Botanica Complutensis
2000, 24, 101-106

ISSN: 0214-4565

Essential Oil Constituents of Sideritis ibanyezii Pau

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Resumen

KARDALI, M., VELASCO-NEGUERUELA, A. & PÉREZ-ALONSO. M. J. 2000. Constituyentes del aceite esencial de *Sideritis ibanyezii* Pau. *Bot. Complutensis* 24: 101-106.

El aceite esencial extraido de las partes aéreas de *Sideritis ibanyezii* Pau, una labiada endémica de España, ha sido analizado mediante la CG capilar y sus componentes identificados por CG/EM en combinación con los índices de retención. Se han identificado cincuenta y seis compuestos que representan el 96.0 % de la cantidad total del aceite esencial y de los cuales 26 han sido detectados por primera vez en esta especie. Son mayoritarios: acetato de α–fenchilo (16.0 %), sabineno (12.8 %) y α–pineno (10.7 %). También se han incluido en el trabajo los datos espectroscópicos de 14 componentes.

Palabras clave: *Sideritis ibanyezii* Pau, Labiatae, Aceite esencial, terpenos, α–pineno, sabineno, acetato de α–fenchilo.

Abstract

KARDALI, M., VELASCO-NEGUERUELA, A. & PÉREZ-ALONSO. M. J. 2000. Essential oil constituents of *Sideritis ibanyezii* Pau. *Bot. Complutensis* 24: 101-106.

The essential oil isolated from the aerial parts of *Sideritis ibanyezii* Pau, an endemic Spanish Labiatae, has been analysed by means of capillary GC and their components identified by GC/MS in combination with retention indices. The fifty six components identified, amounted 96.0 % of the essential oil of which 26 have been detected for the first time in this species. The major components were (α-fenchyl acetate (16,0 %), sabinene (12.8 %) and (-pinene (10.7 %). The mass spectra data of 14 constituents have been included.

Key words: *Sideritis ibanyezii* Pau, Labiatae, essential oil, terpenes, (-pinene, sabinene, (-fenchyl acetate.

INTRODUCTION

Among the plants belonging to the genus *Sideritis* L, widely distributed throughout the Iberian Peninsula, *Sideritis ibanyezii* Pau [= *S. flavovirens* (Rouy) Alcaraz *et*

al.] is endemic to the Murciano-Almeriense province of the Spanish mediterrannean basin. *Sideritis ibanyezii* is a 60 to 70 cm shrub. Its inflorescence has six flowered verticillasters yellowish tint in the angles of the axis, calyces and bracts.

The plant is known in Almería by the common names of "ogarzo" and "zajareña fina", while in Murcia the popular name is "chichifraile" or "rabo de gato". The decoction of the leaves is employed as anti-inflammatory and anti-rheumatic, whereas the infusion is taken for stomach-aches as well as a mild laxative in case of constipation (OBÓN DE CASTRO *et al.*, 1991).

The oils of Spanish *Sideritis* have been studied with some detail (MATEO *et al.*, 1984; MATEO *et al.*, 1988; ADZET *et al.*, 1990; MÁNEZ *et al.*, 1991; BURZACO *et al.*, 1992). The oil of *S. ibanyezii* Pau. has been the subject of only one report (MATEO *et al.*, 1988). The major identified constituents were found to be: α-fenchyl acetate (19.8 %), fenchone (18.6 %), α-pinene (13.4 %), limonene (7.5 %) and 1.8-cineole (7.4 %).

As a part of our research on aromatic endemic flora of Spain we report the results of our investigation on the chemical composition of the volatiles of *S. ibanyezii*.

MATERIAL AND METHODS

Plant Material

Samples of the aerial parts of *Sideritis ibanyezii* Pau. were collected in Cuesta del Capitán Pulpí near Almería, in August 1998. The air-dried plant, 167.6 g, was hydrodistilled for 8 hours in an all-glass Clevenger apparatus in accordance with the method recommended in the REAL FARMACOPEA ESPAÑOLA (1997). The oil was dried over anhydrous sodium sulphate and stored at -15°C in the dark until analysis. The plant material was authentified by Dr. Ginés López. A voucher specimen was deposited at the Herbarium of the Real Jardín Botanico (C.S.I.C.) Madrid, Spain.

Gas Chromatography (GC)

Analytical GC was performed on a Varian 3300 gas chromatograph fitted with a OV-1, capillary methyl silicone column, 50 m × 0.25 mm, 0.25 μm film thickness. Oven temperature was programmed 95-240°C at 4°C/min. Carrier gas was N_2 with a flow rate 1.5 mL/min. Injector temperature 250°C. Split ratio 1/100; injection sample 0.1 μL. Detector used FID at 300°C.

Gas Chromatography-Mass Spectrometry (GC/MS)

Analyses were carried out on a Hewlett-Packard 5890 gas chromatograph fitted with a fused Silica SE-30 capillary column (25 m × 0.22 mm, 0.25 μm film thick-

ness). Carrier gas helium with a flow rate 1.5 mL/min. Column temperature was programmed from 70°-220°C at 5°C/min. Injector temperature 250°C. The chromatograph was coupled to a HP 5971A mass selective detector at 70 eV.

The constituents were identified by comparing their retention indices with those of authentic standards available in the author's laboratory.The latter were either purchased, synthetesized or identified in oils of known composition. The fragmentation patterns of mass spectra were compared with NBS54K and WILEY libraries and with those reported in the literature (ADAMS, 1997; JENNINGS & SHIBAMOTO, 1980; LIBEY, 1991).

RESULTS AND DISCUSSION

The yield based on dried weight of sample was 0.71%. The volatile constituents, the retention time (Rt), percentages and Kovats indices are shown in Table 1. Components are listed in order of their elution from OV-1 column.

The oil of *S. ibanyezii* was characterised by a high content of monoterpenes (72.8 %) and α-fenchyl acetate (16.0 %) was found to be the mayor component. Furthermore, sabinene (12.8%), α-pinene (10.7 %), α-fenchol (6.1 %), 1.8-cineole (5.6 %), β-phellandrene (4.5 %), limonene (4.1 %) and terpinen-4-ol (4.3 %) were the major components found. Our results are in accordance with those of MATEO *et al.* (1988) in which the characteristic constituents of *S. ibanyezii* were fenchane derivatives.

Our oil, however, contains a lower amount of fenchone and a higher percentage of sabinene than that reported by MATEO *et al.* (1988).

In essential oils the biosynthesis of bicyclic monoterpenes as fenchone, α and β-pinenes and sabinene are derived from three diferents pathways (PORTER & SPURGEON, 1981). Terpinen-4-ol is the precursor of sabinene and α-terpineol via the pinenes leads to fenchone or to fenchyl acetate. In our oil sample the pathway to fenchone is suppressed whereas that to fenchyl acetate is maintained. Also the pathway to sabinene is available. In the sample studied by MATEO *et al* (1988) the pathway to fenchone and fenchyl acetate is available whereas that to sabinene seems to be almost eliminated.

ACKNOWLEDGEMENTS

We are indebted to Dr. Ginés López (Real Jardin Botánico C.S.I.C. Madrid) for providing and authentifying the plant material.

Table 1
Chemical composition of the oil of *Sideritis ibanyezii* Pau

Component	K.I	Percentage	Methods--
MONOTERPENES			
1. α-thujene	920	0.8	K.I, MS
2. α-pinene	930	10.7	K.I, MS
3. α-fenchene	942	0.4	K.I, MS
4. camphene	945	0.1	K.I, MS
5. sabinene	962	12.8	K.I, MS
6. β-pinene	972	2.0	K.I, MS
7. β-myrcene	976	0.1	K.I, MS
8. α-phellandrene	996	0.1	K.I, MS
9. δ-3-carene	1004	0.1	K.I, MS
10. α-terpinene	1007	1.3	K.I, MS
11. p-cymene	1010	0.5	K.I, MS
12. limonene	1019	4.1	K.I, MS
13. 1,8-cineole	1019	5.6	K.I, MS
14. β-phellandrene	1019	4.5	K.I, MS
15. γ-terpinene	1044	0.3	K.I, MS
16. *cis*-sabinene hydrate	1052	0.3	K.I, MS
17. fenchone	1070	1.2	K.I, MS
18. α-terpinolene	1076	0.6	K.I, MS
19. linalool	1084	0.2	K.I, MS
20. α-fenchol	1102	6.1	K.I, MS
21. β-fenchol	1109	0.1	K.I, MS
22. *trans*-pinocarveol	1126	0.1	K.I, MS
23. terpinen-4-ol	1161	4.3	K.I, MS
24. α-terpineol	1173	0.3	K.I, MS
25. α-fenchyl acetate	1205	16	K.I, MS
26. bornyl acetate	1267	0.1	K.I, MS
27. isothujyl-3-acetate	1297	0.1	K.I, MS
Total identified monoterpenes		**72.8**	
28. osmorhizol [‡]	1322	0.1	
SESQUITERPENES			
29. δ-elemene	1328	0.5	K.I, MS
30. α-copaene	1372	0.3	K.I, MS
31. β-bourbonene	1380	1.6	K.I, MS
32. β-caryophyllene	1414	2.5	K.I, MS
33. β-gurjunene	1423	0.1	K.I, MS
34. *cis*-muurola-4(14),5-diene [†]	1455	0.3	K.I, MS
35. germacrene D	1465	0.4	K.I, MS
36. *cis*-β-guaiene	1473	0.8	K.I, MS
37. bicyclo-germacrene	1484	0.1	K.I, MS
38. α-muurolene	1488	0.7	K.I, MS
39. γ-cadinene	1503	0.6	K.I, MS
40. *cis*-calamenene	1507	0.2	K.I, MS

Table 1
Chemical composition of the oil of *Sideritis ibanyezii* Pau *(Continuación)*

Component	K.I	Percentage	Methods--
41. δ-cadinene	1509	1.6	K.I, MS
42. β-calacorene †	1526	0.2	K.I, MS
43. bornyl-angelate †	1538	0.6	K.I, MS
44. ledol	1546	0.2	K.I, MS
45. spathulenol	1561	0.7	K.I, MS
46. caryophyllene oxyde	1568	1.6	K.I, MS
47. β-oplopenone †	1586	0.5	K.I, MS
48. 1,10-*di-epi*-cubenol †	1590	0.5	K.I, MS
49. hydroxy calamenene * †	1607	0.3	K.I, MS
50. M^+=220, 136(100)	1618	0.6	
51. *epi*-α -muurolol †	1622	1.1	K.I, MS
52. (-cadinol	1628	1.3	K.I, MS
53. 14-hydroxy-9-*epi*-caryophyllene†	1634	1.6	K.I, MS
54. bisabolol †	1650	2.0	K.I, MS
55. bulnesol †	1655	0.3	K.I, MS
56. 1,6 germacradien-5-ol †	1661	1.4	K.I, MS
57. M^+=220, 91(100)	1675	0.3	
58. nootkatone †	1765	0.3	K.I, MS
Total identified sesquiterpenes		**22.3**	
Total unidentified sesquiterpene alcohols		**0.9**	

K.I = Kovats Indices
* = Correct isomer not found.
† = tentatively identified according to literature data.

Mass data of tentatively identified components:

Component 28: **osmorhizol**: C10H12O2, K.I = 1322, m/z (rel.int.):164[M^+](100), 149(39), 131(38), 103(32), 77(32), 91(26), 55(25), 65(22).

Component 34: ***cis*-muurola-4(14),5-diene**: C15H24, K.I = 1455, m/z (rel. int.): 204[M^+](21), 161(100), 91(53), 105(41), 119(40), 41(40), 133(38), 81(37), 67(29), 147(20), 189(14).

Component 42: **ß-calacorene**: C15H24O, K.I = 1526, m/z (rel. int.): 200[M^+](17), 157(100), 142(48), 115(7), 41(6), 129(5).

Component 43: **bornyl-angelate**: C15H24O2, K.I = 1538, m/z (rel. int.): 236[M^+](0), 83(100), 55(18), 93(11), 67(10), 41(10), 136(8), 109(4).

Component 47: **ß-oplopenone**: C15H24O, K.I = 1586, m/z (rel. int.): 220[M^+](35), 177 (100), 107(58), 91(50), 43 (39), 135 (33), 79 (33), 71 (22).

Component 48: **1,10 *di-epi*-cubenol**: C15H26O, K.I = 1590, m/z (rel. int.): 222[M^+](0), 41(100), 119(79), 161(68), 67(65), 105(38), 109(36)204(31), 179(17), 81(14), 189(7).

Component 49: **hydroxy-calamenene**: K.I = 1607, m/z (rel.int.): 220[M^+](0), 159(100), 97(51), 202(34), 121(28), 79(18), 177(17), 191(16), 109(14), 150(15), 63(9).

Component 53: **14-hydroxy-9-*epi*-caryophyllene**: C15H24O, K.I = 1634, m/z (rel. int.): 220[M^+](4), 91(100), 69(100), 79(84), 41(75), 105(52), 55(41), 133(39), 131(36), 119(36), 187(23), 159(23).

Component 54: **bisabolol**: C15H26O, K.I = 1650, m/z (rel. int.):222[M^+](0), 109(100), 119(89), 43(71), 204(24), 121(21), 55(19), 81(16), 161(8).

Component 55: **bulnesol**: C15H26O, K.I = 1655, m/z (rel. int.):222[M+](9), 204(39), 161(100), 79(40), 107(38), 41(36), 135(9), 119(6).

Component 56: **1,6-germacradien-5-ol**, K.I = 1661, m/z (rel. int.):222[M+](5), 84(100), 81(57), 55(42), 109(39), 41(32), 69(29), 121(29), 93(27), 137(19), 207(13), 161(13), 189(8).

Component 58: **nootkatone**: C15H22O K.I = 1765, m/z (rel. int.):218[M+](0), 91(100), 105(83),), 79(45), 67(42), 133(32), 121(30), 147(18), 53(15), 203(9).

Mass data of unidentified sesquiterpene alcohols:

Component 50: **K.I = 1618**, m/z (rel. int.):220[M+](0), 136(100), 69(56), 41(43), 91(41), 79(38), 109(25), 53(22), 159(18).

Component 57: **K.I = 1675**, m/z (rel. int.):220[M+](32), 91(100), 81(87), 95(70), 109(57), 69(46), 40(30), 177(26), 161(25), 54(23), 191(22), 148(22), 163(21), 54(23).

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Recibido: 30 de Junio de 2000.
Aceptado: 1 de Septiembre de 2000.