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Short communication

## Analysis of the volatile components of *Argyranthemum adauctum* (Link.) Humphries by gas chromatography–mass spectrometry

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### Abstract

The volatile constituents of the essential oil of *Argyranthemum adauctum* (Link.) Humphries extracted by steam distillation have been studied by GC–MS. A total of 60 compounds have been identified representing the 89.8% of the oil. The major constituents were found to be  $\beta$ -pinene (27.4%) and santolinatriene (22.6%). This is the first report on the chemical compounds of the oil of this species. © 2001 Elsevier Science B.V. All rights reserved.

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### 1. Introduction

The genus *Argyranthemum* Webb ex Schutz-Bip., belongs to the family Asteraceae tribe Anthemideae, and comprises 39 species restricted to the archipelagos of the Canaries, Selvagens, Madeira and Desertas in the Macaronesian biogeographic region. It is the largest endemic genus in all the Atlantic oceanic archipelagos with 24 species and 15 subspecies [1]. *Argyranthemum adauctum* (Link.) Humphries inhabits only in the archipelago of the Canaries and it is distributed throughout La Palma, El Hierro, Tenerife and Gran Canaria [2].

Molecular studies have been previously reported showing the origin, distribution, hybridization and subspecies in *Argyranthemum* genus [3–5]. According to these results, the chloroplast DNA data indicated that *Argyranthemum* is a monophyletic

group that has recently speciated. The two major radiations identified in the Canaries are correlated with distinct ecological habitats, one restricted to ecological zones under the influence of the northeastern trades and the other to regions that are not affected by these winds. The patterns of phylogenetic relationships in *Argyranthemum* indicated that inter-island colonization between similar ecological zones was the main mechanism establishing founder populations. This phenomenon, combined with rapid radiation into distinct ecological zones and inter-specific hybridation, was the primary explanation for species diversification.

The biological activity of seven *Argyranthemum* species have been also studied [6]. The acetone extracts from the roots of *A. foeniculaceum* Webb ex Schutz-Bip., *A. adauctum* (Link.) Humphries and *A. frutescens* (L.) Schutz-Bip., were the most active, exhibiting activity against Gram-positive and Gram-negative bacteria and yeasts as *Candida albicans* and *Saccharomyces cerevisiae*.

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Table 1  
Percentage composition of the essential oil of *Argeranthenum adactum* (Link.) Humphries

Compound	<i>I</i>	%
Santolinatriene	887	22.6
α-Thujene	916	0.3
α-Pinene	926	2.3
α-Fenchene	941	0.2
Sabinene	958	1.3
β-Pinene	968	27.4
<i>cis</i> -Pinane	971	t
Myrcene	981	1.0
α-Phellandrene	995	0.2
α-Terpinene	1002	t
<i>p</i> -Cymene	1010	4.5
Limonene	1014	1.3
1,8-Cineole	1016	1.3
( <i>Z</i> )-β-Ocimene	1023	0.8
( <i>E</i> )-β-Ocimene	1034	0.1
γ-Terpinene	1039	0.6
Terpinolene	1066	t
α-Pinene oxide	1071	0.3
<i>trans</i> -Sabinene hydrate	1073	t
Linalool	1074	t
Chrysanthenone	1103	t
Pinocarvone	1141	0.5
Borneol	1147	0.3
Lavandulol	1140	1.2
Terpinen-4-ol	1157	0.6
α-Terpineol	1165	t
Myrtenal	1169	0.9
Myrtenol	1171	0.5
<i>exo</i> -Fenchyl acetate	1214	t
Lavandulyl acetate	1268	0.8
Longicyclene	1353	0.2
α-Copaene	1366	0.2
( <i>E</i> )-Caryophyllene	1408	0.2
α-Humulene	1435	0.9
α-Patchoulene	1444	0.9
( <i>E</i> )-β-Farnesene	1446	0.2
<i>allo</i> -Aromadendrene	1451	0.7
α-Acoradiene	1456	0.5
β-Acoradiene	1459	t
γ-Muurolene	1463	0.5
Germacrene D	1467	0.7
α-Zingiberene	1473	0.6
δ-Selinene	1478	t
α-( <i>E</i> ),( <i>E</i> )-Farnesene	1485	0.2
6-Methyl-α-( <i>E</i> )-ionone	1497	0.4
δ-Cadinene	1503	0.1
β-Sesquiphellandrene	1512	1.0
( <i>E</i> )-Nerolidol	1546	1.9
n.i. 1	1562	5.6
n.i. 2	1562	2.1
( <i>Z</i> )-α-Santalol*	1571	0.4
<i>trans</i> -Sesquisabinene hydrate	1573	2.2

Table 1. Continued

Compound	<i>I</i>	%
Caryophyllene oxide	1577	0.5
Viridiflorol	1582	t
Guaiol	1589	0.7
10- <i>epi</i> -γ-Eudesmol	1596	2.7
<i>epi</i> -α-Cadinol	1627	0.8
<i>epi</i> -α-Muurolol	1630	1.5
α-Muurolol	1635	0.6
<i>epi</i> -α-Bisalolol*	1659	1.8
n.i. 3	1674	0.3
Zerumbone	1710	1.6
α-Sinensal	1732	0.6
14-Oxy-α-muurolene	1745	0.3
14-Hydroxy-α-muurolene	1756	0.2

t=Trace (<0.1%); *I*=Kováts retention index according to *n*-alkanes on the DB-1 column; n.i.=not identified; \*=tentatively identified.

With regard to the chemical constituents of this genus, we have only found a previous study about the essential oils of *A. pinnatifidum* (L. fil.) Lowe and *A. haemotomma* (Lowe) Lowe [7]. The oil yield of these species varied from 0.01% to 0.05% (v/w). Monoterpene hydrocarbons were dominant in each of the samples analysed from each species. The main components of the oil were found to be β-myrcene (28–50 and 39–62%) and germacrene D (10–18 and 10–23%) in *A. pinnatifidum* and *A. haemotomma*, respectively.

In the present work, we report on the chemical composition of the essential oil from the aerial parts of *A. adactum* (Link.) Humphries by gas chromatography–mass spectrometry (GC–MS). A literature search did not yield any reference to earlier reports on the essential oil components of this species.

## 2. Experimental

### 2.1. Plant material

The aerial parts of *A. adactum* were gathered at flowering in Cuevas del Chorro, Tejeda, Gran Canaria (Canary Islands, Spain), 3 April 2000. A voucher specimen MAB-76451 has been deposited at the herbarium of the Biology Faculty in the Complutense University of Madrid, Spain.

## 2.2. Isolation procedure

Plant material was steam distilled in a Clevenger-type apparatus for 8 h, according to the method recommended by the Spanish Pharmacopoeia [8]. The essential oil was dried over anhydrous magnesium sulfate and stored at 4°C in the dark. The yield was 0.38% based on dried mass of sample.

## 2.3. Gas chromatography:

A Varian GC 3300 system was used for GC analysis, fitted with a fused methylsilicone DB-1 column (50 m×0.25 mm I.D., 0.25 µm film thickness). The oven temperature was programmed from 80 to 225°C at 4°C/min. Injection was performed at 280°C in the split ratio 1:100; 0.1 µl of sample was injected. A flow of 1.5 ml/min carrier gas (N<sub>2</sub>) was used. Flame ionisation detection was performed at 300°C.

## 2.4. Gas chromatography–mass spectrometry

Analyses were carried out in a Fison 8000 gas chromatograph fitted with a fused methylsilicone SE-30 and SE-54 columns (50 m×0.25 mm I.D., 0.25 µm film thickness), coupled to an MD 800 mass detector. Column temperature was programmed from 70 to 240°C at 4°C/min. Injection was performed at 250°C. Helium was used as carrier gas (0.5 ml/min). Mass spectra were recorded in the scan mode at 70 eV (35–350 u).

## 2.5. Qualitative and Quantitative analyses

Most constituents were tentatively identified by

comparison of their GC Kováts retention indices (*I*) with those of authentic standards available in the author's laboratory or with GC data previously published [9,10]. Identification was confirmed when possible by comparison of their mass spectra with those stored in the MS database (National Institute of Standards and Technology and Wiley libraries) and with mass spectra literature data [10–13]. Component relative concentrations were obtained directly from GC peak areas.

## 3. Results and discussion

The blue oil isolated from the aerial parts of *A. adauctum* (Link.) Humphries was obtained with 0.38% (v/w) yield. The identified compounds of the oil, their retention indices and percentage composition are given in Table 1 where the components are listed in order to their elution on the DB-1 column.

The essential oil studied was dominated by the monoterpene fraction that amounted 68.2% of the oil. β-Pinene (27.4%) and santolinatriene (22.6%) were found to be the major constituents of the oil. Other minor compounds identified were *p*-cymene (4.5%), 10-*epi*-γ-eudesmol (2.7%), α-pinene (2.3%), *trans*-sesquisabinene hydrate (2.2%), (*E*)-nerolidol (1.9%), zerumbone (1.6%), *epi*-α-muurolool (1.5%), sabinene (1.3%), limonene (1.3%), 1,8-cineole (1.3%), lavandulol (1.2%), myrcene (1.0%) and β-sesquiphellandrene (1.0%). It is worthwhile to mention that the high amount of santolinatriene (22.6%) was not previously reported in this genus. Two compounds, (*Z*)-α-santalol (0.4%) and *epi*-α-bisabolol (1.8%), were tentatively identified according to literature and their mass spectra data (Table

Table 2  
Mass spectra data of unidentified and tentatively identified components

Compound	M <sup>+</sup>	<i>m/z</i> (relative intensity)
n.i. 1: <i>I</i> 1562	220M <sup>+</sup> (5)	43 (100), 91 (85), 93 (80), 119 (80), 71 (70), 105 (67), 79 (65), 107 (58), 77 (50), 55 (45), 145 (20), 173 (10), 187 (10).
n.i. 2: <i>I</i> 1562	220M <sup>+</sup> (20)	94 (100), 79 (95), 67 (70), 55 (67), 41 (57), 131 (42), 109 (36), 205 (20), 164 (15), 149 (10).
( <i>Z</i> )-α-Santalol: <i>I</i> 1571	220M <sup>+</sup> (7)	94 (100), 79 (61), 67 (42), 109 (40), 131 (20), 55 (20), 41 (17), 187 (9).
<i>epi</i> -α-Bisabolol: <i>I</i> 1659	222M <sup>+</sup> (5)	119 (100), 93 (95), 69 (86), 91 (67), 41 (45), 105 (43), 55 (40), 161 (15), 204 (7).
n.i. 3: <i>I</i> 1674	222M <sup>+</sup> (5)	69 (100), 119 (98), 93 (97), 149 (52), 105 (50), 55 (49), 79 (48), 41 (45), 161 (21), 204 (15).

2). The compound  $I=1562$  was the mixture of two components that were separated on the SE-54 column, although neither these nor constituent  $I=1674$  have been identified by the method used in the present work. We think it would be useful to give their mass spectral data (Table 2).

According to our results and with those of the Ref. [7], the essential oils of *Argeranthenum* species studied at the moment are richer in monoterpene than in sesquiterpene compounds. The yield of *A. adaucum* was higher than the yield of the other two species previously reported.

## References

- [1] A. Hansen, P. Sunding, *Sommerfeltia* 17 (1993) 1.
- [2] D. Bramwell, Z.I. Bramwell, *Flores Silvestres de las Islas Canarias*, Rueda, Madrid, 1990.
- [3] J. Francisco-Ortega, R.K. Jansen, A. Santos-Guerra, *Proc. Natl. Acad. Sci. USA* 93 (1996) 4085.
- [4] J. Francisco-Ortega, D.J. Crawford, A. Santos-Guerra, J.A. Carvalho, *Pl. Syst. Evol.* 202 (1996) 137.
- [5] J. Francisco-Ortega, A. Santos-Guerra, A. Hines, R.K. Jansen, *Am. J. Bot.* 84 (1997) 1595.
- [6] A.G. González, R. Estévez-Reyes, A. Estéves-Braun, A.G. Ravelo, I.A. Jiménez, I.L. Bazzocchi, M.A. Aguilar, L. Moujir, *Phytochemistry* 45 (1997) 963.
- [7] J.G. Barroso, L.G. Pedro, A.C. Figueiredo, S.S. Fontinha, A. Looman, J.J.C. Scheffer, *Flavour Fragr. J.* 11 (1996) 211.
- [8] *Real Farmacopea Española*, Ministerio de Sanidad y Consumo, Madrid, 1997.
- [9] R.P. Adams, *Identification of Essential Oils Components by Gas Chromatography–Mass Spectroscopy*, Allured Publishing, IL, 1995.
- [10] W. Jennings, T. Shibamoto, *Qualitative Analysis of Flavor and Fragrance Volatiles by Capillary Gas Chromatography*, Academic Press, New York, 1980.
- [11] L.M. Libbey, *J. Essent. Oil Res.* 3 (1991) 192.
- [12] A.A. Swigar, R.M. Silverstein, *Monoterpenes*, Aldrich, Milwaukee, WI, 1981.
- [13] W.W. Epstein, L.R. McGee, C.D. Poulter, L.L. Marsh, *J. Chem. Eng. Data* 21 (1976) 500.