oxyde, (10) intermedeol.

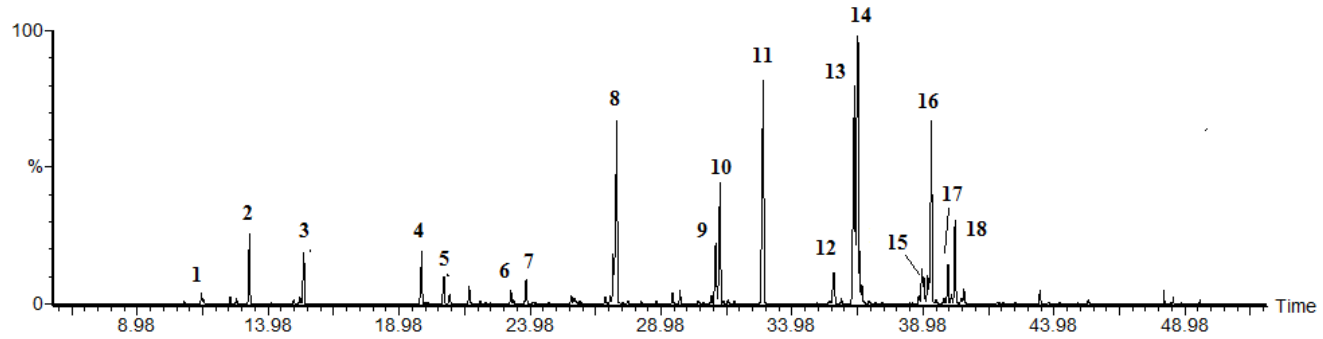

Figure 4. GC/MS chromatogram of Hungarian roots (individual 5) with the identification of the most representative compounds: (1) α-fenchene, (2) myrcene, (3) 1,8-cineole, (4) (*Z*)-*p*-menthen-2-en-1-ol, (5) (*E*)-*p*-menthen-2-en-1-ol, (6) (*Z*)- piperitol, (7) (*E*)-piperitol, (8) bornyl acetate, (9) (Z)-myrtanol acetate, (10) (*E*)-myrtanol acetate, (11) lavandulyl isobutanoate, (12) neryl isobutanoate, (13) lavandulyl 3-methylbutanoate, (14) lavandulyl 2-methylbutanoate, (15) geranyl isobutanoate, (16) neryl 2-methylbutanoate, (17) geranyl 2-methylbutanoate, (18) geranyl isovalerate.

31.

Table 1. Main chemotypes in *Artemisia absinthium* L. according references

Reference	Country	Nr. of detected compounds	Determined chemotypes (main compounds in area %)
Ariño et al. (3)	Spain	17	(*Z*)-chrysanthemyl-acetate (31-44%)+ (*Z*)-epoxyocimene (34-42%)
Bagci et al. (4)	Turkey	31	Chamazulene (29%)
Basta et al. (5)	Greece	68	Caryophyllene-oxide (25%)
Chialva et al. (6)	Italy	34	(*Z*)-epoxyocimene (30-54%)
			β-thujone (41%)
	Romania		β-thujone (15%)
	France		Sabinyl-acetate (32%)
			Chrysanthemyl-acetate (42%)
	Siberia		Sabinyl-acetate (85%)
Derwich et al. (7)	Marocco	–	α-thujone (40%)

Judzentiene and Budiene (8)	Lithuania	15	(*E*)-sabinyl-acetate (22-51%), α-and β-thujones (18-72%)
Pino et al. (9)	Cuba	40	Bornyl-acetate (24%)
Rezaeinodehi et al. (10)	Iran	28	β-pinene (24%)
Sharopov et al. (11)	Tajikistan	41	Myrcene (23%) (*Z*)-chrysanthemyl-acetate (18%)
Simonnet et al. (12)	Switzerland	6	(*Z*)-epoxyocimene (30-40%)

Table 2a. EO Composition of leaves and roots from Hungarian samples

				HUNGARY ROOTS										HUNGARY LEAVES									
				Individuals										Individuals									
				1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Compound[1]	RI[2]	RI(lit)[3]	ID method[4]																				
2-hexenal	856	855	MS, RI	-[5]	-	-	-	-	-	-	-	-	-	-	0.1	0.2	-	-	0.2	-	-	-	0.6
α-thujene	931	930	MS, RI	-	-	-	-	-	-	-	-	-	tr[6]	-	0.3	-	-	-	-	-	-	-	0.3
α-pinene	936	939	MS, RI, std	-	0.7	tr	-	-	0.4	-	-	0.1	1.2	-	0.4	-	-	-	-	0.3	-	-	0.4
α-fenchene	953	953	MS, RI	2.0	42.8	15.2	7.6	2.4	22.5	1.4	1.8	1.0	26.2	-	-	1.9	-	-	0.1	-	-	-	-
camphene	955	954	MS, RI, std	-	-	-	-	-	-	-	-	-	-	-	-	1.0	0.6	-	0.1	-	-	-	-
sabinene	975	975	MS, RI	-	0.2	-	-	-	0.1	-	-	-	0.6	4.3	45.0	3.5	3.2	1.6	8.4	20.1	17.5	10.3	49.3
β-pinene	977	979	MS, RI, std	-	0.9	-	0.2	0.1	0.6	-	0.1	-	1.1	-	-	-	-	-	-	-	-	-	0.3
1-octen-3-ol	982	979	MS, RI	-	-	-	-	-	-	-	-	-	-	-	0.2	0.7	-	0.2	-	-	-	-	-
myrcene	991	990	MS, RI, std	2.4	18.0	15.3	14.4	7.6	6.9	1.2	5.9	0.8	12.2	3.6	37.1		2.7	1.1	7.1	23.9	11.0	3.0	36.4
α-phellandrene	1006	1003	MS, RI	1.5	3.9	0.4	1.9	0.3	tr	-	-	-	0.5	-	0.8	0.3	-	-	-	tr	2.1	7.7	0.2
α-terpinene	1018	1017	MS, RI	-	-	-	-	-	-	-	-	-	0.2	-	-	-	-	0.5		-	-	-	0.1
p-cymene	1027	1025	MS, RI, std	2.1	2.1	-	1.2	0.1	7.1	-	-	-	-	-	0.2	-	tr	-	tr	-	-	-	-
limonene	1031	1029	MS, RI, std	-	1.2	-	0.7	0.4	0.9	-	-	-	-	-	2.2	-	-	0.9	1.4	0.5	2.1	11.4	0.8
1,8-cineole	1034	1031	MS, RI, std	-	1.1	-	0.5	0.4	0.7	0.1	-	tr	2.4	-	0.2	-	-	0.1	0.2	-	-	-	0.2
γ-terpinene	1063	1060	MS, RI	-	-	-	-	-	-	-	-	0.6	0.1	-	0.5	-	-	-	tr	0.6	0.3	-	0.5
(*Z*)-sabinene hydrate	1073	1070	MS, RI	-	-	-	-	-	-	-	-	-	0.1	-	-	-	0.1	-	-	1.0	1.1	0.3	0.3
terpinolene	1086	1089	MS, RI	-	-	-	-	-	-	-	-	-	-	1.2	0.1	0.2	0.4	0.3	0.2	-	-	-	0.1
linalool	1098	1096	MS, RI, std	-	-	-	-	-	-	tr	-	-	-	3.1	2.2	5.3	0.6	1.9	0.1	2.1	3.7	6.8	5.8
α-thujone	1102	1102	MS, RI, std	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1	0.2	-	-	-
β-thujone	1118	1114	MS, RI, std	-	-	-	-	-	-	-	-	-	-	-	-	-	11.1	83.5	4.2	2.3	-	0.1	0.1
(*Z*)-*p*-menth-2-en-1-ol	1124	1122	MS, RI	1.3	5.3	-	2.4	4.6	3.8	5.5	1.1	4.5	10.7	-	-	-	-	-	-	-	-	-	-
(*E*)-*p*-menth-2-en-1-ol	1143	1141	MS, RI	0.3	2.8	-	1.0	2.9	2.0	3.7	0.1	2.8	6.3	-	-	-	-	-	-	-	-	-	-
terpinen-4-ol	1181	1177	MS, RI, std	0.1	-	-	0.1	1.2	-	0.1	-	-	0.1	2.9	0.8	-	0.6	0.2	3.0	2.1	0.3	0.8	0.1
α-terpineol	1188	1188	MS, RI, std	-	-	-	-	-	-	0.1	-	0.2	0.2	-	-	-	-	-	-	-	-	-	-
(*Z*)-piperitol	1194	1196	MS, RI	-	1.0	-	0.4	0.8	0.6	0.3	-	0.2	0.2	-	-	-	-	-	-	-	-	-	-
(*E*)-piperitol	1206	1208	MS, RI	-	1.2	-	0.5	1.3	1.0	1.3	0.2	1.0	2.0	-	-	-	-	-	-	-	-	0.2	-

citronellol	1221	1226	MS, RI	-	-	-	-	-	0.6	1.8	0.2	1.6	3.0	-	-	-	-	-	-	-	-	-	-
nerol	1236	1230	MS, RI	0.1	-	-	tr	1.2	1.0	0.1	-	0.3	0.2	-	-	-	-	-	-	-	-	-	-
(*Z*)-chrysanthemyl acetate	1267	1265	MS, RI	-	-	-	-	-	-	0.1	-	-	-	-	-	-	-	-	-	-	-	-	-
lavandulyl acetate	1286	1290	MS, RI	-	-	-	-	0.2	-	-	-	-	-	-	-	-	-	-	-	-	-	0.8	-
bornyl acetate	1290	1289	MS, RI	3.7	1.7	2.7	5.1	12.9	7.3	12.8	11.9	26.6	13.9	-	-	-	-	-	-	0.6	-	0.6	tr
methyl nerolate	1300	1283	MS, RI	-	-	-	-	-	-	-	-	0.2	0.1	-	-	-	-	-	-	-	-	-	-
methyl geranate	1318	1323	MS, RI	-	-	-	-	-	-	-	-	0.7	-	-	-	-	-	-	-	-	-	-	-
β-terpinyl acetate	1353	1359 (6)	MS, RI	0.1	0.2	-	0.5	0.7	0.1	0.5	2.9	0.1	0.2	-	-	-	-	-	-	-	-	-	-
α-terpineol acetate	1354	1349	MS, RI	0.1	0.5	0.4	0.9	0.6	9.1	0.1	0.1	16	0	-	-	-	-	-	-	-	-	0.3	-
neryl acetate	1359	1362	MS, RI	0.1	1.0	-	2.4	0.2	0.4	0.1	0.4	-	-	-	-	-	-	-	-	-	-	-	-
(*Z*)-myrtanol acetate	1370	1368 (26)	MS, RI	5.7	1.1	5.3	3.1	4.3	1.5	1.4	1.2	0.3	0.5	-	-	-	-	-	-	-	-	-	-
linalyl isobutanoate	1376	1375	MS, RI	-	0.1	-	0.2	0.5	0.1	0.3	0.8	-	0.3	-	-	-	-	-	-	-	-	-	-
(*E*)-myrtanol acetate	1379	1376 (26)	MS, RI	8.3	1.7	8.2	3.9	5.6	1.7	8.2	5.4	11.1	5.8	-	-	-	-	-	-	-	-	-	-
geranyl acetate	1381	1381	MS, RI	-	-	-	-	-	-	0.1	tr	0.2	0.1	-	-	-	-	-	-	-	-	-	-
(*E*)-jasmone	1388	1391	MS, RI	-	-	-	-	-	-	-	-	-	-	0.6	0.4	0.9	-	0.1	0.2	-	-	-	-
β-caryophyllene	1415	1419	MS, RI	-	-	-	-	-	-	-	-	-	-	6.9	3.5	24.8	15.8	1.1	6.0	7.1	2.8	4.4	0.6
lavandulyl isobutanoate	1417	1421	MS, RI	7.9	0.2	9.2	6.5	11.0	3.1	3.7	3.0	2.0	1.1	-	-	-	-	-	-	-	-	-	-
citronellyl propionate	1441	1446	MS, RI	-	-	-	-	-	-	0.1	-	0.4	-	-	-	-	-	-	-	-	-	-	-
neryl propionate	1451	1454	MS, RI	-	-	-	0.1	-	0.1	0.3	0.1	-	0.1	-	-	-	-	-	-	-	-	-	-
α-humulene	1459	1454	MS, RI	-	-	-	-	-	-	-	-	-	-	-	0.2	-	-	-	0.4	0.8	0.3	0.8	0.1
linalyl isovalerate	1467	1468	MS, RI	-	-	-	-	-	-	-	-	0.3	0.1	-	-	-	-	-	-	-	-	-	-
γ-gurjunene	1479	1477	MS, RI	-	-	-	-	-	-	-	-	-	-	2.1	0.2	-	-	0.2	0.2	0.3	1.8	tr	-
citronellol isobutanoate	1482	1483	MS, RI	0.5	0.6	-	1.6	0.2	1.5	-	-	-	-	-	-	-	-	-	-	-	-	-	-
curcumene <ar->	1484	1481	MS, RI	-	-	-	-	-	-	0.1	-	0.1	-	2.8	0.3	-	-	0.8	4.3	1.7	5.0	3.2	-
neryl isobutanoate	1488	1491	MS, RI	5.7	3.0	0.7	9.4	2.3	0.9	1.6	0.7		0.1	-	-	-	-	-	-	-	-	-	-
β-selinene	1490	1490	MS, RI	-	-	-	-	-	-	-	-	-	-	6.8	0.2	-	8.7	0.6	2.2	2.8	2.2	0.3	-
bicyclogermacrene	1499	1500	MS, RI	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.3	0.5	-	-
lavandulyl 3-methylbutanoate + lavandulyl 2-methylbutanoate	1506	1510, 1512	MS, RI	2.9	0.7	1.8	1.9	21.6	5.5	8.1	10.6	7.6	1.2	-	-	-	-	-	-	-	-	-	0.1
geranyl isobutanoate	1508	1515	MS, RI	15.1	0.7	22.8	7.0	2.0	2.9	5.5	11.1	2.1	1.1	1.2	-	-	-	0.3	2.5	0.7	tr	6.4	-
isobornyl isovalerate	1517	1523	MS, RI	-	-	-	-	-	-	0.5	0.1	0.7	0.2	-	-	-	-	-	-	0.2	0.1	-	-
geranyl butanoate	1557	1564	MS, RI	9.4	0.6	3.7	5.6	0.6	-	0.1	0.1	0.2	tr	-	-	-	-	-	-	-	-	-	-

citronellyl 2-methylbutanoate	1568	1577 (27)	MS, RI	1.6	0.6	0.4	1.0	0.3	0.3	1.2	2.7	3.9	0.1	-	-	-	-	-	-	-	-	-	-
neryl 2-methylbutanoate	1574	1579	MS, RI	4.2	0.7	2.2	3.3	2.0	2.3	6.7	5.6	4.1	1.0	-	-	-	-	-	-	-	-	-	-
neryl isovalerate	1581	1583	MS, RI	10.2	0.5	0.8	1.0	0.8	3.3	19.4	9.4	1.8	4.3	-	-	-	-	-	-	-	-	-	-
(*E*)-sesquisabinene hydrate	1576	1579	MS, RI	-	-	-	-	-	-	-	-	-	-	2.5	-	-	1.0	0.3	1.6	2.4	1.0	3.4	tr
caryophyllene oxyde	1577	1583	MS, RI	-	-	-	-	-	-	-	-	-	-	12.2	1.9	19.5	23.1	0.9	1.0	6.2	7.2	11.2	0.4
(*E*)-β-terpinyl pentanoate	1594		MS[6]	-	-	-	-	-	-	0.1	0.5	-	-	-	-	-	-	-	-	-	-	-	-
geranyl 2-methylbutanoate	1597	1601	MS, RI	3.7	3.5	1.5	1.6	1.8	0.1	2.0	3.0	0.3	0.2	-	-	-	-	-	-	2.0	-	2.7	0.1
geranyl isovalerate	1604	1607	MS, RI	1.0	0.7	0.1	1.4	2.7	0.2	2.0	2.7	0.3	0.3	-	-	-	-	-	-	0.3	-	1.7	0.1
(*Z*)-methyljasmonate	1648	1649	MS, RI	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1	-	1.4	0.1
geranyl valerate	1655	1656	MS, RI	-	-	-	-	-	-	0.5	2.1	0.1	0.1	-	-	-	-	-	-	-	-	0.4	-
intermedeol	1661	1666	MS, RI	-	-	-	-	-	-	-	-	-	-	30.2	1.3	-	16.9	3.2	36.7	6.7	18.3	1.6	0.8
sinensal-β	1696	1700	MS, RI	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.5	-	1.0	1.8	0.2	0.3
nuciferyl acetate	1824	1831	MS, RI	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.4	0.1
Azulen-2-ol, 1,4-dimethyl-7-(1-methylethyl)-	1952	1960 (28)	MS, RI	0.2	-	-	1.1	0.6	0.3	3.2	5.7	1.3	1.3	-	-	-	-	-	-	-	-	-	-
geranyl *p*-cymene	1953	1950 (29)	MS, RI	-	-	-	-	-	-	-	-	-	-	2.6	0.2	2.5	2.3	0.3	2.1	1.5	2.5	3.3	0.3
hexadecanoic acid	1962	1960	MS, RI	-	-	0.1	0.1	-	-	-	0.2	-	-	0.3	tr	-	-	-	-	0.4	0.7	0.1	tr
manoyl oxide	1988	1989 (30)	MS, RI	-	-	-	-	-	-	-	-	-	-	-	tr	-	-	-	tr	0.1	0.5	0.1	tr
nuciferol (*Z*)-isobutanoate	1998	1997 (11)	MS, RI	-	-	-	-	-	-	-	-	-	-	5.0	0.2	6.4	0.8	0.3	3.4	6.8	6.2	6.2	0.2
nuciferol (*E*)-isobutanoate	2004	2004 (11)	MS, RI	-	-	-	-	-	-	-	-	-	-	5.3	0.2	30.2	11.1	0.8	5.3	0.6	2.5	5.4	0.7
Hydrocarbon monoterpenes				**8.0**	**69.8**	**30.9**	**26.0**	**10.9**	**48.5**	**2.7**	**7.7**	**2.6**	**42.1**	**9.2**	**86.6**	**6.9**	**6.9**	**4.4**	**17.3**	**45.3**	**33.0**	**32.4**	**88.3**
Ox. Monot. (no esters)				**1.7**	**11.4**	**0.0**	**4.8**	**12.2**	**9.7**	**12.8**	**1.7**	**10.6**	**25.1**	**6.0**	**3.2**	**5.3**	**12.5**	**85.7**	**7.6**	**7.7**	**5.1**	**8.2**	**6.5**
Monoterpenic esters				**80.2**	**18.1**	**59.8**	**56.5**	**70.3**	**40.4**	**75.4**	**74.4**	**78.6**	**30.8**	**1.2**	**0.0**	**0.0**	**0.0**	**0.3**	**2.5**	**3.8**	**0.1**	**13.0**	**0.2**
Hydrocarbon sesquiterpenes				**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.1**	**0.0**	**0.1**	**0.0**	**18.5**	**4.4**	**24.8**	**24.5**	**2.7**	**13.1**	**13.0**	**12.5**	**8.8**	**0.7**
Ox. Sesquiterpenes				**0.2**	**0.0**	**0.0**	**1.1**	**0.6**	**0.3**	**3.2**	**5.7**	**1.3**	**1.3**	**55.2**	**3.6**	**56.0**	**52.9**	**6.0**	**48.0**	**23.6**	**37.0**	**28.3**	**2.5**
Other				**0.0**	**0.0**	**0.1**	**0.1**	**0.0**	**0.0**	**0.0**	**0.2**	**0.0**	**0.0**	**2.9**	**0.5**	**3.4**	**2.3**	**0.5**	**2.3**	**2.0**	**3.7**	**3.5**	**0.9**
Total identified				**90.1**	**99.3**	**90.8**	**88.5**	**94.2**	**98.9**	**94.2**	**89.7**	**93.1**	**99.3**	**93.0**	**98.3**	**96.4**	**99.0**	**99.6**	**90.8**	**95.4**	**91.4**	**94.2**	**99.1**

Table 2b. EO Composition of leaves and roots from Spanish samples

				SPANISH ROOTS										SPANISH LEAVES									
				Individuals										Individuals									
				1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Compound[1]	RI[2]	RI [3](lit.)	ID method[4]																				
2-hexenal	856	855	MS, RI	-[5]	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1	0.1	tr[6]	-
santene	890	889	MS, RI	-	-	-	-	-	-	-	0.1	0.1	-	-	-	-	-	-	-	-	-	-	-
santolinatriene	910	909	MS, RI, std	-	-	-	-	-	-	-	0.1	0.1	-	-	-	-	-	-	-	-	-	-	-
tryciclene	924	927	MS, RI	-	-	-	-	-	-	-	0.2	0.2	-	-	-	-	-	-	-	-	-	-	-
α-pinene	936	939	MS, RI, std	0.1	-	0.3	0.5	-	-	0.3	1.6	2.4	0.1	-	-	-	-	-	-	0.3	0.4	0.3	0.6
α-fenchene	953	953	MS, RI	1.3	0.3	4.2	0.1	0.4	1.1	1.9	12.4	12.1	0.7	-	-	-	-	-	-	-	-	-	-
camphene	955	954	MS, RI, std	-	-	0.3	-	-	-	0.6	2.8	4.5	-	0.2	1.0	0.6	0.8	0.6	0.5	0.2	-	0.4	-
sabinene	975	975	MS, RI	-	-	-	-	-	-	0.1	0.3	0.3	-	0.2	0.1	0.2	0.3	0.3	0.4	-	-	-	0.1
β-pinene	977	979	MS, RI, std	0.1	-	0.5	-	-	-	0.2	0.8	1.4	-	-	0.2	-	-	-	-	1.3	0.1	-	0.4
1-octen-3-ol	982	982	MS, RI	-	-	-	-	-	-	-	-	-	-	-	0.4	-	-	1.5	0.5	-	0.1	-	-
myrcene	991	990	MS, RI, std	6.7	1.2	3.8	0.5	1.6	5.8	4.5	15.5	12.3	1.9	0.5	0.2	0.1	0.3	0.3	0.8	0.3	0.2	0.1	0.3
1,8-cineole	1034	1031	MS, RI, std	0.3	-	0.2	-	-	0.3	0.1	0.8	1.0	-	-	tr	-	-	-	-	-	-	-	-
(*Z*)-β-ocimene	1040	1040	MS, RI, std	-	-	-	-	-	-	-	-	-	-	0.1	-	-	0.1	0.2	0.2	0.1	-	0.1	tr
(*E*)-β-ocimene	1050	1051	MS, RI, std	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2	-	0.3	0.1
γ–terpinene	1063	1060	MS, RI	-	-	-	-	-	-	-	-	-	-	1.6	1.3	1.1	1.4	1.8	1.2	-	-	-	-
isoterpinolene	1082	1086	MS, RI	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.1	0.3	-	0.2	0.2
terpinolene	1086	1089	MS, RI, std	-	-	-	-	-	-	-	-	-	-	0.1	-	-	0.2	-	0.2	-	-	0.1	-
α-pinene epoxide	1101	1099	MS, RI	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2	-	tr	0.1
linalool	1098	1096	MS, RI, std	-	-	-	-	-	-	-	-	-	-	0.3	0.2	0.2	0.3	0.2	0.2	0.7	0.1	0.1	0.1
1-octen-3-ol acetate	1111	1112	MS, RI	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.9	0.8	0.1
α-thujone	1112	1102	MS, RI, std	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	0.6	-
β-thujone	1117	1114	MS, RI, std	-	-	-	-	-	-	-	-	-	-	1.4	1.1	1.1	0.8	1.1	2.6	0.5	0.5	0.6	0.5
(*Z*)-β-epoxyocimene	1142	1132	MS, RI	-	-	-	-	-	-	-	-	-	-	83.5	59.9	69.1	69.0	78.4	73.9	78.5	63.7	80.0	69.6
(*E*)-β-epoxyocimene	1149	1142	MS, RI	-	-	-	-	-	-	-	-	-	-	3.3	2.3	3.5	2.3	3.1	2.4	6.4	3.3	3.6	3.8
camphor	1157	1146	MS, RI, std	-	-	-	-	-		0.2	0.1	-	-	6.1	1.6	3.3	3.8	4.1	5.4	2.7	tr	7.1	tr
(*Z*)-chrysanthemol	1167	1164	MS, RI	-	-	-	-	-	-	-	-	-	-	-	tr	-	-	-	0.2	0.2	0.2	0.3	0.2

borneol	1173	1169	MS, RI, std	-	-	-	-	-	-	-	-	-	-	-	2.5	1.4	1.0	-	-	0.2	0.7	-	0.6
terpinen-4-ol	1181	1177	MS, RI, std	-	-	-	-	-		0.4	0.2	0.4	-	-	-	0.2	-	-	-	0.3	0.1	0.2	0.1
α-terpineol	1194	1188	MS, RI, std	-	-	-	-	-	-	-	-	tr	-	-	-	-	-	-	0.4	0.5	0.7	0.3	0.6
citronellol	1221	1226	MS, RI			0.1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
(*Z*)-geraniol	1231	1229	MS, RI, std	-	-	-	-	-	-	0.2	tr	-	0.2	-	-	-	-	-	-	-	-	-	tr
(*Z*)-chrysanthemyl acetate	1267	1265	MS, RI	-	-	-	-	-	-	0.3	0.1	0.1	0.1	-	21.8	13.2	10.8	0.1	-	2.8	25.8	0.1	16.6
lavandulyl acetate	1286	1288	MS, RI	-	-	-	-	-	-	0.1	0.1	0.1	0.1	-	-	-	-	-	-	-	-	-	-
bornyl acetate	1290	1288	MS, RI, std	55.2	34.2	14.0	18.4	35.2	29.8	35.1	32.3	47.6	27.5	-	-	-	-	-	-	tr	tr		0.1
methyl nerolate	1300	1283	MS, RI	0.2	0.2		0.3	0.2	0.2	0.3	0.1	0.3	0.2	-	-	-	-	-	-	-	-	-	-
methyl geranate	1318	1323	MS, RI	-	-	-	-	-	-	tr	-	0.1	-	-	-	-	-	-	-	-	-	-	-
terpinyl acetate <cis-dihydro-alpha>	1318	1318	MS, RI	-	-	-	-	-	-	0.4	0.4	-	0.5	-	-	-	-	-	-	-	0.2	-	1.0
dihydrocarveol acetate iso	1328	1329	MS, RI	0.2	-	-	0.1	-	0.2	0.2	0.1	0.2	0.1	-	-	-	-	-	-	-	-	-	-
β-terpinyl acetate	1342	1359 (6)	MS, RI	3.4	18.8	33.9	28.4	19.9	19.9	10.1	14.7	0.1	11.4	-	-	-	-	-	-	-	-	-	-
(*Z*)-myrtanol acetate	1370	1381	MS, RI	1.0	0.4	0.2	0.5	0.4	0.8	0.7	0.1	0.3	0.5	-	-	-	-	-	-	-	-	-	-
linalyl isobutanoate	1376	1375	MS, RI	4.3	3.0	0.6	5.6	3.1	6.4	1.6	0.8	1.5	1.3	-	-	-	-	-	-	-	-	-	-
α-copaene	1379	1377	MS, RI	-	-	-	-	-	-	-	-	-	-	-	0.1	-	0.1	-	0.1	tr	0.1	-	0.1
(*E*)-myrtanol acetate	1379	1386	MS, RI	-	-	-	-	0.2	0.3	-	-	-	-	-	-	-	-	-	-	-	-	-	-
geranyl acetate	1381	1381	MS, RI	3.7	2.0	0.5	6.0	2.1	6.3	5.2	3.6	3.5	5.9	-	0.1	-	0.2	-	0.1	-	-	-	-
(*E*)-jasmone	1388	1391	MS, RI	-	-	-	-	-	-	0.4	-	0.1	0.3	-	-	-	-	-	-	-	-	-	-
β-caryophyllene	1415	1419	MS, RI	1.1	1.7	0.3	1.1	1.8	0.5	0.7	0.4	0.8	1.1	0.7	1.5	1.3	2.3	0.9	1.8	0.4	0.2	0.3	0.3
lavandulyl isobutanoate	1417	1421	MS, RI	0.3	0.4	-	0.4	0.4	0.4	0.2	0.2	-	0.5	-	-	-	-	-	-	-	-	-	-
α-humulene	1459	1454	MS, RI	-	-	-	-	-	-	0.1	-	-	-	-	0.1	0.1	0.2	-		tr	tr	tr	tr
geranyl propionate	1467	1478	MS, RI	-	-	-	-	-	-	-	-	-	-	-	0.3	0.6	0.6	-	0.1	-	-	-	-
germacrene-D	1485	1485	MS, RI	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2	-	-	0.5	0.3	0.2	0.4
neryl isobutanoate	1488	1491	MS, RI	2.8	10.7	5.2	10.5	11.3	6.8	2.0	1.6	0.1	5.1	-	-	-	-	-	-	-	-	-	-
β-selinene	1490	1490	MS, RI	-	-	-	-	-	-	-	-	-	-	0.6	1.5	0.7	1.5	0.8	1.1	0.2	0.1	0.1	0.2
bicyclogermacrene	1499	1500	MS, RI	-	-	-	-	-	-	-	-	-	-	-	-	-	0.2	0.1	0.3	tr	-	-	tr
lavandulyl 3-methylbutanoate + lavandulyl 2-methylbutanoate	1506	1510, 1512	MS, RI	0.3	0.3	-	0.5	0.3	0.2	1.1	0.5	0.8	2.7	-	-	-	-	-	-	-	-	-	-
geranyl isobutanoate	1508	1515	MS, RI	1.5	0.8	-	1.4	0.9	0.1	0.2	-	0.1	0.4	-	-	-	-	-	-	-	-	-	-
isobornyl isovalerate	1517	1523	MS, RI	0.5	0.9	0.4	0.1	1.0	0.1	1.4	0.5	1.0	1.3	0.1	0.4	tr	-	0.8	-	-	-	0.1	0.2
geranyl butanoate	1557	1564	MS, RI	0.7	0.5	-	-	-	0.4	0.1	-	-	0.2	-	-	-	-	0.1	0.1	-	-	-	-

citronellyl isovalerate	1568	1577	MS, RI	0.3	0.3	-	0.1	0.4	0.5	0.4	0.1	0.1	0.3	-	-	-	-	-	-	-	-	-	-
neryl 2-methylbutanoate	1574	1579	MS, RI	2.5	4.6	2.3	6.7	0.2	3.6	0.6	0.2	0.2	0.6	-	-	-	-	-	-	-	-	-	-
neryl isovalerate	1581	1583	MS, RI	5.5	13.4	24.7	9.3	12.9	11.5	10.2	7.0	3.0	18.3	-	0.7	tr	0.7	-	0.1	0.2	-	-	0.1
trans-beta-terpinyl pentanoate	1594		MS[7]	-	-	-	-	-	-	-	-	-	-	-	-	0.1	0.1	-	0.2	-	-	-	-
geranyl 2-methylbutanoate	1597	1601	MS, RI	1.2	0.3	-	0.8	-	0.2	1.0	-	0.2	1.4	-	-	-	-	-	-	-	-	-	-
geranyl isovalerate	1604	1607	MS, RI	1.2	0.3	-	0.5	0.5	0.8	1.5	0.1	0.8	1.6	-	-	-	-	-	-	-	-	-	-
(*Z*)-methyljasmonate	1648	1649	MS, RI	-	-	-	-	-	-	-	-	-	-	tr	0.7	0.1		tr	0.3	tr	tr	0.2	0.1
geranyl valerate	1655	1656	MS, RI	0.3	-	0.1	-	-	-	0.5	-	0.1	0.3	-	-	-	-	-	-	-	-	-	-
intermedeol	1661	1666	MS, RI	-	-	-	-	-	-	-	-	-	-	-	0.5	0.9	0.4	1.8	0.5	0.6	0.1	0.3	0.3
chamazulene	1726	1732	MS, RI	-	-	-	-	-	-	-	-	-	-	-	0.7	0.6	0.7	1.6	2.8	1.3	1.3	3.0	1.5
Azulen-2-ol, 1,4-dimethyl-7-(1-methylethyl)-	1952	1960 (28)	MS, RI	2.1	2.0	3.4	0.8	2.3	1.0	2.0	1.1	2.4	4.3	-	-	-	-	-	-	-	-	-	-
hexadecanoic acid	1962	1960	MS, RI	-	-	-	-	-	-	-	-	-	-	0.1	-	0.2	-	0.1	0.2	0.1	0.1	0.1	0.1
nuciferol (*Z*)-isobutanoate	1998	1997 (31)	MS, RI	-	-	-	-	-	-	-	-	-	-	0.4	0.2	0.6	0.5	0.8	1.2	0.2	0.4	0.4	0.2
nuciferol (*E*)-isobutanoate	2004	2004 (31)	MS, RI	-	-	-	-	-	-	-	-	-	-	0.3	0.1	0.4	0.1	0.2	0.7	0.2	0.1	0.1	0.3
Hydrocarbon monoterpenes				**8.2**	**1.5**	**9.1**	**1.1**	**2.0**	**6.9**	**7.6**	**33.8**	**33.4**	**2.8**	**2.7**	**2.8**	**2.0**	**3.1**	**3.2**	**3.4**	**2.3**	**0.6**	**1.1**	**1.5**
Ox. Monot. (no esters)				**1.0**	**0.0**	**0.3**	**0.0**	**0.0**	**0.3**	**0.9**	**1.1**	**1.4**	**0.2**	**94.6**	**67.6**	**78.8**	**77.2**	**86.9**	**85.1**	**90.3**	**69.3**	**92.8**	**75.6**
Monoterpenic esters				**83.6**	**90.3**	**81.9**	**88.2**	**88.1**	**88.4**	**72.9**	**62.4**	**59.9**	**80.0**	**0.1**	**23.3**	**14.0**	**12.4**	**1.0**	**0.6**	**3.0**	**26.0**	**0.2**	**18.0**
Sesquiterpenes				**1.1**	**1.7**	**0.3**	**1.1**	**1.8**	**0.5**	**0.7**	**0.4**	**0.8**	**1.1**	**1.3**	**3.2**	**2.1**	**4.5**	**1.8**	**3.3**	**1.2**	**0.6**	**0.6**	**1.0**
Ox. Sesquiterpenes				**2.1**	**2.0**	**3.4**	**0.8**	**2.3**	**1.0**	**2.0**	**1.1**	**2.4**	**4.3**	**0.8**	**0.8**	**1.9**	**1.0**	**2.8**	**2.4**	**1.0**	**0.6**	**0.8**	**0.8**
Other				**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.0**	**0.1**	**1.1**	**0.8**	**0.7**	**3.2**	**3.5**	**1.5**	**2.4**	**3.9**	**1.7**
Total identified				**96.0**	**95.5**	**95.0**	**91.2**	**94.2**	**97.1**	**84.1**	**98.9**	**97.9**	**88.3**	**99.5**	**98.8**	**99.5**	**98.9**	**98.9**	**98.3**	**99.2**	**99.5**	**99.3**	**98.6**

1. Compounds are listed in order of their elution from a ZB-5 column
2. Kovats retention indices as determined on ZB-5 using homologous series of n-alkanes
3. Retention indices from literature (Adams, R. P., 2007) except for that from other references (marked with superscript letters)
4. Methods of identification: MS, by comparison of the mass spectrum with those from computer mass libraries; RI, by comparison of RI with those from literature; std, by injection of an authentic sample.
5. –: no detected
6. tr: traces (<0.1 %)

7. Tentatively identified. MS, 70 eV, 200ºC, m/z (rel. int.) 136(30), 121(56), 108(20), 107(28), 95(33), 94(30), 93(100), 92(21), 85(34), 82(22), 81(51), 80(34), 79(32), 69(20), 67(28), 57(75), 55(27), 41(72)