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Short communication

Analysis by gas chromatography–mass spectrometry of the essential oil from the aerial parts of *Pimpinella junoniae* Ceb. & Ort., gathered in La Gomera, Canary Islands, Spain

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Abstract

The essential oil from the aerial parts of *Pimpinella junoniae* Ceb. & Ort., growing in La Gomera, Canary Islands, Spain, was studied by gas chromatography and gas chromatography–mass spectrometry, and 43 constituents were identified. The major components were found to be α-zingiberene (20.6%), α-pinene (17.9%), (*E*)-β-farnesene (9.3%), *ar*-curcumene (7.4%), β-phellandrene (7.0%), β-bisabolene (6.1%) and epoxypseudoisoeugenyl 2-methylbutyrate (6.0%). The decomposition product of epoxypseudoisoeugenol derivatives, 5-methoxy-2-methylbenzofuran (5.7%), moderate amounts of other arylpropanoids with the pseudoisoeugenol skeleton (total percentage, 5.2%) and other compounds such as β-sesquiphellandrene (3.0%), *cis*-β-guaiene (1.5%), α-phellandrene (1.5%) and α-bisabolol (1.3%), were also found.

Keywords: *Pimpinella junoniae*; Essential oils; Monoterpenes; Sesquiterpenes; Arylpropanoids; Terpenes

1. Introduction

Pimpinella L. belongs to the plant family Apiaceae (Umbelliferae) subfamily Apioideae, and the genus is present in the Macaronesian Archipelago comprising four species: *Pimpinella cumbrae* Link, *P. dendrotragium* Webb & Berth., *P. anagodendron* Bolle and *P. junoniae* Ceb. & Ort. [1]. This last species is endemic to the Macaronesian Archipelago and inhabits only in La Gomera, in cliffs at the edge of the sea and at an altitude of 600–1200 m, in the Garajonay National Park of the Canary Islands. As a part of a project on the volatile composition of Apiaceae endemic species to the Canary Islands [2–6] we have studied in this work the oil composition of the aerial parts of *P. junoniae* by gas chromatography and gas chromatography–mass spectrometry. Kubeczka and Ullmann [7] surveyed the presence of geijerene and pregeijerene in the root oil of *P. junoniae* and they found 46% of these components. As far as we know there is no other

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previous report on the chemical analysis of *P. junoniae*.

2. Experimental

2.1. Plant material

The air-dried aerial parts of *P. junoniae* were gathered at flowering in Orillas de Isque, above Benchijigua, La Gomera, Canary Islands, Spain (19/7/2002, at an altitude of 1200 m (above sea level) E/280352-N/3110285). Voucher specimen, *Exsiccata* TFC 43696 was deposited at the Herbarium of La Laguna University, La Laguna, Tenerife, Canary Islands, Spain.

2.2. Isolation procedure

The aerial parts of *P. junoniae* were left to dry at room temperature and 219 g of the plant material were coarsely minced and placed in a flask containing 500 ml of water and steam distilled in a Clevenger-type apparatus according to the method recommended in the Spanish Pharmacopoeia [8] for 8 h. The essential oil was dried over anhydrous magnesium sulfate and stored at 4 °C in the dark. Essential oil yield was 2.2% based on dried weight of sample.

2.3. Gas chromatography (GC)

A Varian GC 3300 fitted with a fused-silica capillary column (column A) coated with polymethylsiloxane DB-1 as stationary phase (50 m×0.25 mm I.D., 0.25 μm film thickness) was used for GC analysis. Oven temperature was programmed from 95 °C to 240 °C at 4 °C/min. Injection was performed at 250 °C using a 1:100 split ratio. A flow of 1.5 ml/min carrier gas (N_2) was used. Flame ionization detection was performed at 300 °C.

2.4. Gas chromatography–mass spectrometry

Analyses were carried out on a Hewlett-Packard 5890 gas chromatograph fitted with a fused-silica capillary column coated with crosslinked polymethylsiloxane as stationary phase (Agilent Technologies, 25 m×0.20 mm I.D., 0.33 μm film thickness. Carrier gas He, flow-rate 1 ml/min. Temperature was programmed from 70 °C to 250 °C at 4 °C/min. Samples were injected at 250 °C, using a 1:20 split ratio. Spectra were recorded in the scan mode at 70 eV.

2.5. Qualitative and quantitative analyses

Most constituents were identified by gas chromatography by comparison of their GC retention indices (*I*) with those of the literature [9–15] or with those of standards purchased, synthesized or identified in oils of known composition [16]. A limit *I* value of ±20 *I* units with respect to reference data has been considered as a criterion for positive assignment. Further identification was confirmed when possible by comparison of their mass spectra with those stored in the MS databases (NIST and Wiley libraries) or with mass spectra from the literature [9–15]. Relative component concentrations were obtained directly from GC peak areas.

3. Results and discussion

The components of the oil from the aerial parts of *P. junoniae*, their retention indices, their percentage composition and identification methods are given in Table 1 where the components are listed in order of elution on the DB-1 column.

The major constituents of the essential oil were found to be monoterpene hydrocarbons, sesquiterpene hydrocarbons and arylpropanoids. In the first group, the major components were found to be α-pinene (17.9%), β-phellandrene (7.0%). In the second group, the major components detected were α-zingiberene (20.6%), (*E*)-β-farnesene (9.3%), *ar*-curcumene (7.4%) and β-bisabolene (6.1%). The arylpropanoids amounted to 11.2% of the oil and epoxypseudoisoeugenyl 2-methylbutyrate (6.0%) was the major one. Other representative components of the oil were identified as α-phellandrene (1.5%), myrcene (0.8%), *p*-cymene (0.6%), 5-methoxy-2-methylbenzofuran (5.7%), β-sesquiphellandrene (3.0%), α-bisabolol (1.3%), (*Z*,*Z*)-farnesol (0.7%), *cis*-β-guaiene (1.5%), pseudoisoeugenyl 2-methylbutyrate (3.2%), pseudoisoeugenyl tiglate (0.8%)

Table 1
Percentage composition of the essential oil from the aerial parts of *Pimpinella junoniae* Ceb. & Ort.

Component	I_A	%
α-Pinene	924	17.9
Camphene	938	0.1
Sabinene	961	0.4
β-Pinene	964	0.6
Myrcene	975	0.8
α-Phellandrene	989	1.5
p-Cymene	1005	0.6
β-Phellandrene	1016	7.0
p-Cresol	1052	0.5
m-Cresol	1055	0.2
Terpinolene	1068	0.1
Linalool	1070	0.4
Terpinen-4-ol	1157	0.3
p-Cymen-8-ol	1163	0.2
α-Terpineol	1169	0.1
3-Methoxy-acetophenone	1277	0.1
5-Methoxy-2-methylbenzofuran	1336	5.7
α-Cubebene	1341	0.1
α-Copaene	1360	0.4
β-Bourbonene	1366	0.1
β-Cubebene	1372	0.3
β-Gurjunene	1414	0.1
(*E*)-α-Bergamotene	1416	0.6
(*E*)-β-Farnesene	1438	9.3
γ-Muurolene	1450	0.1
ar-Curcumene	1453	7.4
cis-β-Guaiene	1458	1.5
α-Zingiberene	1469	20.6
trans-β-Guaiene	1479	0.2
β-Bisabolene	1485	6.1
γ-Cadinene	1490	0.1
β-Sesquiphellandrene	1501	3.0
Spathulenol	1556	0.2
α-Bisabolol	1658	1.3
(*Z*,*Z*)-Farnesol	1693	0.7
(*E*,*E*)-Farnesol	1700	0.1
Xanthorrhizol	1730	0.3
Pseudoisoeugenyl 2-methylbutyrate[a]	**1792**	**3.2**
Pseudoisoeugenyl tiglate[a]	**1817**	**0.8**
Epoxypseudoisoeugenyl 2-methylbutyrate[a]	**1844**	**6.0**
Epoxypseudoisoeugenyl tiglate[a]	**1848**	**0.8**
Epoxypseudoisoeugenyl 2-methylbutyrate[a]	**1850**	**0.2**
Epoxypseudoisoeugenyl tiglate[a]	**1873**	**0.2**

I_A, programmed temperature retention indices relative to the homologous series of *n*-alkanes (C_5–C_{25}) on column A; MS, mass spectra data; A, column A retention data.

[a] Correct isomer not determined; characteristic chemosystematic constituents of genus *Pimpinella* shown in bold-face.

and epoxypseudoisoeugenyl tiglate (0.8%). The total amount of monoterpenes was 30.0%, that of sesquiterpenes 52.3%, that of arylpropanoids 11.2% and that of various components (cresols+5-methoxy-2-methylbenzofuran+3-methoxyacetophenone) 6.5%. More detailed results are shown in Table 1 in which the complete list of the identified compounds is given. The arylpropanoids found in this oil are all derivatives of pseudoisoeugenol (4-methoxy-2-propenyl-phenol). Together with C_{12} compounds such as geijerene and pregeijerene, pseudoisoeugenyl esters are important chemosystematic characters in the genus *Pimpinella*. They have been found so far in *P. junoniae* (this paper), *P. cumbrae* Link, *P. anisum* L., *P. peregrina* L., *P. saxifraga* L., *P. nigra* Mill., *P. major* (L.) Hudson, *P. diversifolia* DC., *P. aromatica* Bieb., *P. villosa* Schousboe, *P. tripartrita* Kalenicz. (=*Albovia tripartita* (Kalenicz.) Schischk.), *P. isaurica* Mathews [6,17–19] and only in another genus of *Apiaceae* namely *Ligusticum mucronatum* (Shrenk) Leute [20]. Pseudoisoeugenyl esters have also been found, but only in *Apiaceae*, in in vitro systems [21,22]. It is worth mentioning the absence in our oil from the aerial parts of *P. junionae* of geijerene and pregeijerene detected by Kubezcka and Ullmann [7] in the root oil of *P. junoniae*. In addition, the occurrence of 5-methoxy-2-methylbenzofuran is also interesting as this component is a decomposition product formed from epoxypseudoisoeugenyl esters during hydrodistillation [6,16,18].

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