

Chemical Composition of the Essential Oils of Three Species of Apiaceae Growing Wild in Sicily: *Bonannia graeca*, *Eryngium maritimum* and *Opopanax chironium*

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In the present study the chemical composition of the essential oils from aerial parts of *Bonannia graeca* (L.) Halácsy and *Opopanax chironium* (L.) Kock, and from aerial parts and roots of *Eryngium maritimum* L. was evaluated by GC and GC-MS. α -Pinene (15.2%) and β -pinene were recognized as the main constituents of *B. graeca*, whereas the aerial parts of *O. chironium* contained mainly the diterpene cembrene and the coumarin angelicin. In both aerial parts and roots of *E. maritimum* germacrene D (10.4% and 15.9%, respectively) and 2,4,5-trimethylbenzaldehyde (8.3% and 6.7%) were the most abundant components.

Keywords: Apiaceae, *Bonannia graeca*, *Eryngium maritimum*, *Opopanax chironium*, Essential oil, α -Pinene, Germacrene D, Cembrene.

Bonannia graeca (L.) Halácsy, Apiaceae family, is a rare plant growing in several Mediterranean areas, such as the southern parts of Italy and Greece [1]. It is known for its toxicity against herbivores and for causing the death of lambs feeding on the aerial parts during its blossoming season (June–July). Our previous phytochemical investigations of this species allowed us to isolate a new irregular diterpene, bonandiol [2a], and seven new C-geranylated flavonoids [2b-2d], some of which show good cytotoxic activity [2d].

The genus *Eryngium*, subfamily Saniculoideae, family Apiaceae, is represented by 317 accepted taxa worldwide and is known to contain acetylenes, flavonoids, coumarins and triterpene saponins [3a]. *E. maritimum* L. (sea holly) is a halophytic species commonly found along Mediterranean and Atlantic coast and generally grows in sand hills. The young cooked shoots are used as an asparagus substitute [3b], whereas the cooked or roasted roots are used either as a vegetable or candied [3c]. Sea holly roots were collected on a large scale in the 17th and 18th centuries in England and were candied, then used as restorative, quasi-aphrodisiac lozenges [3d]. The plant is still used in modern herbalism where it is valued, especially for its diuretic action. Aerial parts and roots are reported to be aphrodisiac, aromatic, diaphoretic, diuretic, expectorant, stimulant and tonic [3e, 3f]. Used externally as a poultice, the dried powdered root aids tissue regeneration [3g]. However, literature on possible activities of sea holly only highlights anti-inflammatory and antinociceptive properties [4a], moderate antioxidant and antimicrobial activities [4b] and antimalarial and antileishmanial properties against *Plasmodium falciparum* and *Leishmania donovani*, respectively [4c]. Previous phytochemical studies indicated the presence of saponins [5a], flavonoids [5b] and new oxygenated sesquiterpenes [5c].

Opopanax chironium (L.) Koch is a plant indigenous to the Western Mediterranean area that grows one to three feet high and produces a large, yellow inflorescence [6a]. A consumable resin with a pleasant and persistent smell, with antispasmodic and deobstruent activities, also used in the treatment of menstrual disorders, asthma, chronic

visceral afflictions [6b] can be extracted from *O. chironium* by cutting the plant at the base of a stem and sun-drying the juice that flows out. The composition of the aerial parts and roots of *O. chironium* has been largely investigated. C-17 acetylenes [7a] and various phthalides were identified in the roots [7b], whereas the ethereal extract of the roots of *O. chironium* cultivated in France from seeds collected in the city of Olympie (Greece) yielded peucedin oxide acetate, a new natural product with an irregular diterpene skeleton, besides the known coumarins gaudichaudin, columbianadin, peucedanin and officinalin isobutyrate [7c]. Furthermore, the presence of two distinct chemotypes was evidenced: the one from Sicily afforded, besides known coumarins, two new dihydrofuranocoumarins, while in the extract from the Sardinian chemotype, were identified different coumarins including the two prenylated furanocoumarins heraclenin and imperatorin that showed powerful apoptotic activity in Jurkat leukemia cells [7d].

As a continuation of our researches on Sicilian plants [8], we decided to investigate on the chemical composition of the essential oils of these three species, all belonging to the Apiaceae family and all growing in the central part of Sicily. No reports have been published on the essential oil composition of *B. graeca* and *O. chironium*, whereas from the essential oil of a population of *E. maritimum* collected in Corsica four new oxygenated sesquiterpenes have been identified, although the full profile of the oil has not been reported [5c].

Hydrodistillation of *B. graeca* aerial parts (BG) gave a pale yellow oil. Overall, 36 compounds were identified, representing 95.7% of the total components. These are listed in Table 1 according to their retention indices on a HP 5MS column and are classified on the basis of their chemical structures into several classes. The only significant class is represented by monoterpene hydrocarbons (87.3%) with α -pinene (60.9%) present in large amount, followed by β -pinene (12.1%), β -phellandrene (3.6%) and sabinene (3.6%).

Hydrodistillation of *E. maritimum* aerial parts (EA) and flowers (EF) gave two pale yellow oils. Overall, 70 compounds were identified

Table 1: Composition of essential oils from *B. graeca* aerial parts (BG), *E. maritimum* aerial parts (EA) and flowers (EF), and *O. chironium* aerial parts (OP).

COMPONENT	K ^a	LRI ^b	BG	EA	EF	OP	Identification ^c
Hydrocarbons			1.0	10.3	8.9	8.2	
1,3,5-Trimethylbenzene	965	1230		1.8	1.3		1, 2
1,2,4-Trimethylbenzene	1003	1292		0.8	1.3		1, 2
Undecane	1100	1100				0.5	1, 2, 3
Dodecane	1200	1200				0.3	1, 2, 3
α -Ionene	1208					0.7	1, 2
Dehydro- <i>ar</i> -ionene	1355	1730				0.5	1, 2
Naphthalene, 1,2-dihydro-2,5,8-trimethyl	1358					0.5	1, 2
Tricosane	2300	2300		2.0	2.2		1, 2, 3
Pentacosane	2500	2500		2.5	1.8		1, 2, 3
Heptacosane	2700	2700		3.2	2.3		1, 2, 3
Octacosane	2800	2800				0.5	1, 2, 3
Nonacosane	2900	2900				3.6	1, 2
Hentriacontane	3100	3100	0.6				1, 2
Tritriacontane	3300	3300	0.4				1, 2
Carbonylic compounds			0.3	14.6	9.0	11.7	
Phenylacetaldehyde	1044	1663				0.5	1, 2, 3
Cryptone	1193	1696	0.3	t			1, 2
Undecan-2-one	1287	1593		2.1			1, 2
2,4,5-Trimethylbenzaldehyde	1304	1895		8.3	6.7		1, 2, 3
(<i>E,E</i>)-2,4-Decadienal	1315	1827				0.6	1, 2
2,4,6-Trimethylbenzaldehyde	1335	1927		4.2	2.3		1, 2, 3
(<i>E</i>)-Geranylacetone	1453	1867				3.3	1, 2
(<i>E</i>)- β -Ionone	1484	1958				3.7	1, 2
Hexahydrofarnesylacetone	1845	2131				2.5	1, 2
(<i>E,E</i>)-Farnesylacetone	1918	2389				1.1	1, 2
Monoterpene hydrocarbons			87.3	6.7	4.2	1.0	
Tricyclene	928	1014		t			1, 2
α -Thujene	931	1023	0.8		t		1, 2
α -Pinene	938	1076	60.9	1.2	2.0		1, 2, 3
Camphene	953	1076	0.4	0.6	t		1, 2, 3
Sabinene	973	1132	3.6				1, 2
β -Pinene	980	1118	12.1				1, 2, 3
Myrcene	993	1174	2.8				1, 2, 3
α -Phellandrene	1005	1150	0.1				1, 2, 3
α -Terpinene	1012	1189	0.5			1.0	1, 2, 3
<i>p</i> -Cymene	1026	1278	0.3	2.2	2.0		1, 2, 3
β -Phellandrene	1029	1218	3.6	1.1	0.1		1, 2
Limonene	1030	1203	0.8	0.5	t		1, 2, 3
(<i>Z</i>)- β -Ocimene	1038	1045	0.2				1, 2, 3
(<i>E</i>)- β -Ocimene	1049	1265	0.5				1, 2, 3
γ -Terpinene	1057	1256	0.4	1.1	0.1		1, 2, 3
Terpinolene	1057	1256	0.3				1, 2, 3
Sesquiterpene hydrocarbons			2.4	37.8	61.8	27.9	
α -Cubebene	1352	1466		1.5	0.7	1.8	1, 2
α -Longipinene	1355	1484		0.6	1.2		1, 2
α -Copaene	1377	1497		3.5	2.8	2.4	1, 2
Isoledene	1379	1665			0.1	1.1	1, 2
β -Patchoulene	1382	1485				1.9	1, 2
β -Cubebene	1382	1547	0.7	1.0	1.8		1, 2
(<i>E</i>)- β -Damascenone	1383	1787				3.7	1, 2
β -Bourbonene	1385	1535		1.2	2.0		1, 2
β -Elemene	1387	1600		1.9	1.5	1.4	1, 2
α -Elemene	1398	1685		0.9	1.8		1, 2
Longifolene	1403	1587		1.3	0.9		1, 2
α -Cedrene	1411	1569				0.8	1, 2
β -Caryophyllene	1415	1612				3.2	1, 2, 3
Widdrene	1433	1620			1.5		1, 2
Aristolene	1434	1552		0.7	2.6		1, 2
γ -Elemene	1435	1652			1.4		1, 2
α -Guaiene	1437	1530		1.2	2.3		1, 2
(<i>E</i>)- β -Farnesene	1452	1672			5.1		1, 2
α -Humulene	1455	1689			1.3		1, 2
<i>allo</i> -Aromadendrene	1463	1667	0.3		1.3		1, 2
Germacrene D	1477	1726		10.4	15.9	2.7	1, 2
γ -Muurolene	1478	1704		1.1	t		1, 2
α -Amorphene	1487	1679		0.2	2.3	2.7	1, 2
Eremophilene	1489	1743			t		1, 2
<i>epi</i> -Bicyclosesquiphellandrene	1489	1734			0.7		1, 2
β -Guaiene	1490	1612		0.8	1.4		1, 2
Bicyclogermacrene	1491	1726	0.1		4.7		1, 2
Valencene	1495	1740		0.7	0.8		1, 2
α -Selinene	1498	1744				1.8	1, 2
α -Muurolene	1500	1740		1.5	1.1		1, 2
γ -Cadinene	1515	1776		1.4	0.8		1, 2
δ -Cadinene	1526	1773	0.8	2.5	2.8		1, 2
Cadina-1,4-diene	1538	1799				1.0	1, 2
1 <i>S</i> - <i>cis</i> -Calamenene	1541	1839		2.9	1.7	1.8	1, 2
α -Calacorene	1541	1918		1.4	0.8		1, 2
Germacrene B	1558	1818	0.5			1.6	1, 2
Calarene or β -Gurjunene	1677	2256		1.1	0.5		1, 2
Oxygenated monoterpenes			4.1	1.7	0.2	8.7	
Yomogi alcohol	994	1405		t	t		1, 2
α -Terpineol	1005	1150				1.8	1, 2, 3
(<i>Z</i>)-Sabinene hydrate	1063	1555	0.1				1, 2
<i>cis</i> -Linalool oxide (furanoid)	1067	1482				0.9	1, 2, 3
α -Pinene oxide	1097	1384	0.5				1, 2
Linalool	1098	1553	0.5			2.9	1, 2, 3
β -Thujone	1115	1451	0.2		t		1, 2
α -Campholenal	1128	1487		0.2			1, 2
<i>cis</i> -Verbenol	1144	1663		t	0.2		1, 2

Camphor	1145	1532		0.4			1, 2, 3
(Z)-Sabinol	1169		0.1				1, 2
Terpinen-4-ol	1176	1611	0.8				1, 2, 3
p-Cymen-8-ol	1185	1856	0.5				1, 2
α -Terpineol	1189	1706	0.8				1, 2, 3
Myrtenol	1196	1804	0.2				1, 2
Safranal	1201	1613			0.9		1, 2
cis-Verbenone	1208	1723		1.1	t		1, 2, 3
trans-Verbenone	1217	1725	0.4				1, 2
Nerol	1226	1808			0.8		1, 2
Geraniol	1235	1857			0.9		1, 2
Eucarvone	1276	1465			0.5		1, 2, 3
Oxygenated sesquiterpenes			0.6	12.3	9.4	0.9	
cis- α -Copaen-8-ol	1553	2076			1.2		1, 2
Spathulenol	1578	2150	0.5	4.5			1, 2, 3
Viridiflorol	1593	2103		1.2	t		1, 2
Isocaryophyllen-14-al (β -Betulenal)	1621	2143		0.3			1, 2
Caryophylla-2(12),6(13)-dien-5 β -ol (Caryophylladienol I)	1640	2316		1.1			1, 2
t-Muurolo	1641	2209	0.1	2.8	1.8		1, 2
α -Cadinol	1642	2255		0.1	t		1, 2
14-Hydroxy- β -caryophyllene	1643	2345		0.5	0.2		1, 2
Aromadendrene oxide	1648	2398		1.4	2.2		1, 2
α -Eudesmol	1653	2252		0.1	0.3		1, 2
Vulgarol B	1691	2367			0.6		1, 2
(E,E)-Germacrene-3,7(11),9-trien-6-one (Germacrene)	1698	2219			1.0		1, 2
Selin-7(11)-en-4-ol (Juniper camphor)	1697	2320		0.3	2.1		1, 2
(E,Z)-Farnesol	1743	2313				0.9	1, 2
Diterpenes						14.6	
Cembrene						14.6	1, 2
Fatty acids and derivatives			t	2.3	3.6	6.1	
γ -Decalactone	1470	2183		2.3	3.6		1, 2
Benzyl benzoate	1760	2655	t				1, 2, 3
Tetradecanoic acid	1767	2675				2.1	1, 2, 3
Hexadecanoic acid	1957	2932				4.0	1, 2, 3
Phenolic compounds				1.4	4.3		
Carvacrol methyl ether	1245	1975		0.3			1, 2, 3
Carvacrol	1299	2239		1.1			1, 2, 3
4-Vinylguaiacol	1312	2180				3.4	1, 2
Eugenol	1353	2186				0.9	1, 2, 3
Coumarins						6.4	
Psoralen	1830					1.9	1, 2
Angelicin	1835					4.5	1, 2, 3
Others				2.6	0.5	0.8	
2-Pentylfuran	1002	1243				0.8	1, 2
Dihydroedulan II	1286	1504		2.6	0.5		1, 2
Total amount of compounds			95.7	89.7	97.6	90.6	

^a: Linear retention index on a HP 5MS column; ^b: Linear retention index on a HP Innowax column ^c: 1: linear retention index, 2: mass spectrum, 3: co-injection with authentic compound; ^d: Mass of compounds in mg/100 mg oil; t, trace (<0.1%).

(56 in EA and 60 in AF), representing 89.7% and 97.6% of the total components, respectively (Table 1). The two oils presented a similar composition and also the identity of the most dominant components was the same. Sesquiterpene hydrocarbons form the main class representing 37.8% and 61.8% of the two oils, respectively, with germacrene D as the most abundant component of both oils (10.4% in EA and 15.9% in EF). The second principal component of the oil of both aerial parts (EA) and flowers (EF) was 2,4,5-trimethylbenzaldehyde (8.3% and 6.7%). In addition, the aerial parts of *E. maritimum* contain a good amount of spathulenol (4.5%), which was not present in the flowers. Although oxygenated sesquiterpenes are well represented (12.3% in EA and 9.4% in EF) with spathulenol (4.5%) as main compound of this class, but present only in aerial parts, it has to be pointed out that the four oxygenated sesquiterpenes, 4 β H-muurolo-9-en-15-al, 4 β H-cadin-9-en-15-al, 4 β H-muurolo-9-en-15-ol and 4 β H-cadin-9-en-15-ol, isolated from the population collected in Corsica [5c], were not found in our sample.

Hydrodistillation of *O. chironium* aerial parts (OC) gave a pale yellow oil. Overall, 44 compounds were identified, representing 90.6% of the total components (Table 1). Although sesquiterpene hydrocarbons were the most abundant class (27.9%) with (*E*)- β -damascenone (3.7%) and β -caryophyllene (3.2%) as main compounds, the principal product of the oil was cembrene (14.6%), the only diterpene detected. (*E*)- β -Ionone (3.7%) and (*E*)-geranylacetone (3.3%) were the main components of the carbonylic compounds class (11.7%); of interest is the presence of two coumarins, angelicin (4.5%), the second product of the oil, and

psoralen (1.9%). The presence of coumarins is in agreement with previous investigations carried out on the acetone extract of *O. chironium* [7d] and on the dichloromethane extract of *O. persicum*, a species endemic of Turkey, Iran, Iraq and Transcaucasia [9].

As stated by Chizzola [14], different volatiles can be identified in the essential oils from Apiaceae, but monoterpenes are frequently found and particularly α -pinene is amongst the major compounds in many species. This is in agreement with the composition of *B. graeca*, where α -pinene is present in large amount (60.9%). Sesquiterpenes are also frequent oil compounds in Apiaceae species. In fact, *E. maritimum* and *O. chironium* are rich in sesquiterpene hydrocarbons, even if the main compounds differ. In various species of *Eryngium* different isomers of trimethylbenzaldehyde have been found, and this conforms to the finding of 2,4,5-trimethylbenzaldehyde both in aerial parts and flowers of *E. maritimum*. As regards the presence of the two coumarins angelicin and psoralen in *O. chironium* oil, furanocoumarins are usually not recovered in distilled oils, but they have been found previously in various Apiaceae, for instance in the genera *Pastinaca* and *Heracleum*. Diterpenes are instead more common in the family and can be found above all in *Eryngium* species, while the diterpene cembrene, which we found in a good amount in *O. chironium* oil, is rare in the Apiaceae family.

Experimental

Plant material: The aerial parts of *B. graeca* (L.) Halácsy (BG) were collected at Quacella, Piano Battaglia, 80 km SE of Palermo, Sicily, Italy, in July 2012. *E. maritimum* L. aerial parts (EA) and

flowers (EF) were collected at full flowering stage at Salinelle Beach, Cefalù, 50 km E of Palermo Sicily, in June 2012. The aerial parts of *O. chironium* (L.) Koch (OC) were collected at Piano Zucchi, 70 km SE of Palermo, Sicily, Italy, in July 2012. Typical specimens were identified by Prof. F.M. Raimondo, University of Palermo, and have been deposited in the Herbarium Mediterraneum of the Palermo University, Palermo, Italy (voucher numbers PAL 12/670, PAL 12/689, PAL 12/700, respectively).

Isolation of the essential oil: For the isolation of the essential oils, the air-dried samples (lots of 25 g) were ground in a Waring blender and then subjected to hydrodistillation for 3 h using *n*-hexane as a solvent, according to the standard procedure previously described [10]. The oils were dried over anhydrous sodium sulfate and stored under N₂ at +4°C in the dark until tested and analyzed. The hydrodistillation yielded 0.07% (BG), 0.93% (EA), 0.84% (EF) and 0.08% (OC), respectively, of yellowish oils.

Gas chromatography-mass spectrometry: Analytical gas chromatography was carried out on a Perkin-Elmer Sigma 115 gas chromatograph fitted with a HP-5 MS capillary column (30 m x 0.25 mm, 0.25 µm film thickness), as described previously [15].

Identification of components: Most constituents were identified by GC by comparison of their retention indices (LRI) with either those of the literature [11-13] or with those of authentic compounds available in our laboratories. The linear retention indices were determined in relation to a homologous series of *n*-alkanes (C₈-C₂₈) under the same operating conditions. Further identification was achieved by comparison of their MS on both columns, either with those stored in NIST 02 and Wiley 275 libraries or with MS from the literature [12,13] and our home-made library.

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