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Volatiles from Selected Apiaceae Species Cultivated in Poland—Antimicrobial Activities

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Abstract: As part of our ongoing research on phytoconstituents that can act as promising antimicrobial agents, the essential oils of nine selected Apiaceae plants, cultivated in Poland, were studied. The volatiles of the aerial parts with fruits (*herba cum fructi*) of *Silaum silaus*, *Seseli devenyense*, *Seseli libanotis*, *Ferula assa-foetida*, *Glehnia littoralis* and *Heracleum dulce*, in addition to the fruits (*fructi*) of *Torilis japonica* and *Orlaya grandiflora* as well as of the aerial parts (*herba*) of *Peucedanum luxurians* were investigated through Gas Chromatography–Mass Spectrometry to identify more than 60 different metabolites. The essential oils from *S. devenyense*, *H. dulce*, *T. japonica* and *P. luxurians* are reported for the first time. All examined species were also assayed for their antimicrobial activities against several human pathogenic Gram-positive and -negative bacteria and fungi. The species *H. dulce*, *S. devenyense* and *S. libanotis* exerted the strongest antimicrobial activity, mostly against Gram-positive bacteria strains (MIC values 0.90–1.20 mg/mL). To the best of our knowledge, this is the first attempt to determine the antimicrobial activity of the above Apiaceae species.

Keywords: Apiaceae; gas chromatography-mass spectrometry; volatiles; antimicrobial activity; coumarins

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1. Introduction

Aromatic plants and their essential oils have been used therapeutically for centuries, while many scientific studies are conducted, describing their remarkable healing properties. Essential oils are complex mixtures of natural volatiles, characterized by a strong odor and formed by aromatic plants as secondary metabolites. They are also proven to exert antimicrobial activity against a large number of bacteria and fungi [1].

Apiaceae is considered as one of the most important plant family, including 3780 species and 434 genera [2]. They are mainly distributed in the Mediterranean basin with high economic importance for the food and cosmetic industry [3]. Plant secondary products typically found in Apiaceae are essential oils, including terpenoids and phenylpropanoids, coumarins and furanocoumarins, sesquiterpenelactones, polyacetylenes (polyines), and further compounds derived from acetate units, such as alkylphthalides and the toxic piperidine alkaloids [4]. Plants of the Apiaceae family are used widely in folk medicine for the treatment of several human ailments [5]. In several scientific studies, they have shown antimicrobial and antioxidant activity, and they are considered as promising sources of bioactive agents [5–8].

In the framework of our ongoing research on umbelliferous plants [1,9–16], we report in this study the chemical analyses of volatiles from nine plants of Apiaceae family, which are cultivated in Poland, which to our knowledge have scarcely been studied phytochemically before.

The incidence of microbial infections has increased dramatically together with emergence of antimicrobial resistant strains [15], thus discovering alternative potentially effective treatments for such infectious diseases is a challenge. Furthermore, phytoconstituents are widely considered as promising agents for antimicrobial therapy [15].

The aim of our study is to evaluate the chemical profile and the antimicrobial activity of nine selected Apiaceae species (Table 1).

Table 1. Apiaceae species analyzed in this study.

Plant Species Studied	Plants Parts Studied	Yield %
Silaum silaus (L.) Schinz & Thell.	aerial parts with fruits (*herba cum fructi*)	0.10
Seseli devenyense Simonkai		0.18
Seseli libanotis (L.) W.D.J.Koch		0.20
Glehnia littoralis F. Schmidt ex Miq.		0.15
Ferula assa-foetida L.		0.32
Heracleum dulce Fisch., C.A.Mey. & Avé-Lall.,		0.18
Torillis japonica (Houtt.) DC.	fruits (fructi)	0.25
Orlaya grandiflora (L.) Hoffm		0.22
Peucedanum luxurians Tamamsch.	aerial parts (herba)	0.14

The obtained essential oils have been chemically analyzed through GC and GC/MS. Moreover, they have been investigated for their potential antimicrobial activity against Gram-positive and negative bacteria as well as against human pathogenic fungi, as essential oils are known as potential sources of novel compounds with antibacterial properties.

2. Materials and Methods

2.1. Plant Material

The aerial parts and fruits of all studied plant material were collected from three botanical gardens: Botanical Garden of University of Marie Curie-Skłodowska (UMCS), Lublin, Poland; Botanical Garden Adam Mickiewicz University, Poznan, Poland; Pharmacognostic Garden, Dept. of Pharmacognosy, Medical University of Lublin as well as from wild (Lublin region). Species cultivated in Botanical Garden of UMCS were *Seseli libanotis* (voucher specimen: 56_2018) and *Orlaya grandiflora* (voucher specimen: 49_2018). *Peucedanum luxuriansn* was collected in Botanical Garden of Poznań (voucher specimen: 7973_S003). *Torilis japonica* was collected in natural state (190_2019). The rest studied species were cultivated in Pharmacognostic Garden of Lublin: *Silaum silaus* (voucher specimen: 52_2019), *Seseli devenyense* (voucher specimen: 44_2019), *Glehnia littoralis* (voucher specimen: 180_2019), *Ferula asa-foetida* (voucher specimen: 22_2019). Plant material from the Botanical Garden of Poznan was identified by Grażyna Naser while all the rest species (from Lublin) was confirmed by dr Agnieszka Dąbrowska from Botanical Garden of UMCS.

2.2. Experimental

The air dried and powdered plants were submitted to hydrodistillation. About 10 g of the dried whole fruits, crushed leaves and finely chopped stems were subjected to hydro distillation for 2 h in a Clevenger type apparatus containing 200 mL of distilled water. After recording the yield of oil, n-pentane was added to collect the oil, which was stored at −20 °C until GC/MS and GC analyses. The collected essential oils were dried over anhydrous sodium sulphate.

2.3. GC Analysis

The GC analyses were carried out on a Perkin-Elmer 8500 gas chromatograph with FID, fitted with a Supelcowax-10 fused silica capillary column (30 m $\times$ 0.32 mm i.d., 0.25 μm film thickness). The column temperature was programmed from 60 to 280 °C at a rate of 2.5 °C/min. The injector and detector temperatures were programmed at 230 and 300 °C, respectively. Helium was used as carrier gas, flow rate 1 mL/min.

The GC-MS analyses were performed with an Agilent 7820A Gas Chromatograph System (Shanghai, China) linked to Agilent5977B mass spectrometer system (Santa Clara, CA, USA) equipped with a 30 m length, 0.25 mm id and 0.5 μm film thickness HP5-MS capillary column. The initial column temperature is 60 °C and then increases at a rate of 3 °C/min to a maximum temperature of 280 °C, where it remains for 15 min. Total analysis time was 93 min. Helium was used as a carrier gas at a flow rate of 2.2 mL/min, split ratio 1:10, injector temperature 220 °C, and ionization voltage 70 eV. The compound identification was conducted using the NIST14 library and bibliographic data [17].

2.4. Antimicrobial Activity

In vitro antibacterial study of the studied volatiles was carried out via the agar dilution method in 96-well plates, by measuring the MIC values against two Gram-positive bacteria: *Staphylococcus aureus* (ATCC 25923), *Staphylococcus epidermidis* (ATCC 12228), four Gram-negative bacteria: *Escherichia coli* (ATCC 25922), *Enterobacter cloacae* (ATCC 13047), *Klebsiella pneumoniae* (ATCC 13883) and *Pseudomonas aeruginosa* (ATCC 227853), as well as against three human pathogen fungi: *Candida albicans* (ATCC 10231), *C. tropicalis* (ATCC 13801) and *C. glabrata* (ATCC 28838). Stock solutions of the samples were prepared at 10 and 1 mg/mL, respectively. Serial dilutions of the stock solutions in broth medium (100 μL of Müller–Hinton broth or on Sabouraud broth) were prepared in a microtiter plate (96 wells). All tested organisms have a final cell concentration of 10^7 cell/mL. Then 1 μL of the microbial suspension (the inoculum, in sterile distilled water) was added to each well. For each strain, the growth conditions and the sterility of the medium were checked, and the plates were incubated as referred above. MICs were determined as the lowest concentrations preventing visible growth. Standard antibiotic netilmicin and amoxicillin (at concentrations 4–88 μg/mL) were used in order to control the sensitivity of the tested bacteria, while 5-fluocytosine and amphotericin B (at concentrations 0.5–25 μg/mL) were used as controls against the tested fungi. The experiments were repeated three times, and the results were expressed as average values [18].

3. Results and Discussion

3.1. Chemical Analysis

Silaum silaus (L.) Schinz & Thell., or pepper saxifrage, occurs from Europe to West Siberia and North Caucasus. Plants flowers in summer and fruits are developed by autumn. Whole plant has been used to treat bladder diseases, and leaves are edible as potherbs [19]. The analysis of the essential oil from the aerial parts of *S. silaus* (Table 2) showed the presence of 14 metabolites (87.18% of the total) among which α-pinene (22.48%), myristicin (20.01%), methyl eugenol (9.80%), methyl isoeugenol (7.60%), o-cymene (6.47%), E-*β*-ocimene (5.97%) and γ-terpinene (4.41%) were the most abundant ones. These results are in agreement with previous bibliographic data for *S. silaus* samples from different areas in Austria. In that study, myristicin was the main compound of the essential oil from the fruits (approx. 60%), followed by E-*β*-ocimene and α-pinene, while of the leaves and stems, α-pinene (30%) predominated, with E-β-ocimene and myristicin as further major compounds [19]. The abundant chemical category of the compounds in this oil is the monoterpene hydrocarbons followed by phenylpropene and alcohols (Table 3).

Table 2. The composition of Apiaceae essential oils.

Compounds	*Silaum silaus*	*Seseli devenyense*	*Seseli libanotis*	*Glehnia littoralis*	*Ferula assa-foetida*	*Torilis japonica*	*Orlaya grandiflora*	*Peucedanum luxurians*
α-pinene	22.48	0.84	1.90	0.50	5.24	-	-	-
camphene	-	0.2	0.20	-	-	-	-	-
sabinene	0.65	-	18.37	-	1.28	-	-	-
myrcene	3.02		1.25	-	18.74	-	-	1.33
β-pinene	-	0.48	0.57	2.30	-	-	-	-
propyl octanoate	-	-	-	18.80	-	-	-	-
β-elemene	-		1.97	-	-	18.12	-	-
γ-elemene	-	-	2.20	5.94	-	-	-	-
δ-elemene	-	-	-	-	-	-	-	5.10
β-caryophyllene	-	3.30	28.70	-	-	11.02	18.83	8.84
limonene	-	0.48	-	-	4.01	-	-	-
β-phellandrene	-	-	13.16	16.26	0.18	-	-	-
δ-3-carene	2.49	0.05	-	1.21	1.45	-	-	-
p-cymene	-	0.17	1.66	0.55	-	-	-	-
o-cymene	6.47		-	-	-	-	-	-
tricyclene	-	-	0.41	-	-	-	-	-
geranyl acetate	-	5.31	-	-	-	-	-	-
Z-β-ocimene	-	0.38	-	-	0.16	-	-	-
E-β-ocimene	5.97	0.08	-	-	0.38	-	-	-
α-amorphene	-	7.97	0.60	-	-	-	8.56	-
eugenol	0.10	-	-	-	8.05	-	-	-
methyl eugenol	9.80	-	-	-	20.75	-	-	-
Z-methyl isoeugenol	0.95	-	-	-	-	-	-	-
γ-terpinene	4.41	0.11	0.36	-	2.83	-	-	-
meta-tolualdeyde	-	0.35	-	-	0.21		-	-
terpinolene	0.34	0.06	-	-	1.93	-	-	-
anethole	-		-	1.81	0.11	-	-	
β-cubebene	-	-	-	-	0.35	-	-	-
α-humulene	-	-	-	-	-	0.97	-	
trans-β-farnesene	-	-	1.36	1.73	-	-	-	16.35
germacrene D	2.80	4.70	1.96	0.65	5.75	9.33	7.27	13.76
bicyclo-germacrene	-	-	1.67	-	-	-		-
α-germacrene	-	-	-	-	-	8.29	-	-
α-muurolene	-	3.57	-	-	-	-	-	

Table 2. *Cont.*

Compounds	*Silaum silaus*	*Seseli devenyense*	*Seseli libanotis*	*Glehnia littoralis*	*Ferula assa-foetida*	*Torilis japonica*	*Orlaya grandiflora*	*Peucedanum luxurians*
γ-muurolene	-	3.67	-	-	-	-	-	-
E-methyl isoeugenol	7.60	-	-	-	25.46	-	-	-
α-zingiberene	-	-	-	-	-	-	-	10.58
β-sesquiphellandrene	-	17.79	-	-	-	-	-	3.72
δ-cadinene	-	-	-	0.79	0.70	1.12	10.83	-
α-cadinene	-	-	-	-	-	-	2.48	-
myristicin	20.01	-	-	-	-	-	-	-
palmitic acid	-	-	-	16.45	-	-	-	-
spathulenol	0.09	5.70	12.80	0.59	0.31		–	-
germacrene B	-	-	-	4.06	-	-	0.33	-
calamenene	-	-	-	0.42	-	-	-	-
t-cadinol	-	-	-	-	0.71	-	5.33	-
1,6 -germacradien-5-ol	-	-	-	-	-	38.46	-	
4,5-dehydro-isolongifolene	-	-	-	2.48	-	-	-	-
linoleic acid	-	-	-	9.70	-	-	-	-
oleic acid	-	-	-	3.17	-	-	-	-
unknown compounds	-	29.09	-	-	-	-	28.64	26.50
Total (%)	87.18	84.30	89.14	87.41	98.6	87.31	82.27	86.18

-: not detected.

Table 3. Chemical categories (% area) in the studied Apiaceae essential oils.

Chemical Categories	*S. silaus*	*S. devenyense*	*S. libanotis*	*G. littoralis*	*F. assa-foetida*	*H. dulce*	*T. japonica*	*O. grandiflora*	*P. luxurians*
Monoterpene hydrocarbons	45.83	2.85	37.88	20.82	36.2	-	-	-	1.33
Sesquiterpene hydrocarbons	2.80	41.0	38.46	16.07	6.8	2.01	48.85	48.3	58.35
Phenylpropene	20.01	-	-	1.81	0.11	-	-	-	-
Aldehydes	-	0.35	-	-	0.21	-	-	-	-
Alcohols	18.54	5.70	12.80	0.59	55.28	-	38.46	5.33	-
Esters	-	5.31	-	18.80	-	-	-	-	-
Fatty acids	-	-	-	29.32	-	27.84	-	-	-
Coumarins	-	-	-	-	-	58.38	-	-	-
Unknown	-	29.09	-	-	-	-	-	28.64	26.50

Seseli devenyense Simonkai (*Seseli elatum* subsp. *osseum* (Crantz) P.W.Ball.) was studied exhaustively previously, by our scientific team [12,13] as a source of several coumarins, which have been isolated and structurally determined, while its essential oil has never been studied before. In the present work, *S devenyense* yielded 0.18% of essential oil, consisting of 19 components (Table 2) with β-sesquiphellandrene (17.8%), amorphene (8%), spathulenol (5.7%) and geranyl acetate (5.30%) as main ones. Sesquiterpene hydrocarbons is the abundant chemical category with percentage 41% of the total (Table 3).

Seseli libanotis (L.) *W.D.J. Koch* is an aromatic plant widely distributed from Central Europe to West Siberia. In Turkish folk medicine, the aerial parts of the plant were popularly used against inflammations as well as antinociceptive agent probably due to its coumarins' content. The leaves of *S. libanotis* are consumed as a vegetable in Turkey [1]. The essential oil composition from different geographic areas in Austria has been studied, and monoterpenes such as α-pinene, sabinene and β-myrcene and the sesquiterpene germacrene D were present in all essential oils from its aerial parts [20]. Root's volatiles have been also studied and were dominated by α-pinene [20], while in a study on the fruits of the plant [1] sabinene and β-phellandrene appeared as the most abundant metabolites. Volatiles obtained from the aerial parts of the plant from Iran has shown trans-caryophyllene (20%) as the main constituent, followed by limonene, α-pinene and caryophyllene oxide [21]. The essential oil from *S. libanotis*, in the present study (yield 0.20%), appeared a rich chemical profile (Table 2) with 17 identified metabolites (89.14%), dominated by β-carryophyllene (28.70%), sabinene (18.37%), together with β-phellandrene (13.16%) and spathulenol (12.80%) as major ones. In this oil the percentage of monoterpene and sesquiterpene hydrocarbons is equally high (~38%).

Glehnia littoralis F. Schmidt ex Miq. essential oils from aerial and root parts have been investigated previously only in Japan, and the main constituents of the essential oils were found to be α-pinene, limonene, β-phellandrene, germacrene B, spathulenol, β-oplopenone, panaxynol, propyl octanoate, hexadecanoic acid and linoleic acid [22]. Moreover, oral administration of certain extracts of *Glehnia* root prolonged pentobarbital-induced sleeping time due to inhibition of liver metabolizing enzymes and have caused analgesic effects in vivo in mice [23]. In this study, the composition of the essential oil (yield 0.15%) of the aerial parts together with fruits (Table 2) is comparable to previously investigated essential oil from aerial and root parts [22] as propyl octanoate (18.80%), palmitic acid (16.45%), β-phellandrene (16.26%), γ-elemene (5.94%) and germacrene B (4.06%) were the most abundant compounds. It is noteworthy that this is the only essential oil with high percentage of fatty acids (29.32%), followed by monoterpene and sesquiterpene hydrocarbons as well as by esters.

Ferula assa-foetida L. is a perennial herb distributed throughout the Mediterranean area and central Asia. It is reputed in Iranian and Indian traditional medicine for its therapeutic applications against a number of different disorders [24,25] and in food industry, due to the occurrence of essential oils and/or mainly oleoresin possessing strong aromatic scent [26]. It contains mainly sesquiterpene coumarins, phenolics and volatile compounds (especially sulfur compounds) [26,27]. The most frequent compounds that occurred among the main constituents of *Ferula* oils were α-pinene, β-pinene, myrcene and limonene (among monoterpene hydrocarbons); linalool, α-terpineol and neryl acetate (among oxygenated monoterpenes); β-caryophyllene, germacrene B, germacrene D and δ-cadinene (among sesquiterpene hydrocarbons); caryophyllene oxide, α-cadinol, guaiol and spathulenol (among oxygenated sesquiterpenes) and sec-butyl-(Z)-propenyl disulfide and sec-butyl-(E)-propenyl disulfide (among sulfur-containing compounds) [24]. In our study, the essential oil (yield 0.32%) exerted a rich chemical profile of 20 constituents (Table 2) belonging to monoterpene and sesquiterpene hydrocarbons. Methyl isoeugenol (25.46%), methyl eugenol (20.75%), myrcene (18.74%), germacrene D (5.75%), α-pinene (5.24%), and limonene (4.01%) have been detected in *F. assa-foetida*, while it is characteristic the absence of sulfur-containing compounds (butyl-propenyl disulfides) which have been referred in other chemical studies and the fact that alcohols is the abundant category (more than 50%).

Furthermore, the aerial parts of *Heracleum dulce* Fisch., C.A.Mey. & Avé-Lall., not having been previously studied phytochemically, showed a unique chemical profile (Table 4) as it contained mainly coumarins (58.38%), several of which have been identified and a high percentage of fatty acids.

Table 4. The composition of the essential oil from *Heracleum dulce.*

Compounds	*H. dulce*
Psoralene	0.73
palmitic acid	0.77
psoralene-8-hydroxy (xanthotoxol)	4.87
xanthotoxin	2.88
bergapten	1.04
germacrene D	2.01
linoleic acid	7.10
oleic acid	19.46
8-heptadecenoic acid	0.51
coumarin	0.84
coumarin	18.04
coumarin	5.58
coumarin	5.39
coumarin	13.33
coumarin	0.61
coumarin	0.47
allo-imperatorin	0.75
coumarin	3.85
Hexadecyl oleate	0.67
Total (%)	88.90

Torilis japonica D.C. (Japanese name "Jabujirami") is widespread in East Asia (China, Korea, Mongolia and Russia), also naturalized in the warmer areas of Europe. Its fruits were used as a substitute medicament of the She-Chuang-Zi (*Cnidium monnieri* fructi, snowparsley), known for promoting healthy libido and fertility levels. They have been studied phytochemically twice before and had afforded to new hemiterpenoid pentol and monoterpenoid glycosides [28] as well as guaiane-type sesquiterpenoid glycosides [29]. The essential oil of the plant, to the best of our knowledge, has never been investigated before. In the present study, through the chemical investigation of its volatiles (yield 0.25%), the metabolites 1,6-germacradien-5-ol (38.46%), β-elemene (18.12%), β-caryophyllene (11.02%), germacrene D (9.33%) and α-germacrene (8.29%) appeared as the main compounds (Table 2). In this essential oil, only sesquiterpenes and alcohols are present.

The essential oil of the aerial parts of *Orlaya grandiflora* (L.) Hoffm., the white laceflower, growing wild in Central Balkan area, has been reported once before [30], where sabinene, a-pinene followed by γ-terpinene, β-caryophyllene and germacrene D have been identified as abundant compounds. The volatiles from the fruits essential oil of *O. grandiflora* (yield 0.22%) have been examined in this study, where β-caryophyllene (18.83%), δ-cadinene (10.83%), α-amorhene (8.56%) and germacrene D (7.27%) appeared as the major constituents and all of them belong to sesqiterpenes (Table 2). It is obvious that out of the identification of germacrene D in both oils, their chemical profiles did not show any other similarities.

Finally, herba of *Peucedanum luxurians* was studied phytochemically before, as a source of rare bioactive furanocourmarins with unique structures by our scientific team [3,6–8], while its volatiles have never been studied until now. *P luxurians* is an endemic plant from Armenia, growing in the area around Mount Ararat [31]. In the present study, the analysis revealed the presence of *trans*-β-farnesene (16.35%), germacrene D (13.76%) α-zingiberene (10.58%) and β-caryophyllene (8.84%), as the most abundant constituents (Table 2). Among its constituents, one (26.50%) remained unidentified, which unfortunately due to the low yield of the oil (0.14%) was not possible to be further isolated and structurally determined, while the majority of the identified compounds belong to the sesquiterpenes (Table 3).

3.2. Antimicrobial Activity Evaluation

All essential oils assayed against a panel of nine human pathogenic microbia, two Gram-positive (*Staphylococcus aureus*, *S. epidermidis*), four Gram-negative (*Escherichia coli, Pseudomonas aeruginosa, Klebsiella pneumoniae* and *Enterobacte cloacae*) as well as against three fungi strains (*Candida albicans, C. tropicalis* and *C. glabrata*). According to the results presented in Table 5, the essential oils of *G. littoralis* and *T. japonica* appeared completely inactive against all assayed microbial strains. *S. silaus* showed a moderate activity against Gram-positive bacteria *S. aureus* and *S. epidermidis* (MIC values 1.25, 1.48 mg/mL, respectively) and a very weak activity against Gram-negative bacteria (MIC values 7.38–13.45 mg/mL), while being inactive against all *Candidas'* strains. *O. grandiflora* compared to *S. silaus* exerted a stronger activity specifically against both Gram-positive strains (1.52 and 1.60 mg/mL). *S. libanotis* aerial parts' volatiles exerted moderate activity against Gram-positive bacteria (MIC 1.35, 1.47 mg/mL, respectively) and weak activities against all the Gram-negative bacteria and the fungi. Corresponding results to that of *S. libanotis* were revealed from *S. devenyense* (MIC 1.35, 1.20 mg/mL). These results are in agreement with previously published data, where Gram-negative bacteria are less sensitive to essential oils obtained from plants belonging to the Apiaceae family [1]. The essential oil from *F. assa-foetida* showed a weak activity against all tested microorganisms, while *P. luxurians* appeared together with *H. dulce* as the most active among all assayed essential oils exerting activity against all assayed microorganisms. More specifically *H. dulce* showed strong activity against Gram-positive bacteria (MIC values 0.90 and 0.87 mg/mL) and a moderate one against the rest Gram-negative ones (MIC values 3.30–4.05 mg/mL), while it was the only one, which exhibited activity (weak) against the three assayed fungi (MIC values 4.0–4.9 mg/mL). *P. luxurians* expressed also strong activity against Gram-positive bacteria (MIC values 1.0–1.20 mg/mL) and weaker against Gram-negative one (MIC values 2.80–5.76 mg/mL) and the tested fungi (MIC values 4.87–6.89 mg/mL).

Table 5. Antimicrobial activity of the tested essential oils compared to common antimicrobial agents (mg/mL).

	S. aureus	***S. epidermidis***	***P. aeruginosa***	***E. cloacae***	***K. pnaumoniae***	***E. coli***	***C. albicans***	***C. tropicalis***	***C. glabrata***
S. silaus	1.80	1.25	8.70	13.45	10.27	7.38	>20	>20	>20
S. devenyense	1.35	1.20	12.80	12.00	11.62	13.41	10.70	9.65	9.00
S. libanotis	1.35	1.47	5.68	6.00	6.32	6.70	12.35	11.45	10.80
G.littoralis	>20	>20	>20	>20	>20	>20	>20	>20	>20
F. assa-foetida	7.23	6.80	5.70	4.65	5.23	4.35	7.65	5.43	4.30
H. dulce	0.90	0.87	3.30	3.84	4.05	3.92	4.90	4.78	4.00
T.japonica	>20	>20	>20	>20	>20	>20	>20	>20	>20
O. grandiflora	1.60	1.52	8.70	9.60	12.32	15.70	16.30	12.27	11.90
P. luxurians	1.20	1.00	2.80	>20	5.76	3.43	6.89	5.94	4.87
itraconazol	nt	nt	nt	nt	nt	nt	1.0×10^{-3}	0.1×10^{-3}	1×10^{-3}
5-flucytocine	nt	nt	nt	nt	nt	nt	0.1×10^{-3}	1.0×10^{-3}	9.7×10^{-3}
amphotericin B	nt	nt	nt	nt	nt	nt	1.0×10^{-3}	0.5×10^{-3}	0.4×10^{-3}
amoxicillin	1.8×10^{-3}	1.5×10^{-3}	2.5×10^{-3}	2.7×10^{-3}	3.1×10^{-3}	2.1×10^{-3}	nt	nt	nt
netilmicin	3.0×10^{-3}	2.9×10^{-3}	7.0×10^{-3}	7.8×10^{-3}	6.8×10^{-3}	3.1×10^{-3}	nt	nt	nt

nt: not tested.

4. Conclusions

The analyses of the essential oils of nine selected Apiaceae plants, all of them cultivated in Poland, resulted to some new data for *Seseli devenyense, Heracleum dulce, Torillis japonica* and *Peucedanum luxurians* as they have never been studied before for their volatiles. Moreover, the essential oils from *Silaum silaus* and *Orlaya grandiflora* have been analyzed for the second time, showing differences in their chemical profile probably due to different cultivation, climate and geographic conditions [32–34]. *Glehnia littoralis* essential oil, cultivated in Europe, was analyzed for the first time, while *Seseli libanotis* was studied for the second time in Europe showing differences in comparison with published data. *Ferula assa-foetida* was also analyzed in this study due to its wide use and in order to compare its chemical profile with previously reported data.

In general, the identified compounds showed a great variability among investigated Apiaceae species. Among approx. 60 different metabolites, which were identified, sesquiterpene germacrene D was the only metabolite common in all nine essential oils. It is noteworthy that the chemical profile of *Heracleum dulce* was completely different from all the other studied species, as it contains mainly coumarins. Moreover, it is also of interest that the high proportion content of myristicin in the *S. silaus* essential oil, which together with α-pinene, and α-caryophyllene were also present in many other plants of the Apiaceae family.

The essential oils or some of their constituents are very effective against a large variety of organisms including bacteria and fungi. As typical lipophiles, they disrupt the structure of the cytoplasmic membrane and permeabilize them. In bacteria, the permeabilization of the membranes is associated with loss of ions and reduction of membrane potential [1,15].

Throughout the antimicrobial tests, *Peucedanum luxurians* together with *Heracleum dulce* appeared as the most active among all assayed essential oils, exerting activity against all assayed microorganisms. These results are in agreement with bibliographic data, as selected *Peucedanum* plants (*P. paniculatum, P. alsaticum, P. cervaria, P. graveolens, P. ruthenicum, P. zenkeri and P. ostruthium*) have been used for centuries as antibacterial agents, and for some of them, the activity was confirmed by biological and pharmacological studies, showing moderate or high activity against different human pathogens [15].

Additionally, *Heracleum dulce* essential oil was full of coumarins, and its exerted bioactivity could be contributed mainly to these compounds. Coumarins, naturally plant-derived metabolites, possess a wide variety of known bioactivities. Series of coumarin analogues naturally-isolated coumarins, as well as their chemically modified analogs, are being extensively studied due to their broad spectrum, low toxicity, and lower drug resistance properties [9,11,13–15]. Moreover, isolated furanocoumarins, from different Apiaceae species (like imperatorin, bergapten, ostruthin, and isoimperatorin) were found to be very active antimicrobial agents [35–37]. The above data suggest that several among the studied essential oils may be an alternative promising way to treat various infections with further extension towards cosmetic and pharmaceutical applications.

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References

1. Skalicka-Wozniak, K.; Los, R.; Glowniak, K.; Malm, A. Comparison of Hydrodistillation and Headspace Solid-Phase Micro-extraction Techniques for Antibacterial Volatile Compounds from the Fruits of *Seseli libanotis*. *Nat. Prod. Commun.* **2010**, *5*, 1427–1430. [PubMed]
2. Sayed-Ahmad, B.; Talou, T.; Saad, Z.; Hijazi, A.; Merah, O. The Apiaceae: Ethnomedicinal family as source for industrial uses. *Ind. Crop. Prod.* **2017**, *109*, 661–671. [CrossRef]
3. Kamte, S.L.N.; Ranjbarian, F.; Cianfaglione, K.; Sut, S.; Dall'Acqua, S.; Bruno, M.; Afshar, F.H.; Iannarelli, R.; Benelli, G.; Cappellacci, L.; et al. Identification of highly effective antitrypanosomal compounds in essential oils from the Apiaceae family. *Ecotoxicol. Environ. Saf.* **2018**, *156*, 154–165. [CrossRef]
4. Chizzola, R. Essential Oil Composition of Wild Growing Apiaceae from Europe and the Mediterranean. *Nat. Prod. Commun.* **2010**, *5*, 1477–1492. [CrossRef] [PubMed]
5. Zengin, G.; Sinan, K.I.; Ak, G.; Mahomoodally, M.F.; Paksoy, M.Y.; Picot-Allain, C.; Glamocilja, J.; Sokovic, M.; Jekő, J.; Cziá-ky, Z.; et al. Chemical profile, antioxidant, antimicrobial, enzyme inhibitory, and cyto-toxicity of seven Apiaceae species from Turkey: A comparative study. *Ind. Crops Prod.* **2020**, *153*, 112572. [CrossRef]
6. Hasheminya, S.-M.; Dehghannya, J. Chemical composition, antioxidant, antibacterial, and antifungal properties of essential oil from wild *Heracleum rawianum*. *Biocatal. Agric. Biotechnol.* **2021**, *31*, 101913. [CrossRef]
7. Pateiro, M.; Munekata, P.E.; Sant'Ana, A.S.; Domínguez, R.; Rodríguez-Lázaro, D.; Lorenzo, J.M. Application of essential oils as antimicrobial agents against spoilage and pathogenic microorganisms in meat products. *Int. J. Food Microbiol.* **2021**, *337*, 108966. [CrossRef]
8. Süzgeç-Selçuk, S.; Dikpınar, T. Phytochemical evaluation of the Ferulago genus and the pharmacological activities of its coumarin constituents. *J. Herb. Med.* **2021**, *25*, 100415. [CrossRef]
9. Melliou, E.; Magiatis, P.; Mitaku, S.; Skaltsounis, A.-L.; Chinou, E.; Chinou, I. Natural and Synthetic 2,2-Dimethylpyranocoumarins with Antibacterial Activity. *J. Nat. Prod.* **2005**, *68*, 78–82. [CrossRef]
10. Chinou, I.; Widelski, J.; Fokialakis, N.; Magiatis, P.; Glowniak, K. Coumarins from *Peucedanum luxurians*. *Fitoterapia* **2007**, *78*, 448–449. [CrossRef]
11. Widelski, J.; Popova, M.; Graikou, K.; Glowniak, K.; Chinou, I. Coumarins from *Angelica lucida* L.-Antibacterial Activities. *Molecules* **2009**, *14*, 2729–2734. [CrossRef] [PubMed]
12. Widelski:, J.; Melliou, E.; Fokialakis, N.; Magiatis, P.; Glowniak, K.; Chinou, I. Coumarins from the Fruits of *Seseli devenyense*. *J. Nat. Prod.* **2005**, *68*, 1637–1641. [CrossRef]
13. Widelski, J.; Grzegorczyk, A.; Malm, A.; Chinou, I.; Głowniak, K. Antimicrobial activity of petroleum ether and methanolic extracts from fruits of Seseli devenyense Simonk. and the herb of *Peucedanum luxurians* Tamam. *Curr. Issues Pharm. Med. Sci.* **2015**, *28*, 257–259. [CrossRef]
14. Widelski, J.; Kukula-Koch, W.; Baj, T.; Kedzierski, B.; Fokialakis, N.; Magiatis, P.; Pozarowski, P.; Rolinski, J.; Graikou, K.; Chinou, I.; et al. Rare Coumarins Induce Apoptosis, G1 Cell Block and Reduce RNA Content in HL60 Cells. *Open Chem.* **2017**, *15*, 1–6. [CrossRef]

15. Widelski, J.; Vlad Luca, S.; Skiba, A.; Chinou, I.; Marcourt, L.; Wolfender, J.L.; Skalicka-Woźniak, K. Isolation and antimicrobi-al activity of coumarin derivatives from fruits of *Peucedanum luxurians* Tamamsh. *Molecules* **2018**, *23*, 1222. [CrossRef] [PubMed]
16. Kontaratou, V.; Widelski, J.; Wojtowicz, I.; Glowniak, K.; Chinou, I. Volatiles from three Apiaceae species. In Proceedings of the 5th International Symposium on Chromatography of Natural Products, Lublin, Poland, 19–22 June 2006.
17. Adams, R.P. *Identification of Essential Oil Components by Gas Chromatography/Mass Spectrometry*; Allured Publishing Corporation: Carol Stream, IL, USA, 2007; Volume 456.
18. Atsalakis, E.; Chinou, I.; Makropoulou, M.; Karabournioti, S.; Graikou, K. Evaluation of Phenolic Compounds in Cistus cre-ticus Bee Pollen from Greece. Antioxidant and Antimicrobial Properties. *Nat. Prod. Commun.* **2017**, *12*, 1813–1816.
19. Chizzola, R. Variability of the Volatile Oil Composition in a Population of *Silaum silaus* from Eastern Austria. *Nat. Prod. Commun.* **2008**, *3*, 1141–1144. [CrossRef]
20. Chizzola, R. Chemodiversity of Essential Oils in Seseli libanotis (L.) W.D.J. Koch (*Apiaceae*) in Central Europe. *Chem. Biodivers.* **2019**, *16*. [CrossRef]
21. Masoudi, S.; Esmaeili, A.; Ali khalilzadeh, M.; Rustaiyan, A.; Moazami, N.; Akhgar, M.R.; Varavipoor, M. Volatile Constitu-ents of *Dorema aucheri* Boiss., *Seseli libanotis* (L.) WD Koch *var. armeniacum* Bordz. and *Conium maculatum* L. Three Umbel-liferae Herbs Growing Wild in Iran. *Flavour Fragr. J.* **2006**, *21*, 801–804. [CrossRef]
22. Miyazawa, M.; Kurose, K.; Itoh, A.; Hiraoka, N. Comparison of the Essential Oils of Glehnia littoralis from Northern and Southern Japan. *J. Agric. Food Chem.* **2001**, *49*, 5433–5436. [CrossRef] [PubMed]
23. Okuyama, E.; Hasegawa, T.; Matsushita, T.; Fujimoto, H.; Ishibashi, M.; Yamazaki, M.; Hosokawa, M.; Hiraoka, N.; Anetal, M.; Masuda, T. Analgesic Components of Glehnia Root (*Glehnia littoralis*). *J. Nat. Med.* **1998**, *52*, 491–501.
24. Sahebkar, A.; Iranshahi, M. Volatile Constituents of the Genus Ferula (*Apiaceae*): A Review. *J. Essent. Oil Bear. Plants* **2011**, *14*, 504–531. [CrossRef]
25. Mohammad, N.S.; Dehpour, A.A.; Ebrahimzadeh, M.A.; Fazel, N.S. Antioxidant activity of the methanol extract of Ferula assafoetida and its essential oil composition. *Grasas Aceites* **2009**, *60*, 405–412. [CrossRef]
26. Farhadi, F.; Iranshahi, M.; Taghizadeh, S.F.; Asili, J. Volatile sulfur compounds: The possible metabolite pattern to identify the sources and types of asafoetida by headspace GC/MS analysis. *Ind. Crop. Prod.* **2020**, *155*. [CrossRef]
27. Kavoosi, G.; Tafsiry, A.; Ebdam, A.A.; Rowshan, V. Evaluation of Antioxidant and Antimicrobial Activities of Essential Oils from *Carum copticum* Seed and *Ferula asafoetida* Latex. *J. Food Sci.* **2013**, *78*, T356–T361. [CrossRef] [PubMed]
28. Kitajima, J.; Suzuki, N.; Tanaka, Y. ChemInform Abstract: New Guaiane-Type Sesquiterpenoid Glycosides from Torillis japonica Fruit. *Chem. Pharm. Bull.* **1998**, *46*, 1743–1747. [CrossRef]
29. Kitajima, J.; Suzuki, N.; Ishikawa, T.; Tanaka, Y. New Hemiterpenoid Pentol and Monoterpenoid Glycoside of Torillis japonica Fruit, and Consideration of the Origin of Apiose. *Chem. Pharm. Bull.* **1998**, *46*, 1583–1586. [CrossRef]
30. Kapetanos, C.; Karioti, A.; Bojović, S.; Marin, P.; Veljić, M.; Skaltsa, H. Chemical and Principal-Component Analyses of the Essential Oils of Apioideae Taxa (*Apiaceae*) from Central Balkan. *Chem. Biodivers.* **2008**, *5*, 101–119. [CrossRef]
31. Sarkhail, P. Traditional uses, phytochemistry and pharmacological properties of the genus *Peucedanum*: A review. *J. Ethnopharmacol.* **2014**, *156*, 235–270. [CrossRef]
32. Şanli, A.; Karadoğan, T. Geographical Impact On Essential Oil Composition Of Endemic Kundmannia Anatolica Hub.-Mor. (*Apiaceae*). *Afr. J. Tradit. Complement. Altern. Med.* **2017**, *14*, 131–137. [CrossRef]
33. Mekinić, I.G.; Šimat, V.; Ljubenkov, I.; Burčul, F.; Grga, M.; Mihajlovski, M.; Lončar, R.; Katalinić, V.; Skroza, D. Influence of the vegetation period on sea fennel, *Crithmum maritimum* L. (*Apiaceae*), phenolic composition, antioxidant and anticholinesterase activities. *Ind. Crop. Prod.* **2018**, *124*, 947–953. [CrossRef]
34. Msaada, K.; Hosni, K.; Ben Taarit, M.; Chahed, T.; Kchouk, M.E.; Marzouk, B. Changes on essential oil composition of coriander (*Coriandrum sativum* L.) fruits during three stages of maturity. *Food Chem.* **2007**, *102*, 1131–1134. [CrossRef]
35. Schinkovitz, A.; Gibbons, S.; Stavri, M.; Cocksedge, M.J.; Bucar, F. Ostruthin: An Antimycobacterial Coumarin from the Roots of *Peucedanum ostruthium*. *Planta Medica* **2003**, *69*, 369–371. [CrossRef] [PubMed]
36. Gökay, O.; Kühner, D.; Los, M.; Götz, F.; Bertsche, U.; Albert, K. An efficient approach for the isolation, identification and evaluation of antimicrobial plant components on an analytical scale, demonstrated by the example of *Radix imperatoriae*. *Anal. Bioanal. Chem.* **2010**, *398*, 2039–2047. [CrossRef] [PubMed]
37. Ngwendson, J.N.; Bedir, E.; Efange, S.M.N.; Okunji, C.O.; Iwu, M.M.; Schuster, B.G.; Khan, I.A. Constituents of *Peucedanum zenkeri* seeds and their antimicrobial effects. *Pharm.-Int. J. Pharm. Sci.* **2003**, *58*, 587–589.