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Short communication

Analysis by gas chromatography–mass spectrometry of the essential oils from the aerial parts of *Rutheopsis herbanica* (Bolle) Hans. & Kunk., gathered in Fuerteventura (Canary Islands)

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Abstract

The essential oil from the aerial parts of *Rutheopsis herbanica* (Bolle) Hans. & Kunk., growing in Fuerteventura, Canary Islands, Spain, was studied by gas chromatography and gas chromatography–mass spectrometry, and 42 constituents were identified. The major components were found to be α-pinene (29.4%), dillapiole (21.3%), limonene (14.1%), β-pinene (13.2%) and myristicin (10.0%). As far as we know, this is the first report on the essential oil composition of this species.

Keywords: Essential oils; *Rutheopsis herbanica*; Pinenes; Volatile organic compounds; Terpenes

1. Introduction

Rutheopsis Hans. & Kunk. (Apiaceae, Apioideae, Apieae) is a monotypic genus comprising the species *Rutheopsis herbanica* (Bolle) Hans. & Kunk. [1] (=*Ruthea herbanica* Bolle) [2]. This species is a small umbelliferous plant with white flowers endemic to the Macaronesian Archipelago and inhabiting only the volcanic black rocks and ashes of Fuerteventura and Lanzarote of the Canary Islands. As part of a project on the volatile composition of Apiaceae and Asteraceae species of the Canary Islands [3–6], we have studied the oil composition of the aerial parts of *R. herbanica* by gas chromatography and gas chromatography–mass spectrometry. This plant contains an essential oil with a sweet odour resembling that of parsley but as far as we know, no data have been published on its volatile components.

2. Experimental

2.1. Plant material

The air-dried aerial parts of *R. herbanica* were gathered at flowering in La Oliva, Fuerteventura, Canary Islands, Spain (8/3/2002). Voucher specimens, TFC-43625 and TFC-43628 were deposited at

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the Herbarium of La Laguna University, Santa Cruz de Tenerife, Canary Islands, Spain.

2.2. Isolation procedure

The aerial parts of *R. herbanica* were left to dry at room temperature and 290 g of the plant material were coarsely minced and placed in a flask containing 500 ml water and steam distilled in a Clevenger-type apparatus according to the method recommended in the Spanish Pharmacopoeia [7] for 8 h. The essential oil was dried over anhydrous magnesium sulphate and stored at 4 °C in the dark. Essential oil yield was 1.0% based on dried mass of sample.

2.3. Gas chromatography (GC)

A Varian GC 3300 system fitted with a fused-silica capillary column (column A) coated with poly(dimethylsiloxane) 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 90 to 240 °C at 4 °C/min. Injection was carried out 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 carried out at 300 °C.

2.4. Gas chromatography–mass spectrometry (GC–MS)

Analyses were carried out with two different instruments:

1. A Trace GC–MS Thermo Finigan apparatus fitted with a Restek RTX-5 capillary column [column B, poly(diphenyldimethylsiloxane) containing 5% diphenylsiloxane monomer, 30 m×0.25 mm I.D., 0.25 μm, film thickness]. Temperature was programmed from 70 to 250 °C at 5 °C/min. Helium was used as carrier gas at a flow-rate of 1 ml/min. Samples were injected at 275 °C, using a 1:50 split ratio. Spectra were recorded in the scan mode at 70 eV.
2. A Hewlett-Packard 6890 gas chromatograph fitted with a HP-Innowax capillary column (column C, poly(ethylene glycol), 50 m×0.20 mm I.D., 0.20 μm film thickness) coupled to an HP 5973A mass selective detector. Column temperature was programmed from 70 to 190 °C at 5 °C/min and helium was used as carrier gas at a flow-rate of 1 ml/min. Samples were injected at 275 °C, using a 1:25 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 using columns A and C with phases of different polarity, by comparison of their GC retention indices (I) with those of literature [8–14] or with those of standards purchased, synthesized or identified in oils of known composition. 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 (columns B and C) with those stored in the MS databases [US National Institute of Standards and Technology (NIST) and Wiley libraries] or with mass spectra from literature [8–13]. Relative component concentrations were obtained directly from GC peak areas.

3. Results and discussion

The components of the oil from the aerial parts of *R. herbanica*, their retention indices on columns A and C, 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 (column A).

The major constituents of the essential oil were found to be monoterpene hydrocarbons and arylpropanoids. In the first group, the major components were found to be α-pinene (29.4%), limonene (14.1%) and β-pinene (13.2%). In the second group, the main components detected were dillapiole (21.3%) and myristicin (10.0%). Other representative components of the oil were identified as phellandral (3.8%), myrcene (1.5%), α-terpinene (1.4%), sabinene (1.1%), β-phellandrene (1.1%), β-caryophyllene (0.8%) and elemicin (0.4%). The total amount of monoterpenes was 66.5%, that of sesquiterpenes 1.4% and that of arylpropanoids 31.7%. The complete list of the identified compounds ap-

Table 1
Percentage composition of the essential oil from the aerial parts of *R. herbanica* (Bolle) Hans. & Kunk.

Component	I_A	I_C	%	Identification
n-Hexanal	772	1094	t	A, C, MS
n-Hexanol	839	1320	t	A, C, MS
α-Thujene	903	1038	0.2	A, C, MS
α-Pinene	**912**	**1038**	**29.4**	A, C**, MS**
Camphene	924	1088	0.1	A, C, MS
Sabinene	941	1135	1.1	A, C, MS
β-Pinene	**949**	**1128**	**13.2**	A, C, MS
Myrcene	949	1167	1.5	A, C, MS
α-Phellandrene	970	1180	t	A, C, MS
α-Terpinene	980	1197	1.4	A, C, MS
p-Cymene	982	1287	t	A, C, MS
Limonene	**998**	**1216**	**14.1**	A, C, MS
β-Phellandrene	998	1226	1.1	A, C, MS
(*Z*)-β-Ocimene	1024	1234	t	A, C, MS
(*E*)-β-Ocimene	1038	1255	t	A, C, MS
γ-Terpinene	1053	1257	t	A, C, MS
1,3,4-Trimethyl-3-cyclohexene -1-carboxaldehyde*	1053	1525	t	MS
Terpinolene	1069	1298	t	A, C, MS
β-Cyclocitral	1105	1608	0.3	A, C, MS
Lavandulol	1125	1682	t	A, C, MS
Borneol	1130	1706	0.1	A, C, MS
Terpinen-4-ol	1141	1638	0.1	A, C, MS
α-Terpineol	1161	1704	0.1	A, C, MS
Verbenone	1176	1738	t	A, C, MS
Phellandral	1185	1613	3.8	A, C, MS
Bornyl acetate	1260	1589	t	A, C, MS
α-Copaene	1339	1525	t	A, C, MS
β-Cedrene	1381	1620	t	A, C, MS
β-Caryophyllene	1386	1614	0.8	A, C, MS
(*E*)-α-Bergamotene	1397	1595	t	A, C, MS
(*E*)-β-Farnesene	1408	1670	0.1	A, C, MS
α-Humulene	1417	1686	0.1	A, C, MS
γ-Muurolene	1429	1698	t	A, C, MS
γ-Curcumene	1432	–	0.1	A, MS
ar-Curcumene	1436	–	0.2	A, MS
Valencene	1451	1755	t	A, C, MS
Myristicin	**1482**	**2258**	**10.0**	A, C, MS
Elemicin	1517	2228	0.4	A, C, MS
Caryophyllene oxide	1541	1972	t	A, C, MS
Carotol	1560	–	0.1	A, MS
Dillapiole	**1582**	**2338**	**21.3**	A, C, MS
Apiole	1642	–	t	A, MS
n.i. $C_{20}H_{34}O$	1990	>2500		MS

t = trace amount (<0.1%); I_A and I_C = programmed temperature retention indices relative to the homologous series of *n*-alkanes (C_5–C_{25}) on columns A and C; MS = mass spectral data; A = column A retention data; C = column C retention data. Values in bold = major constituents; * = tentative identified.

pears in Table 1. The arylpropanoids found in this oil, myristicin, elemicin, apiole and dillapiole are commonly found in the Apiaceae, Piperaceae and Myristicaceae plant families. In the Apiaceae are present frequently in the subfamily Apioideae. Parsley apiole or apiole [1,3-benzodioxole-4,7-dimethoxy-5-(2-propenyl)] is a characteristic constituent of parsley [*Petroselinum crispum* (Miller)

A.W. Hill] and its isomer dillapiole [1,3-benzodioxole-4,5-dimethoxy-6-(2-propenyl)] is a major component in dill (*Anethum graveolens* L.), sea-fennel (*Crithmum maritimum* L.) and also in *Astidamia latifolia* (L. fil.) Baillon, a species also endemic to the Canary Islands. Myristicin and elemicin have been found in the seeds and roots of many Apiaceae of economic importance in the food industry such as celery (*Apium graveolens* L.), dill, fennel (*Foeniculum vulgare* Miller), parsley, parsnip (*Pastinaca sativa* L.), and carrot (*Daucus carota* L.). Myristicin presents pharmaceutical interest [15] and dillapiole is used at present in the pharmaceutical and cosmetics industries [16]. The oil of *R. herbanica* appears to be a good source of myristicin (10.0%) and dillapiole (21.3%). Among other *Rutheopsis* components it is worth mentioning phellandral (3.8%) which was first detected in the Apiaceae in the oil of *Phellandrium aquaticum* L. [17] and an unidentified oxygenated diterpene $C_{20}H_{34}O$ with mass spectrum *m*/*z* (rel. int.): 290 [M^+](4), 69 (100), 109 (85), 41(60), 93(45), 81(40), 121(30), 135(20), 275(5), which suggests an acyclic structure.

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