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Journal of Chromatography A, 1074 (2005) 235–239
JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma

Short communication

Essential oil composition of the different parts of *Eryngium bourgatii* Gouan from Spain☆

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Received 7 December 2004; received in revised form 18 February 2005; accepted 10 March 2005
Available online 2 April 2005

Abstract

The essential oil extracted from the different parts of *Eryngium bourgatii* Gouan: stems + leaves (E.b.SL), inflorescences (E.b.I) and roots (E.b.R), have been extracted by steam distillation and analysed by gas chromatography (GC) and gas chromatography coupled to mass spectrometry (GC–MS). Quantitative but not qualitative differences have been found between the analysed parts. The principal compounds from the inflorescences oil were found to be phyllocladene (37.6%) and bicyclogermacrene (15.1%), while the oil from stems and leaves showed phyllocladene (20.4%), γ-muurolene (11.8%) and (*E*)-caryophyllene (10.1%) as main ones. The oil from the roots presented γ-muurolene (15.4%) and phyllocladene (15.0%) as major constituents. It is worth mentioning the presence of a diterpene, phyllocladene, as main compound of the essential oil. This is the first report on the essential oil of this species.

Keywords: *Eryngium bourgatii*; Apiaceae; Essential oil; Phyllocladene; Diterpene; Bicyclogermacrene; γ-Muurolene; (*E*)-Caryophyllene

1. Introduction

Eryngium L. genus belongs to the Apiaceae family and, with about 250 species, it has a cosmopolitan distribution practically all around the world. Fourteen of the 26 species described in Flora Europaea grow in the Iberian Peninsula [1]. Although *Eryngium bourgatii* Gouan grows wildly in Spain and France, has been used as an ornamental plant in other countries because of the colour of its leaves and inflorescences. It is perennial with stems 15–45 cm erect, basal leaves slightly coriaceous, persistent. Inflorescences usually bluish and fruits sparsely scaly [2]. In Iberian Peninsula, *E. bourgatii* habits dry stony places on Pyrenees and mountain systems (Fig. 1).

The chemistry, genetic diversity and properties of several species of *Eryngium* have been previously studied [3–19], but the essential oils of only few species have been previously reported. The chemical composition of *E. creticum* [20], *E. foetidum* [21–25], *E. maritimum* L. [26], *E. paniculatum* Cav. [27], *E. expansum* F. Muell [28], *E. pandanifolium* Cham. and Schlecht. [28], *E. rostratum* Cav. [28], *E. vesiculosum* [28–29] and *E. yucifolium* Michx. [30] have been analysed by gas chromatography (GC) and gas chromatography coupled to mass spectrometry (GC–MS) being the main constituents in most of them sesquiterpenes.

In the present work, we contribute to the knowledge of the essential oils of *Eryngium* species with the chemical composition of the different parts of *E. bourgatii* L. This is the first report on the essential oil of this species.

2. Materials and methods

2.1. Plant material

Few specimens of *E. bourgatii* were gathered in Puerto de Navacerrada, Madrid (Spain) in 22-VII-2000 (30TVL1516).

☆ Part of this paper has been presented as a poster at the 34th International Symposium on Essential Oils, Würzburg (Germany), 7–10 September 2003.

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doi:10.1016/j.chroma.2005.03.036

Fig. 1. Distribution of *E. bourgatii* in the Iberian Peninsula.

A voucher specimen (MACB-77654) has been lodged at the Herbarium of the Faculty of Biology, Complutense University, Madrid, Spain.

2.2. Isolation of volatile oils

The oils from the different air dried parts of *E. bourgatii* were isolated by steam distillation with cohobation for 8 h according to the method recommended in the Spanish Pharmacopoeia. The oils were dried over anhydrous sodium sulphate and stored at 4 °C in the dark. The samples' yield was based on dry weight were 0.33, 0.11 and 0.20 for inflorescences, stems + leaves and roots respectively.

2.3. Gas chromatography

Analytical gas chromatography was carried out on a Varian 3300 gas chromatograph fitted with a fused methyl silicone DB-1 column (50 m × 0.25 mm), 0.25 μm film thickness. Temperature was programmed from 95 to 240 °C at 4 °C/min. Injection was performed at 250 °C in the split mode (1:100). Nitrogen was used as the carrier gas (1.5 mL/min). Flame ionisation detection (FID) was performed at 250 °C. Injection volume for all the samples was 0.1 μL.

2.4. Gas chromatography–mass spectrometry

GC–MS was carried out on a Hewlet-Packard 5890 gas chromatograph fitted with a fused silica SE-30 capillary column (50 m × 0.22 mm), 0.25 μm film thickness, coupled to a HP 5971A mass-selective detector. Column temperature was programmed from 70 to 220 °C at 4 °C/min and helium was used as carrier gas. Mass spectra were recorded in the scan mode at 70 eV. In order to confirm the identification of some compounds, the oil samples were also analysed on a VG Quattro mass spectrometer operating at 70 eV ionisation 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 as carrier gas.

2.5. Qualitative analyses

Most constituents were tentatively identified by GC by comparison of their retention indices with those of authentic standards available in the author's laboratory or with retention indices from Refs. [31–35]. Further identification was achieved by GC–MS. Other constituents were either synthesised or identified in oils of known composition. The fragmentation patterns of mass spectra were also compared with those stored in the spectrometer data base using the Wiley.L built-in libraries.

3. Results and discussion

The yield from the different parts analysed of *E. bourgatii* (E.b.I = 0.33, E.b.SL = 0.11, E.b.R = 0.20) is not very high. Only the inflorescences seem to contain little high amount of essential oil although the values are very similar. We have only studied one sample of a population so we do not know if the yield could be influenced by external factors and change during the phenology of the plant as we have previously reported for Asteraceae species [36]. In that case, could be interested to analyse which part of the plant shows more changes.

The components identified from the different parts of *E. bourgatii*, their retention indices and their percentage composition are summarised in Table 1 where all the compounds are arranged in order of their elution on the DB-1 column although the retention indices of compounds confirmed on DB-wax column have been also included.

The main constituents of the oil extracted from the inflorescences were found to be phyllocladene (37.6%) and bicyclegermacrene (15.1%). The oil of the stems and leaves only shared phyllocladene (20.4%), with the inflorescences, as principal compound, but it also contained γ-muurolene (11.8%) and (*E*)-caryophyllene (10.1%). Finally the oil of the roots showed γ-muurolene (15.4%) and phyllocladene (15.0%) as major constituents, mentioned in any of the previous fractions. Other constituents of the oil were identified as (*E*)-caryophyllene (8.3%), carotol (6.0%), γ-muurolene (4.4%) and α-*neo*-clovene (3.4%) in the inflorescences, β-elemene (5.2%), caryophyllene oxide (4.6%), *iso*-acorone (2.6%), spathulenol (2.3%), α-cadinol (2.1%), 14-hydroxy-9-*epi*-(*E*)-caryophyllene (2.1%) and δ-cadinene (2.0%) in the stems and leaves while in the roots were δ-cadinene (7.4%), bicyclogermacrene (5.4%), 14-hydroxy-9-*epi*-(*E*)-caryophyllene (3.1%), spathulenol (2.1%) and α-cadinol (2.1%). Five compounds could not be identified although their mass spectral fragmentation patterns have been included at the end of Table 1.

The chemical composition of the different fractions is similar. Phyllocladene has been identified as main constituent in all of them. The other principal compounds have changed from one fraction to another although all of them are present in the different parts analysed. These differences could be caused because the compounds have distinct functions or because they could be precursors of other components. Besides, the natural habit where this species grows, exposed it to high temperature during the summer and low one during the winter could explain the presence of phyllocladene. This compound

Table 1
Essential oil composition of the different parts of *E. bourgatii* from Spain

Compound	*I*	E.b.I	E.b.SL	E.b.R
α-Pinene	932 (1012)	1.0	1.5	0.2
Sabinene	963 (1113)	t	t	t
β-Pinene	970 (1097)	t	0.4	0.3
3-*p*-Menthene	976	t	1.3	1.1
Myrcene	985 (1160)	0.1	0.1	0.0
Mesitylene	989	t	t	0.1
n-Decane	1000	t	t	t
α-Phellandrene	1005 (1157)	t	t	t
1,2,4-Trimethyl benzene	1021 (1275)	t	–	–
p-Cymene	1023 (1264)	t	–	–
Limonene	1026 (1191)	t	0.1	0.2
β-Phellandrene	1027 (1201)	t	–	–
1,8-Cineole	1029 (1204)	t	–	–
(*Z*)-β-Ocimene	1031 (1232)	t	–	–
(*E*)-β-Ocimene	1041 (1249)	t	–	–
γ-Terpinene	1058 (1240)	t	–	–
Cryptone	1087 (1669)	0.1	0.1	0.5
Linalool	1096 (1549)	0.4	0.9	0.8
6-Camphenol	1106	t	t	0.1
trans-3-Caren-2-ol	1111	t	0.2	t
Chrysanthenone	1122	t	–	–
α-Terpineol	1183 (1700)	t	t	0.2
iso-Pinocampheol	1190	t	0.1	–
(*E*)-Ocimenone	1252	t	t	0.2
(*E*)-Anethol	1300	t	–	–
δ-Elemene	1333 (1468)	0.2	t	0.1
α-Cubebene	1345 (1455)	t	0.1	0.1
β-Ylangene	1350 (1573)	t	t	t
α-Copaene	1366 (1480)	t	0.1	0.1
Daucene	1370	t	0.7	0.4
(*E*)-β-Damascenone	1371	t	–	–
β-Bourbonene	1376 (1515)	0.7	0.2	–
β-Elemene	1387 (1587)	1.1	5.2	0.6
α-Gurjunene	1406 (1528)	0.1	–	–
(*E*)-Caryophyllene	1410 (1594)	8.3	10.1	1.6
β-Gurjunene	1426 (1595)	t	0.2	0.2
γ-Elemene	1429 (1636)	t	0.1	6.0
Aromadendrene	1433 (1605)	0.4	0.3	0.1
α-Guaiene	1434	t	–	–
α-Patchoulene	1443	t	–	–
α-*neo*-Clovene	1445	3.4	0.2	t
α-Humulene	1447 (1667)	0.5	0.9	0.2
(*E*)-β-Farnesene	1452 (1770)	1.0	1.2	0.9
cis-Muurola-4(14)-5-diene	1454	t	–	–
γ-Himachalene	1461	t	–	–
γ-Gurjunene	1463	t	–	–
γ-Muurolene	1465 (1675)	4.4	11.8	15.4
Germacrene D	1476 (1713)	0.7	0.8	0.4
Viridiflorene	1487 (1695)	t	0.4	0.4
Bicyclogermacrene	1493 (1750)	15.1	1.8	5.4
α-Bulnesene	1498 (1642)	t	–	–
α-Muurolene	1499 (1724)	0.4	1.0	0.6
Sesquicineole	1509	t	–	–
β-Bisabolene	1513 (1727)	0.3	0.2	0.4
(*Z*)-γ-Bisabolene	1514	t	–	–
δ-Cadinene	1522 (1760)	1.6	2.0	7.4
Cadina-1,4-diene	1528 (1783)	t	0.1	0.1
α-Calacorene	1538	t	0.2	0.1
α-Cadinene	1539	0.2	0.6	0.4
1-*nor*-Bourbonanone	1548	t	–	–
β-Calacorene	1553	t	0.3	–
Eremophyllene	1554	1.0	1.9	0.2
cis-Muurol-5-en-4-α-ol	1556	0.1	0.4	–

Table 1 (*Continued*)

Compound	*I*	E.b.I	E.b.SL	E.b.R
n.i. 1 ($C_{15}H_{24}O$)	1557	0.3	1.7	0.8
n.i. 2 ($C_{15}H_{24}O$)	1559	0.4	t	5.3
Germacrene B	1563	0.1	0.2	–
Ledol	1570	t	–	–
Spathulenol	1576 (2133)	1.6	2.3	2.1
Germacrene D-4-ol	1578	t	t	0.3
Palustrol	1579 (1931)	t	–	–
Caryophyllene oxide	1580 (1987)	1.7	4.6	1.0
Globulol	1583 (2064)	1.3	0.2	0.6
Viridiflorol	1590 (2091)	1.1	t	1.1
Carotol	1594 (2026)	6.0	0.7	0.6
Guaiol	1595	t	–	–
β-Oploplenone	1597	t	–	–
n.i. 3 ($C_{15}H_{24}O$)	1602	t	0.5	1.2
1,10-Di-*epi*-cubenol	1611	t	–	–
10-*epi*-γ-Eudesmol	1623	0.3	1.3	0.8
Cedr-8-(15)-en-9-α-ol	1625	0.1	0.1	0.2
epi-α-Cadinol	1630 (2177)	t	–	–
epi-α-Muurolol	1631 (1890)	0.4	0.3	0.3
α-Muurolol	1650 (2246)	0.1	0.3	0.1
α-Cadinol	1651 (2243)	1.3	2.1	2.1
14-Hydroxy-9-*epi*-(*E*)-caryophyllene	1662 (1924)	1.5	2.1	3.1
Kusinol	1665	0.3	0.5	0.3
n.i. 4 ($C_{15}H_{26}O$)	1674	0.7	3.4	1.7
(*E*)-Nerolidolol acetate	1693	0.2	0.2	0.5
14-Hydroxy-α-muurolene	1757 (2026)	0.1	0.9	0.1
n.i. 5 ($C_{15}H_{24}O$)	1770	0.3	1.6	3.3
14-Hydroxy-δ-cadinene	1788	0.3	0.4	t
iso-Acorenone	1812	0.2	2.6	0.4
Sclarene	1935	1.3	0.2	2.0
Phyllocladene	1985	37.6	20.4	15.0
Monoterpene hydrocarbons		1.1	3.4	1.8
Oxygenated monoterpenes		0.4	1.2	1.3
Sesquiterpene hydrocarbons		38.5	38.7	40.9
Oxygenated sesquiterpenes		16.7	19.1	14.1
Diterpene hydrocarbons		38.9	20.6	17.0
Oxygenated diterpenes		0.0	0.0	0.0
Total		95.6	83.0	75.10

I = Kováts retention indices on DB-1 column on DB-wax in parenthesis; t = traces (%<0.1); n.i. = not identified; E.b. = *E. bourgatii*; I = inflorescences; SL = stems and leaves; R = roots; n.i. 1 K.I. = 1557 ($C_{15}H_{24}O$), 220[M^+](10), 123(100), 131(75), 109(43), 91(40), 146(39), 163(27), 187(9), 202(5); n.i. 2 K.I. = 1559 ($C_{15}H_{24}O$), 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. 3 K.I. = 1602 ($C_{15}H_{24}O$), 220[M^+](5), 161(100), 105(65), 43(60), 107(50), 93(45), 119(40), 204(38), 69(35), 138(30), 189(25), 177(18); n.i. 4 K.I. = 1674 ($C_{15}H_{26}O$), 222[M^+](10), 84(100), 81(65), 109(50), 41(43), 55(42), 121(40), 69(39), 95(28), 161(25), 137(30), 204(10), 189(8); n.i. 5 K.I. = 1770 ($C_{15}H_{24}O$), 220[M^+](10), 159(100), 93(52), 79(46), 105(35), 177(30), 121(25), 135(20), 43(20), 207(20), 187(8).

could be used as a thermo regulator in winter while in summer still as main constituent because it has high molecular weight that impedes its evaporation to be use as hydro regulator, although an exhausted study should be done to confirm this hypothesis.

The similarities of the chemical composition of the different parts of *E. bourgatii* are also presented in the terpenoid contents. In spite of the high percentage of phyllocladene in all the fractions, the sesquiternes are predominant with a 55.2% of the total oil in the inflorescences, 57.8% in the stems and leaves and 55.0% in the roots. Most of them are hydrocarbons (Table 1). The diterpenes are also well represented with 38.9%, 20.6% and 17% in the inflorescences, stems and leaves and roots, respectively. In this case all of them hydrocarbons.

The essential oil composition of the different parts of *E. bourgatii* is very similar, most of the differences found were quantitative. It is worth mentioning the presence of a diterpene, phyllocladene, as main compound of the essential oil. In fact, according to Refs. [16–30] is the first time that a diterpene is reported as a principal compound for an *Eryngium* species. Other species as *E. pandanifolium* (bornyl acetate, 20.8%), *E. paniculatum* [27] (α-pinene, 19.1%) and *E. yucifolium* [30] (leaves: terpinolene, 17.8%; roots: terpinolene, 25.8%) contain monoterpenes as main compounds but most of the species studied until the date are richer in sesquiterpenes [16–30]. On the other hand, it is also worth mentioning the presence of 2,4,5-trimethylbenzaldehyde or isomers that are very common in the essential oils of *Eryngium* species being major compound in some of them

as *E. foetidum* 2,4,5-trimethylbenzaldehyde (20.5%), 2,3,6-trimethylbenzaldehyde (5.5–23.7%) [21–25], the roots of *E. maritimum* 2,3,4-trimethy-benzaldehyde (24.5%) [26], *E. expansum* 2,3,6-trimethylbenzaldehyde (8.0%) [29] and the roots of *E. yucifolium* 2,3,6-trimethylbenzaldehyde (13.9%) [30] although we have not detected it.

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