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The Essential Oil Composition of *Eryngium galioides* Lam.—An Endemic Species of the Iberian Peninsula

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Abstract: The *Eryngium* L. genus belongs to the *Apiaceae* family and, with about 250 species, has a cosmopolitan distribution. Only fourteen of the twenty-six species described in Flora Europaea grow in the Iberian Peninsula. One of these is *Eryngium galioides* Lam., a small annual plant (2–30 cm) that grows in open dry places in the mid-west of the Iberian Peninsula. For this study, the whole plant (aerial parts and roots) of this species was gathered in Guadalajara (Spain). The essential oil of this population was extracted by hydro-distillation and analyzed by gas chromatography (GC) and gas chromatography coupled to mass spectrometry (GC-MS). It is worth noting that this species gave rise to a relatively high essential oil yield (0.48%) in comparison with other species of this genus. *E. galioides* oil consisted of a complex mixture of more than 70 compounds. The main constituents of this oil were identified as valencene (49.7%) and a phyllocladene isomer (23.7%), both representing more than the 70% of the total oil. Other representative compounds of this oil were found to be β-chamigrene (6.0%), γ-muurolene (3.4%), (*E*)-caryophyllene (3.0%) and β-elemene (1.6%). As far as we know, this is the first report about the chemical composition of *E. galioides* essential oils. With this work, we contribute to the knowledge of this genus and provide a chemical and botanical basis to promote the in vitro cultivation of *E. galioides* as a source of essential oils rich in bio-actives for application in different fields.

Keywords: *Eryngium galioides*; *Eryngium*; Apiaceae; essential oil; chemical composition; valencene and phyllocladene isomer

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1. Introduction

The Apiaceae is known worldwide as the parsley family, comprising about 434 genera and nearly 3.780 species of plants distributed throughout a wide variety of habitats mainly in the north temperate regions of the world [1]. Many of those species are economically important as leaf, root vegetables, herbs, spices and garden ornamentals and widely cultivated, including such species as *Apium graveolens* L. (Celery), *Daucus carota* L. (Carrot), *Foeniculum vulgare* Mill. (Fennel), *Anethum graveolens* L. (Dill), *Petroselinum crispum* (Mill.) Nyman ex A.W. Hill (Parsley), *Coriandrum sativum* L. (Coriander), *Carum carvi* L. (Caraway), *Cuminum cyminum* L. (Cumin) and *Pimpinella anisum* L. (Anise). Moreover, most of the species analyzed to date have different biological activities (antibacterial, antifungal, herbicidal, insecticidal or repellent) that support their culinary use not only as a flavoring [2]. However, other species are source of other type of bio-active compounds such *Conium maculatum* L. (Hemlock) that has been used as poison [3,4].

The genus *Eryngium* L., which belongs to this family and comprises about 250 species, has a cosmopolitan distribution. It exhibits great morphological and habitat diversity and includes annual and perennial herbs with hairless and spiny leaves that present dome-shaped umbels of steely blue or white flowers with whorls of spiny basal bracts. Only fourteen of the twenty-six species described in *Flora Europaea* grow wildly in the Iberian Peninsula [5].

Eryngium galiodes Lam. is a small annual plant (2–30 cm), rarely biennial, that is spinescent in the inflorescences. The roots are more or less fasciculated, dark brown. Stems, 0.1–0.25 cm in diameter at the base, range from almost undivided to profusely branched, often from the base itself, and are straw colored. Basal leaves (2–8 × 0.2–0.12 cm), are sparse, linear-lanceolate or oblanceolate. The cauline leaves are scattered and scarcely branched. Inflorescences on hemispherical capitula, barely visible from the involvement, are sessile or almost so. It produces small fruits in mericarps (1.5 mm), mostly naked, with elongated scales on top [6]. It grows in open dry places in the mid-west of the Iberian Peninsula according to the vouchers that have been revised from different Portuguese and Spanish herbaria (Figure 1). According to the European Nature Information System (EUNIS) and following the International Union for de Conservation of the Nature (Unión Internacional para la Conservación de la Naturaleza: UICN) status, *E. galioides* is considered endangered [7].

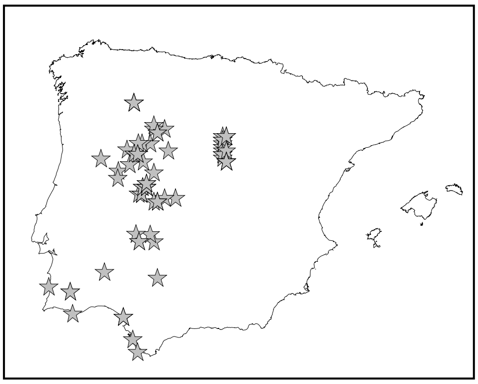

Figure 1. Distribution of *Eryngium galiodes* Lam. in the Iberian Peninsula.

A genus like this with a wide distribution has been the object of different studies. Focusing on the last 20 years, we have found 74 papers describing essential oils [8–56], 3 reviews [57–59] and 23 studies of their biological activities [60–81]. Although more than 70 papers have been published related to this genus, only 37 of the approximately 250 described species have been reported. Most of them relative to the chemical composition of the essential oils. The species analyzed to date in alphabetical order are *Eryngium alpinum* [8], *Eryngium amethystinum* [8–11], *Eryngium aquifolium* [12], *Eryngium barrelieri* [13], *Eryngium billardieri* [14,15], *Eryngium bornmuelleri* [16], *Eryngium bourgatii* [17], *Eryngium bungei* [18], *Eryngium caeruleum* [19,20], *Eryngium campestre* [9,10,21,22], *Eryngium caucasicum* [23,24], *Eryngium corniculatum* [25], *Eryngium creticum* [26,27], *Eryngium dilatatum* [28], *Eryngium duriaei* [29,30], *Eryngium eriophorum* [31], *Eryngium expansum* [32], *Eryngium floribundum* [31], *Eryngium foetidum* [33–38], *Eryngium glaciale* [39], *Eryngium horridum* [31], *Eryngium maritimum* [40–45], *Eryngium nudicaule* [31], *Eryngium palmatum* [46], *Eryngium palmatum* [9,46–49], *Eryngium paludosum* [48], *Eryngium pandanifolium* [31,32], *Eryngium paniculatum* [49], *Eryngium planum* [50], *Eryngium pseudothoriifolium* [51], *Eryngium pyramidale* [52], *Eryngium rostratum* [32], *Eryngium serbicum* [47], *Eryngium thorifolium* [51], *Eryngium tricuspidatum* [53], *Eryngium triquetrum* [54,55] and *Eryngium vesiculosum* [32–56]. In addition to the culinary use of some of these species [74,78], a number of biological activities of any of these activities have been ascribed to them, inlcuding analgesic [52], antibacterial [67,69,76], anti-inflammatory [52,72], antimicrobial [62,66,81], antioxidant [65,67,69,78], antiprotozoal [80], cytotoxic [64,66,69], insecticidal [74], molluscicidal and parasiticidal [68] activity. Other less common activities include their use as a corrosion inhibitor [75] or preservative [61,70] and their effectiveness in hyperglycemia [63], improving long-term memory [71], and percutaneous absorption [77].

As far as we know, the essential oils of only eight of the fourteen species that grow in the Iberian Peninsula have been studied to date. Table 1 shows the species studied, the part of the plant used, the main compounds identified and the oil yield of each one. According to these results, the essential oils of these species are richer in sesquiterpenes than in other terpenoids. However, this is not a general rule, as the habitat where each one grows and the size (biotype) of the species seem to be more significant. The species growing under hard climatic conditions and at high altitude that are geophytes or hemicryptophytes contain a great amount of diterpenes—compounds making up the predominant fraction of the oil in *Eryngium bourgatii* [17] and *E. glaciale* [38]. In fact, altitude has been described to affect the chemical composition of the Iberian endemic species, *E. duriaei* [28]. The populations that grow below 1700 m showed α-neocallitropsene (28–53%), β-betulenal (8.5–15.8%) and 14-hydroxy-β-caryophyllene (5.8–13.7%) as their main compounds, while caryophyllene oxide (47%) and *E*-caryophyllene (6%) were identified in the analyzed population over this altitude [28]. On the other hand, species growing close to wet areas or in seasonal lakes while, normally therophytes, such as *E. corniculatum*, exhibited monoterpenes as the largest fraction of the oils [25]. The chemical composition of other species (e.g., *E. campestre*) growing under similar climatic conditions seem to be affected by the type of soil of each population [22].

Table 1. Main constituents of the essential oils of the *Eryngium* species-growing wild in the Iberian Peninsula.

Species	Main Components	Yield (%)	Ref.
E. aquifolium Cav.	**inflorescences oil:** germacrene D (30.3%) and sesquicineole (26.7%)	0.81	[12]
	stems and leaves oil: germacrene D (46.0%) and myrcene (13.8%)	0.41	
	roots oil: phyllocladene isomer (63.6%)	0.18	
E. bourgatii Gouan	**inflorescences oil:** phyllocladene (37.6%) and bicyclogermacrene (15.1%)	0.33	[17]
	stems and leaves oil: phyllocladene (20.4%), γ-muurolene (11.8%) and (*E*)-caryophyllene (10.1%)	0.11	
	roots oil: γ-muurolene (15.4%) and phyllocladene (15.0%)	0.20	
E. campestre L.	**inflorescences oil:** germacrene D (30.3–40.3%), β-curcumene (0.7–22.2%), myrcene (3.0–21.7%), (*E*)-β-farnesene (0.1–19.0%).	0.1–0.4	[22]
	stems and leaves oil: germacrene D (31.1–42.4%), myrcene (0.5–23.15)	0.1–0.2	
E. corniculatum Lam.	**inflorescences oil:** 2,4,6-trimethylbenzaldehyde (50.8%), α-pinene (4.0%)	0.82	[25]
	stems and leaves oil: 2,4,6-trimethylbenzaldehyde (50.0%), 2,4,5-trimethylbenzaldehyde (3.8%)	0.49	
	roots oil: 2,4,6-trimethylbenzaldehyde (29.8%), phyllocladene isomer (13.0%), (*E*)-nerolidol (9.4%)	0.22	

Table 1. *Cont.*

Species	Main Components	Yield (%)	Ref.
Eryngium dilatatum Lam.	**inflorescences oil:** α-cadinol (3.8%), bicyclogermacrene (3.5%), octanal (3.1%) and spathulenol (2.5%)	0.29	[28]
	stems and leaves oil: octanal (8.1%), α-cadinol (3.7%), δ-cadinene (3.6%), (*E*)-caryophyllene (2.6%), bicyclogermacrene (2.5%) and spathulenol (2.4%)	0.33	
	roots oil: spathulenol (4.6%), α-cadinol (4.4%), khusinol (3.2%), α-muurolol (3.1%) and δ-cadinene (2.6%)	0.14	
E. duriaei J. Gay ex Boiss.	**populations below 1700 m:** α-neocallitropsene (28–53%), β-betulenal (8.5–15.8%) and 14-hydroxy-β-caryophyllene (5.8–13.7%)	0.2–0.3	[29]
	population over 1700 m: caryophyllene oxide (47%) and *E*-caryophyllene (6%)		
Eryngium duriaei subsp. juresianum (M. Laínz) M. Laínz	**aerial parts:** α-neocallitropsene (26.0%), isocaryophyllen-14-al (16.2%), 14-hidroxy-β-caryophyllene (13.4%), caryophyllene oxide (7.6%) and (*E*)-β-caryophyllene (6.3%).	0.15	[30]
E. glaciale Boiss.	**inflorescences oil:** phyllocladene isomer (43.5%), (*E*)-caryophyllene (15.2%) and valencene (11.5%)	0.16	[39]
	stems and leaves oil: phyllocladene isomer (41.3%)	0.26	
	roots oil: phyllocladene isomer (49.4%) and linalool (19.1%)	0.30	

Two species with wide distribution, *E. campestre* and *E. maritimum*, showed similar variations growing out of the Iberian Peninsula. Table 2 compiles their main components and oil yield together with their provenance for these samples.

Table 2. Main constituents of the essential oils of the *Eryngium* species-growing wild out of the Iberian Peninsula.

Species	Region	Main Components	Yield (%)	Ref.
E. campestre L.	Italy (Perugia)	**aerial parts:** germacrene D (13.8%), allo-aromadendrene (7.7%), spathulenol (7.0%) and ledol (5.7%)	0.04	[10]
	Algeria (Tlemcen)	**aerial parts:** germacrene D (15.2%), campestrolide (10.3%), spathulenol (4.8%) and α-cadinol (5.5%)	0.1–0.2	[21]
E. maritimum L.	Latvia	**leaves (wild plants):** 4βH-muurol-9-en-15-al > germacrene D > spathulenol > 4βH-cadin-9-en-15-ol	0.15–0.54	[40]
		leaves (cultivated plants): germacrene D (61.13–75.05%) > eudesma-4,7-diene-1β-ol > cumene > α-muurolene	0.15–0.54	

Table 2. *Cont.*

Species	Region	Main Components	Yield (%)	Ref.
E. maritimum L.	Poland (Poznań)	**leaves:** 2,3,4-trimethylbenzaldehyde (11.3%) and germacrene D (10.5%)	0.06	[41]
		fruits: germacrene D (45.2%)	0.3	
		roots: hexadecanoic acid (18.5%), menthol (16.8%) and menthone (10.9%)	0.01	
	Tunisia	**fruits:** germacrene D (13.62–31.71%), 15-hydroxy-α-muurolene (12.04–18.58%) and germacrene B (6.77–15.04%).	0.31–0.93	[42]
	Corsica and Sardinia	**aerial parts:** germacrene D (13.7–45.9%), 4βH-cadin-9-en-15-al (18.4–27.6%), 4βH-cadin-9-en-15-ol (2.2–14.3%) and 4βH-muurol-9-en-15-al (4.3–9.3%)	0.06–0.13 fresh weight	[43]
		roots: 2,4,5-trimethylbenzaldehyde (39.8%), 2,3,6-trimethylbenzaldehyde (29.0%) and α-muurolene (23.5%)	0.06–0.13 fresh weight	
	Sicily (Palermo)	**aerial parts:** germacrene D (10.4%) and 2,4,5-trimethylbenzaldehyde (8.3%)	0.93	[44]
		roots: germacrene D (15.9%) and 2,4,5-trimethylbenzaldehyde (6.7%)	0.84	
	Corsica (Quercionu)	**aerial parts:** isolation of 4βH-muurol-9-en-15-al, 4βH -cadin-9-en-15-al, 4βH-muurol-9-en-15-ol and 4βH-cadin-9-en-15-ol	0.08	[45]

The aim of this study was to analyze the essential oils of *E. galioides* and compare its chemical composition with those of other Iberian species studied to date. This study contributes to the knowledge of the chemical composition of the *Eryngium* genus species. As far as we know, this is the first report on the volatile components of this species, which is endemic to the Iberian Peninsula.

2. Materials and Methods

2.1. Plant Material

Several specimens of *Eryngium galioides* were gathered at flowering in Puebla de Beleña (30TVL7827) (22-VI-2000), Guadalajara, Castilla-La Mancha (Spain). A voucher specimen (MACB-75554) was lodged at the Herbarium of the Faculty of Biology, Complutense University, Madrid, Spain.

2.2. Isolation of Volatile Oils

All the samples of *Eryngium galioides*, including inflorescences, stems, leaves and roots were air-dried. Because of the small size, the complete plant was subjected to hydro distillation with cohobation for 8 h according to the method recommended in the Spanish Pharmacopoeia [82] to obtain its essential oils. The oil was dried over anhydrous magnesium sulphate and stored at 4 °C in the dark. The yield (%) of the essential oil was calculated on a dry weight basis. The yield, on a dry weight basis, of the essential oil analyzed was 0.48%.

2.3. Gas Chromatography (GC)

GC analysis was carried out on a Varian 3300 gas chromatograph fitted with a fused silica methyl silicone DB-1 column (50 m × 0.25 mm, 0.25 µm film thickness). The temperature was programmed from 95 to 240 °C at 4 °C min^{-1}. Injection was performed at 250 °C in the split mode (1:100). Nitrogen was used as the carrier gas (1.5 mL min^{-1}). Detection was carried out using a flame ionization detector (FID) (Palo alto, California, USA)at 300 °C. The injection volume for all the samples was 0.1 µL of pure oil.

2.4. Gas Chromatography–Mass Spectrometry (GC-MS)

GC-MS analyses were carried out on a 6890 gas chromatograph coupled to an HP 5973 mass selective detector (both from Agilent Technologies, Santa Clara, CA, USA). A fused silica SE-30 capillary column (50 m × 0.22 mm, 0.25 µm film thickness) was used for separation. The column temperature was programmed from 70 to 220 °C at 4 °C min^{-1}, and Helium at 1 mL min^{-1} was used as carrier gas. Mass spectra were recorded in the scan mode (35–450 m/z range) at 70 eV.

In order to confirm the identification of several compounds, the oil samples were also analyzed on a VG Quattro gas chromatograph-mass spectrometer operating at 70 eV ionization energy. The GC column used was a DB-Wax (60 m × 0.32 mm, ×0.25 µm) programmed from 35 ° to 220 °C at 3 °C min^{-1}, with Helium (1 mL min^{-1}) as carrier gas.

2.5. Qualitative and Quantitative Analyses

Most constituents were tentatively identified by GC through a comparison of their retention indices with those of authentic standards available in the authors' laboratory or retention indices from literature [83–89]. Further identification was achieved by GC-MS: the fragmentation patterns of experimental mass spectra were compared with those stored in the commercial spectrometer data base using the WILEY.L built-in library. Other constituents were either synthesized or identified in oils of known composition.

Semiquantitative analysis (%) was carried out directly from peak areas in the GC profile.

3. Results and Discussion

The whole plant of *Eryngium galioides* provided a pale-yellow essential oil (0.48% extraction yield on a dry weight basis). Despite the small size of this species, its yield was higher than the mean of the other *Eryngium* species growing in the Iberian Peninsula (Table 1). A reason for this could be that the habitat where it grows is not as hard as that of other species such as *E. buorgatii* and *E. glaciale* growing in high mountains, but harder than others as *E. corniculatum*, which lives on the margins of seasonal lakes and, therefore, disposes of water during its flowering and fruiting. In agreement with previous references [10,12,17,21,22,25,28–30,39–45], our results indicate that the species of this genus are perfectly adapted to the environment in which they develop, and that may affect the yield of their essential oils. It would, however, be interesting to analyze the plasticity of these species under controlled conditions to understand the possible effect of climate change on their survival and distribution. Some of these species are catalogued as vulnerable or endangered, so this could help us to understand the possible risk in that scenario.

The components identified in the *Eryngium galioides* essential oil under study, their retention indices, and their percent composition are summarized in Table 3, where they are all arranged by their elution order on the DB-1 column. The retention indices of these compounds on the DB-Wax column are also listed in brackets in that table. As is known, essential oils are mixtures of aromatic and aliphatic compounds in different concentrations, all of which contribute to the perceived aroma of the plant. In our case, a total of 71 compounds were identified, representing the 97.3% of the total oil analyzed. It is worth noting that only two compounds, valencene (49.7%) and a phyllocladene isomer (23.7%), were identified as the main components of this oil, the sum of both comprising more than the 70% of the total oil. The remainder of the components that contribute to the scent of this species did not obtain a percentage over 6.0%. Some of these could be considered representative, including β-chamigrene (6.0%), γ-muurolene (3.4%), (*E*)-caryophyllene (3.0%), β-elemene (1.6%), nonane (1.4%), δ-cadinene (1.0%) and spathulenol (1.0%).

Table 3. Essential oil composition (in %) from the whole plant (roots + steams + leaves + flowers) of *Eryngium galioides* Lam. from Spain.

Compound	*I*	I^{1it}	%.	IM
nonane	869	900	1.4	MS,1
α-pinene	932 (1012)	939	0.2	MS,2
heptanol	955 (1181)	959	t	MS,1
sabinene	963 (1113)	969	t	MS,2
β-pinene	970 (1097)	974	t	MS,2
myrcene	985 (1160)	988	0.3	MS,2
octanal	993 (1286)	988	0.2	MS,1
α-phellandrene	1005 (1157)	1002	t	MS,2
o-cimene	1019 (1268)	1022	t	MS,2
limonene	1026 (1191)	1024	t	MS,2
(*Z*)-β-ocimene	1031 (1232)	1032	t	MS,1
benzene acetaldehyde	1032	1036	t	MS,1
(*E*)-β-ocimene	1041 (1249)	1044	t	MS,1
γ-terpinene	1058 (1240)	1054	t	MS,2
octanol	1063 (1172)	1063	t	MS,2
fenchone	1074 (1392)	1083	t	MS,2
linalool	1096 (1549)	1095	t	MS,2
undecane	1100	1100	t	MS,2
cis-thujone	1117	1101	t	MS,1
cryptone	1180 (1669)	1183	0.3	MS,1
α-terpineol	1183 (1700)	1186	0.2	MS,1
n-decanal	1202	1201	t	MS,2
pulegone	1231	1233	t	MS,2
(*E*,*Z*)-2,4-decadienal	1301 (1229)	1292	t	MS,1
carvacrol	1303	1298	t	MS,2
2,4,5-trimethyl benzaldehyde	1305 (1896)	--	t	MS,1
δ-elemene	1333 (1468)	1335	t	MS,2
α-longipinene	1351	1350	t	MS,1
α-copaene	1366 (1480)	1374	0.3	MS,2
daucene	1370	1380	t	MS,1
β-elemene	1387 (1587)	1389	1.6	MS,2
α-gurjunene	1406 (1528)	1409	t	MS,2
(*E*)-caryophyllene	1410 (1594)	1417	3.0	MS,2
α-*trans*-bergamotene	1432 (1583)	1432	t	MS,1
α-guaiene	1433	1437	t	MS,2
aromadendrene	1434 (1605)	1439	0.2	MS,2
α-humulene	1447 (1667)	1452	0.3	MS,2

Table 3. *Cont.*

Compound	***I***	***I*^1it**	**%.**	**IM**
(*E*)-β-farnesene	1452 (1770)	1454	0.2	MS,2
β-acoradiene	1456	1469	0.8	MS,1
β-chamigrene	1461	1476	6.0	MS,1
γ-muurolene	1465 (1675)	1478	3.4	MS,2
β-selinene	1482 (1704)	1489	t	MS,2
valencene	**1485**	**1496**	**49.7**	MS,2
α-selinene	1492 (1727)	1498	0.1	MS,2
α-bulnesene	1498 (1642)	1509	t	MS,2
7-*epi*-α-selinene	1519 (1764)	1520	0.8	MS,1
δ-cadinene	1522 (1760)	1522	1.0	MS,2
n.i. 1	1559	--	0.5	--
selina-3,7(11)-diene	1560	1545	0.3	MS,1
caryophyllenyl alcohol	1569	1570	0.2	MS,1
spathulenol	1576 (2133)	1577	1.0	MS,2
caryophyllene oxide	1580 (1987)	1582	0.4	MS,2
globulol	1583 (2064)	1590	0.3	MS,2
viridiflorol	1590 (2091)	1592	0.3	MS,1
carotol	1594 (2026)	1594	0.2	MS,1
β-oplopenone	1597	1607	0.1	MS,1
n.i. 2	1606	--	0.4	--
epi-α-muurolol (+cubenol)	1631 (1890)	1640	t	MS,1
β-eudesmol	1638 (2239)	1649	t	MS,2
α-cadinol	1639 (2243)	1652	0.4	MS,1
selin-11-en-4-α-ol	1645	1658	t	MS,1
14-hydroxy-9-*epi*-(*E*)-caryophyllene	1662 (1924)	1668	t	MS,1
khusinol	1665	1679	0.2	MS,1
acorenone	1673	1692	t	MS,1
(*E*)-sesquilavandulyl acetate	1775	1739	t	MS,1
cedr-8-(15)-en-9-α-ol acetate	1776	1741	t	MS,1
14-hydroxy-α-muurolene	1787 (1550)	1779	0.1	MS,1
notkatone	1798	1806	t	MS,1
bis-(2-methylpropyl) phthalate	1804	--	t	MS,1
neophytadiene	1810	--	t	MS,1
(*E*,*E*)-farnesyl acetate	1824	1845	t	MS,1
phyllocladene isomer	**1857**	**--**	**23.7**	MS,1
phytol	1922 (2620)	1942	0.1	MS,1

I = Linear retention indices on DB-1 column and on DB-Wax column in parenthesis; I^{1it} = literature linear retention index on DB-5 column [85]; IM = identification method; MS = mass spectra data; 1 = retention data according to literature values; 2 = retention data according to authentic standards; t = traces (% < 0.1); n.i.= not identified; E.d. = *Eryngium galioides*; n.i. 1 *I* = 1559, 220[M^+] (35), 135 (100), 107 (88), 159 (85), 91 (83), 121 (81), 177 (79), 81 (60), 41 (45), 55 (40), 137 (39), 69 (30), 161 (23), 205 (20), 189 (10); n.i. 2 *I* = 1606, 220[M^+] (15), 159 (100), 93 (65), 119 (45), 177 (43), 107 (35), 135 (34), 79 (30), 41 (28), 67 (20), 149 (15), 204 (15), 189 (10); Phyllocladene isomer *I* = 1857, 272[M^+] (1), 91 (100), 55 (83), 115 (78), 117 (70), 129 (55), 159 (53), 41 (48), 77 (47), 103 (45), 141 (40), 173 (15), 187 (10), 229 (8), 256 (5). Main compounds on bold.

The *Eryngium* species studied to date that grow in the Iberian Peninsula show two patterns: *E. bourgatii*, *E. campestre*, *E. corniculatum*, *E. glaciale*, and *E. dilatatum* share the same principal compounds in their different fractions, while the root fraction of *E. aquifolium* and *E. maritimum* does not have the same components (Tables 1 and 2). As in the case of *E. galioides*, it would have been interesting to analyze the phenology of its essential oils when it was harvested to check if the season affects its metabolism and the production of terpenoids. The small size of this species did not allow for its fractionation, but one of its main compounds—phyllocladane, or a phyllocladene isomer—is present in the other existing species studies. According to our results and those previously published on the species of *Eryngium* growing in the Iberian Peninsula, there is no major compound that could be considered as characteristic of the genus. Other compounds that were present in the majority of them were germacrene D, trimethylbenzaldehyde and phyllocladene. However more studies would need to be carried out to determine if any of them or the combination of a few were characteristic of the essential oils of this genus, as well as to determine the phenology of these species and check if the above-mentioned compounds appear in a specific season or biological state of the plant (flowering, fruiting, etc.).

The classification of terpenoids present in *E. galioides* essential oil appears in Figure 2, together with the main compound of each class. The sesquiterpene group (71.2%) was the predominant group, followed by the diterpene group (23.8%). Monoterpenes (0.7%) were insignificant, representing less than 1% of the total oil. In all the groups analyzed (sesquitepenes, diterpenes and monoterpenes, respectively), the hydrocarbon compounds (67.7%, 23.7%, 0.5%) were more abundant than the oxygenated components (3.5%, 0.1%, 0.2%). However, this distribution does not correspond to the number of compounds.

Although more than twenty compounds were identified as monoterpenes in the oil, most of them were detected as traces. On the other hand, diterpenes were the second-most-abundant fraction, comprising only two compounds. Regarding sesquiterpenes, this class was the most equitable and showed the highest percentage composition (71.2%) with the largest number of compounds. Our results on the terpenoid fraction agree with those previously reported [17–39]. Most of the *Eryngium* species studied to date that inhabit open and dry areas have sesquiterpenes as the predominant fraction, whereas the species that grow close to lakes or wet soils have high amounts of monoterpenes [25]. Other species of *Eryngium* growing under hard climatic conditions exhibited diterpenes as the main components [17–39]. *E. campestre* seems to modify its chemical composition according to the type of soil [22]. This could also be one of the reasons that none of the compounds described to date for this genus could be used for chemotaxonomy proposes.

As we have previously mentioned, different species of this genus have been studied for their biological activities [60–81]. However, only three of them correspond to species that appear in the Iberian Peninsula [10,21,30,42,43,72,75]. *Eryngium duriaei* subsp. *Juresianum*, from Portugal, showed antifungal activity against several dermatophyte species, with the main compounds identified from the volatiles being α-neocallitropsene (26.0%), isocaryophyllen-14-al (β-Betulenal) (16.2%) and 14-Hydroxy-β-caryophyllened (13.4%) [30]. Moreover, the essential oils also were anti-inflammatory in human chondrocytes [72]. The bio-activity of *Eryngium campestre* has been also reported. This species, growing in Italy, exhibited cytotoxic activity against tumor cell lines (HCT116 colon carcinoma, breast carcinoma and melanoma) but weak acetylcholinesterase inhibition [10]. Additionally, its essential oils, from Algeria, presented chemical variability according to the geographical samples studied and inhibited the growth of Gram-positive strains while also exhibiting cytotoxicity activity (anti-leishmanial and anti-trypanosomal) [21]. Finally, the essential oil of the same species, growing in Iran, was demonstrated to be efficient as a preservative in controlling the microbial growth of cherries [61]. The essential oils of the last species, *Eryngium maritimum*, were also consistently different depending on the material used (leaves, aerial parts, roots or fruits, Table 2) but presented antioxidant and anticorrosive activities. The oils from the Tunisian fruits showed antioxidant activity significantly higher than Trolox [42]. This activity has been also reported for this species growing in Italy and tested in different fractions (flowers, leaves, stems and roots) [43]. The essential oils of this species growing in France were proposed to serve as an environmentally friendly inhibitor of the corrosion of mild steel in HCl media [75].

As far as we know, this is the first report about *Eryngium galioides*, and based on the data, we believe it would be interesting to investigate the bio-activities of this species. In fact, valencene, which was detected as the main compound with a percentage composition close to 50%, has been previously reported to exhibit antimicrobial, antioxidant, anti-inflammatory and antitumor activities [90,91]. The small size of this species and its conservation state are advantages in terms its use for extracting this active compound. However, its in vitro cultivation would make it possible to extract this bio-active in large quantities. To this end, research should be carried out either to propagate this species under laboratory conditions to reinforce the populations more affected, or to generate larger amounts of this plant to make the extraction of essential oils rich in this bio-active possible. Phyllocladane, another major compound of this species, has also been reported for its biological activity [92,93] and, therefore, would contribute to reinforcing the interest in *E. galioides* as a natural source of bio-actives for different applications. Furthermore, it is accepted that the complex mixtures of the essential oils with bio-active properties have synergy and are more effective than purified bio-active compounds.

Therefore, with this report, we contribute to the knowledge of *E. galioides*, an endemic species of interest. It should be considered a starting point for further studies that can provide a better understanding of this species and its potential bio-active properties.

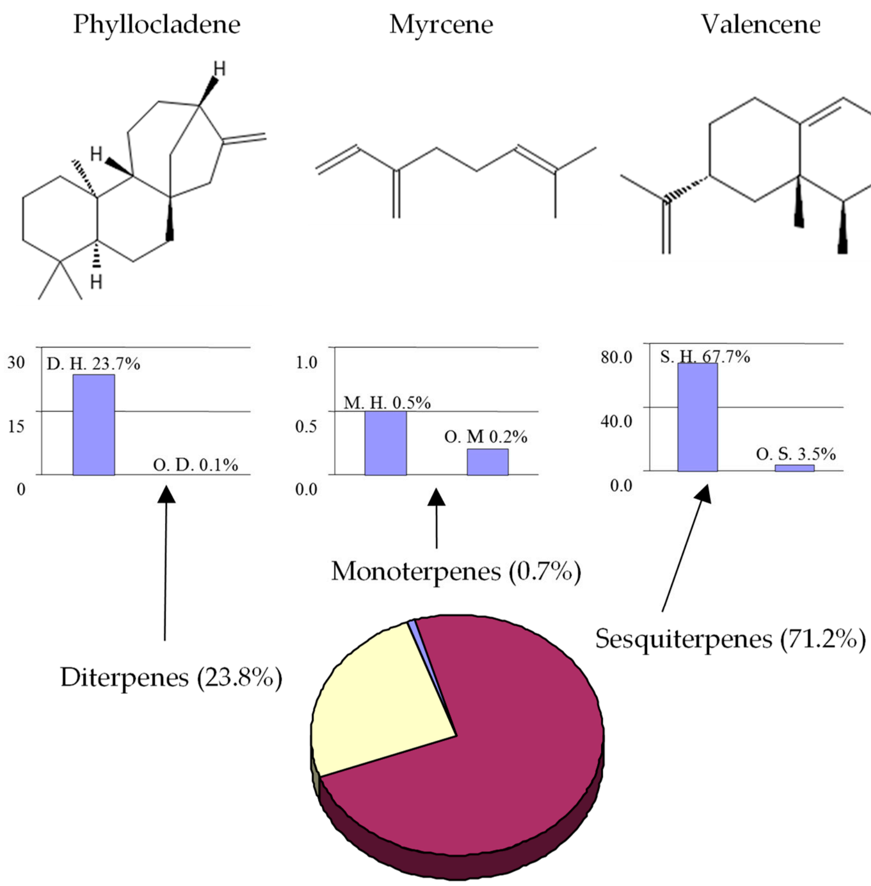

Figure 2. Classification of terpenoids in the essential oil of *Eryngium galioides* Lam. and the main compound of each class (M. = Monoterpenes; S. = Sesquiterpentes; D. = Diterpenes; H. = hydrocarbons; O. = Oxygenated).

4. Conclusions

This is the first report about the chemical composition of the essential oils of *E. galioides* Lam. from the Iberian Peninsula and represents an advance in the knowledge of this scarcely studied species.

The yield of *E. galioides* essential oil is higher than the average of other *Eringium* species growing in the Iberian Peninsula.

The chemical composition of the essential oils of *E. galioides* was characterized by two bio-active compounds: valencene (49.7%) and a phyllocladene isomer (23.7%), constituting more than 70% of the total volatiles identified. All these promising features, as regards the production of bio-active essential oils, make research on the in vitro cultivation of this species worthy of consideration to overcome the present limitations of the available number of wild samples.

The Iberian Peninsula species of the *Erynigum* genus, studied to date and growing under comparable conditions, share the predominance of sesquiterpenes in their essential oils, with major components and relative concentrations being dependent on the species considered.

The ecological conditions seem to affect, to a noticeable extent, the chemical composition of this genus. **Author Contributions:** Conceptualization, J.P.-P., M.J.P.-A., A.C.S. and J.J.B.;

Methodology, J.P.-P., M.J.P.-A., A.C.S. and J.J.B.; Formal analysis, J.P.-P., R.A.-C., A.C.S. and J.J.B.; Investigation, J.P.-P., M.J.P.-A., R.A.-C., A.C.S. and J.J.B.; Resources, J.P.-P.; Writing—original draft, J.P.-P., A.C.S. and J.J.B.; Writing—review & editing, J.P.-P., R.A.-C., A.C.S. and J.J.B.; Supervision, J.P.-P., A.C.S. and J.J.B.; Project administration, J.P.-P. All authors have read and agreed to the published version of the manuscript.

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