Asian Journal of Chemistry

Vol. 21, No. 8 (2009), 6369-6374

Chemical Composition of the Essential Oils from Flowers of Senecio vernalis and Senecio platyphyllus var. platyphyllus

Asu Usta, Osman Üçüncü, Tayyibe Beyza Cansu, Salih Terzioglu[†] and Nurettin Yayli^{*} Department of Chemistry, Faculty of Arts and Sciences, Karadeniz Technical University, 61080 Trabzon, Turkey Fax: (90)(462)3253196; Tel: (90)(462)3772486 E-mail: yayli@ktu.edu.tr

Two essential oil samples obtained by hydrodistillation from the flowers of *Senecio vernalis* Valdst. & Kit., (Asteraceae) and *Senecio platyphyllus* DC. var. *platyphyllus*, were analyzed by GC-FID and GC-MS. 69 compounds in the oil of *S. vernalis*, representing 93.4 % and 48 compounds in the oil of *S. platyphyllus* var. *platyphyllus*, representing 94.4 %, were identified. The essential oils were rich in monoterpene (53.3 %) and sesquiterpene (76.1 %) hydrocarbons with β -pinene (13.0 %) and (E)-caryophyllene (28.6 %) as the major compounds, respectively.

Key Words: *Senecio vernalis, Senecio platyphyllus* var. *platyphyllus*, Essential oils, GC-FID, GC-MS.

INTRODUCTION

In Turkey, the genus *Senecio* L. of the family Asteraceae is represented by 39 species (14 of those which are endemic)¹⁻⁴. A specie of *Senecio* (*S. aureus* L.) is used in folk medicine to induce menstrual periods and to relief menopausal complains⁵. This genus is rich in sesquiterpene hydrocarbons⁴.

Previous works on the essential oils from *Senecio* included *Senecio squalidus* L., *Senecio aegyptius* var. *discoideus* Boiss., *Senecio graveolens* Wedd., *Senecio farfarifolius* Boiss., *Senecio nutans* Sch.-Bip., *Senecio longipenicillatus* Sch.-Bip. and *Senecio trapezuntinus* Boiss. *p*-Cymene (29.3 %) and α -phellandrene (24.7 %) were major constituents in the herb oil of *S. squalidus*⁶. The main constituent was 1,10-epoxyfuranoeremophilane (46.4 to 69.0 %) in the oils of the flower, leaf, stem and root of *S. aegyptius* var. discoideus⁴. α -Terpinene (60 %), *p*-cymene (14 %), terpinen-4-ol (5.5 %) and α -phellandrene (4 %) were major compounds in the leaf essential oil of *S. graveolens*⁷. In the essential oil obtained from the flower of *S. farfarifolius*, α -pinene (48.3 %) and 1,8-cineole (10.3 %) were found as main components⁸. The essential oils from the aerial parts of *S. nutans* showed that oxygenated

[†] Department of Forest Botany, Faculty of Forestry, Karadeniz Technical University, 61080 Trabzon, Turkey.

monoterpene hydrocarbons predominate in the oils⁹. The major components in the essential oil of *S. longipenicillatus* were α -pinene, (48.3 %), α -humulene (15.8 %) and germacrene D (15.5 %)¹⁰. The main compound in the essential oils from flower, leaf and stem of *S. trapezuntinus* was (E)- β -farnesene (26.3, 16.9 and 31.2 %, respectively)¹¹. In this paper we report the composition of the essential oils of *Senecio vernalis* Valdst. & Kit. and *Senecio platyphyllus* DC. var. *platyphyllus*.

EXPERIMENTAL

Whole plants of *S. vernalis* Valdst. & Kit. and *S. platyphyllus* DC. var. platyphyllus were collected in Torul-Karaca Cave, Gümüshane and Besikdüzü-Sisdagi, Trabzon (at height of *ca.* 1580 and 1650 m) in the northwestern part of Turkey in July 2007. The plants were authenticated immediately after collection¹⁻³. Voucher specimens were deposited in the Herbarium of the Faculty of Forestry, KATO (KATO: 16083 and 16087, respectively), Karadeniz Technical University, Turkey.

Isolation of the essential oils: The flowers of the fresh plant materials were separated, frozen with liquid nitrogen and grounded into small pieces. Essential oils of *S. vernalis* and *S. platyphyllus* var. platyphyllus were obtained from the fresh flowers (*ca.* 96 and 160 g each, respectively) by hydrodistillation in a Clevenger-type apparatus¹²⁻¹⁶ with cooling bath (-12 °C) system (4 h) (yields: 0.16 and 0.12 % (w/w), respectively). The obtained oils were dissolved in HPLC grade *n*-hexane (0.5 mL), dried over anhydrous sodium sulphate and stored at 4-6 °C in a sealed brown vial. One μ L of the essential oils was directly injected separately into GC and GC-MS instrument.

Gas chromatography analysis: The capillary GC-FID analysis was performed using an Agilent-5973 Network System, equipped with a FID (supplied with air and hydrogen of high purity) and a split inlet. The chromatographic column used for the analysis was HP-5 capillary column ($30 \text{ m} \times 0.32 \text{ mm}$ i.d., film thickness 0.25 µm). Helium was used carrier gas, at a flow rate of 1 mL/min. The injections were performed in splitless mode at 230 °C. One µL essential oil solution in hexane (HPLC grade) was injected and analyzed with the column held initially at 60 °C for 2 min and then increased to 240 °C with a 3 °C/min heating ramp. The identity of each compound was supported by comparing their retention indices (RI) to published values. The sample was analyzed twice and the percentage composition of oil was computed from the GC peak areas without using correction factors.

Gas chromatography-mass spectrometry (GC-MS) analysis: GC-MS analysis of the essential oils was performed using an Agilent-5973 Network System. A mass spectrometer with an ion trap detector in full scan mode under electron impact ionization (70 eV) was used. The chromatographic column used for the analysis was HP-5 capillary column (30 m \times 0.32 mm i.d., film thickness 0.25 µm). Helium was used carrier gas, at a flow rate of 1 mL/min. The injections were performed in

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splitless mode at 230 °C. One μ L essential oil solution in hexane (HPLC grade) was injected and analyzed with the column held initially at 60 °C for 2 min and then increased to 240 °C with a 3 °C/min heating ramp.

Identification of components: Retention indices of all the components were determined by Kovats method¹⁷ using *n*-alkanes (C₆-C₃₂) as standards. Identification of individual components was made by comparison of their retention times with those of available analytical standards (α -pinene, camphene, β -pinene, α -terpinene, linalool, geraniol, *n*-docosane, *n*-tricosane, *n*-tetracosane and *n*-pentacosane) and by computer search, matching mass spectral data with those held in Nist and Wiley library of mass spectra and literature comparison^{12-16,18-21}.

RESULTS AND DISCUSSION

The GC-FID and GC-MS of the essential oil of S. vernalis and S. platyphyllus var. platyphyllus are presented in Table-1. Total 85 essential components were identified with HP-5 column. Sixty-nine components were identified from the oil of S. *vernalis*, representing 93.4 % of the total oil. The major constituents were β -pinene (13.0 %) and α -pinene (10.5 %). In addition, Δ -3-carene (10.4 %), germacrene D (8.6 %), α -phellandrene (8.3 %), Z- β -ocimene (4.7 %) and α -humulene (4.5 %) were identified as the main constituents. In the essential oil of S. platyphyllus var. platyphyllus, 48 components were identified, representing 94.4 % of the total oil and E-caryophyllene (28.6 %), germacrene D (23.4 %) and E- β -farnesene (6.8 %) were the main compounds. In the oil of S. vernalis, 12 monoterpenes (53.3 %) 14 sesquiterpenes (18.5%), 18 oxygenated monoterpenes (13.4%), 11 others (4.4%), seven oxygenated sesquiterpenes (3.8%), one diterpenoid (0.1%) and in the oil of S. platyphyllus var. platyphyllus 12 sesquiterpenes (76.1%), 7 oxygenated sesquiterpenes (9.6%), 17 others (7.0%), 5 monoterpene hydrocarbons (1.2%), 3 oxygenated monoterpenes (0.5%), one diterpenoid (0.3%) were identified. The qualitative and quantitative determination of essential oil of S. vernalis and S. platyphyllus var. platyphyllus showed that monoterpenes (53.3 %) and sesquiterpenes (76.1 %) were major constituents in the oils, respectively. Generally, the number of volatile compounds present in S. vernalis is greater than in S. platyphyllus var. platyphyllus.

E-Caryophyllene (28.6 %), germacrene D (23.4 %), E-β-farnesene (6.8 %), bicyclogermacrene (5.0 %) and E,E-α-franesene (4.7 %) components were the main compounds in *S. platyphyllus* var. *platyphyllus*. Whereas, the main constituents in the essential oil of *S. vernalis* was monoterpene hydrocarbons and major components were β-pinene (13.0 %), α-pinene (10.5 %), Δ-3-carene (10.4 %), α-phellandrene (8.3 %) and Z-β-ocimene (4.7 %). In comparison with the previously reported composition of the essential oils of *Senecio* species, sesquiterpene hydrocarbons were the major constituents^{4,6-11,19,20}. The results clearly indicate that the major constituents of the essential oil were different and *S. platyphyllus* var. *platyphyllus* gave less volatile (Table-1) which can be explained by the environmental factors and the subspecies of the plant used. 6372 Usta et al.

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Compd	Compounds		Area (%)	
No.		RI^a —	A	В
Monoterpenes		53.3	1.2	
1	a Dinana	939	10.5	0.4
2	Camphene	956	0.1	0.4
3	Thuia-2.4-(10)-diene	963	0.1	
4	ß-Pinene	978	13.0	0.2
5	Myrcene	993	2.6	
6	α-Phellandrene	1003	8.3	0.3
7	α -Terpinene	1019	0.4	
8	Δ-3-Carene	1033	10.4	
9	(Z) - β -Ocimene	1040	4.7	0.2
10	(E) - β -Ocimene	1051	1.8	012
10	Bergamal	1057	1.0	0.1
12	v Terpinene	1060	0.6	0.1
12	Terpinolene	1000	0.8	
Oxygena	ted monoterpenes	13.4	0.5	
14	<i>cis</i> -Sabinene hydrate	1069	0.2	
15	Linalool	1100	0.2	03
16	<i>cis-p</i> -Menth-2-en-1-ol	1122	0.6	0.0
17	α -Campholenal	1124	0.2	
18	allo-Ocimene	1132	0.3	
19	trans-Pinocarveol	1141	1.6	
20	trans-Verbenol	1148	1.2	
21	Pinocarvone	1165	1.0	
22	Terpinen-4-ol	1179	1.2	
23	Myrtenal	1196	2.6	
24	Myrtenol	1198	0.8	
25	Verbenone	1207	1.2	
26	Nerol	1233	0.1	
27	Thymol methyl ether	1236		0.1
28	Cumin aldehyde	1242	0.4	
29	Carvone	1244	0.1	
30	Geraniol	1256	tr	0.1
31	Perilla aldehyde	1274	0.3	
32	α -Terpinen-7-al	1285	0.2	tr
33	Carvacrol	1303	0.7	
Sesquiter	penes	18.5	76.1	
34	α-Cubebene	1350	tr	0.1
35	α-Copaene	1375	0.8	0.3
36	β-Bourbonene	1385	0.1	
37	β-Cubebene	1389	0.1	
38	β-Elemene	1391	0.6	1.6
39	α-Gurjunene	1409	0.1	
40	(E)-Caryophyllene	1419	1.5	28.6
41	α-Humulene	1455	4.5	3.9
42	(E)-B-Farnesene	1460		6.8

TABLE-1 IDENTIFIED COMPONENTS IN THE ESSENTIAL OILS FROM THE FLOWERS OF *S. vernalis* AND *S. platyphyllus* var. *platyphyllus*

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43	allo-Aromadendrene	1460	0.3	
44	Germacrene D	1487	8.6	23.4
45	Bicyclogermacrene	1498	0.7	5.0
46	α-Muurolone	1499	0.2	
47	(E,E) - α -Farnesene	1508		4.7
48	Δ-amorphene	1513	tr	
49	γ-Cadinene	1514	0.2	
50	A-Cadinene	1523	0.7	1.3
51	a-Cadinene	1539		0.3
52	a-Calacorene	1546	0.1	0.1
Oxygenated sesquiterpenes		3.8	9.6	
53	(F)-B-Damascenone	1386	tr	
54	(E)-Nerolidol	1566	0.2	
55	Carvonhyllene oxide	1582	1.1	34
56	Viridiflorol	1502	1.1	1.0
57	Humulene epoxide II	1608	16	1.0
58	1-epi-Cubenol	1628	0.3	0.5
59	ani a Muurolol	1644	0.5	1.8
60	cy Codinal	1656	0.4	1.0
61	Creation of Creati	1000		1.7
01 62		1/29	0.1	0.5
62	14-Hydroxy-∆-cadinene	1807	0.1	07
63 D:	Hexahydro farnesylacetone	1848	0.1	0.7
Diterper	noid	0.1	0.3	0.2
64	cis-Phytol	2121	0.1	0.3
Others	1	4.4	7.0	0.1
65	1-Nonene	896	1.2	0.1
66	Benzaldenyde	962	0.1	0.1
6/	6-Methyl-5-nepten-2-one	988		0.3
68	o-Cymene	1026		0.2
69	Benzene acetaldenyde	1044		0.4
70	Acetophenone	1067		0.5
/1	1-Undecene	1094	0.2	1.6
72	1-Octen-3-yl- acetate	1115	0.2	0.4
73	<i>p</i> -Methyl acetophenone	1180	1.1	0.4
74	(E)-Cinnamaldenyde	12/2	0.1	tr
15	1-Iridecene	1293	0.1	0.5
/6	(2E,4E)-Decadienal	1319		0.1
70	Eugenol	1360	tr	0.5
/8	Methyl hexadecanoate	1929	0.1	0.3
/9	Hexadecanoic acid	1977	0.4	0.2
80	Ethyl hexadecanoate	1995	0.1	0.3
81	Methyl linoleate	2096	0.9	0.4
82	Docosane	2201	0.1	tr
83	Tricosane	2300	0.1	0.8
84	Tetracosane	2401	tr	0.1
85	Pentacosane	2501	0.1	0.4
Total oil content			93.4	94.4
Total nu	umber of identified compounds	69	48	

tr (trace) \leq 0.04; A: S. vernalis, B: S. platyphyllus var. platyphyllus.

^aRI calculated from retention times relative to that of *n*-alkanes (C_6-C_{32}) on the non-polar HP-5 column. % Area obtained by FID peak-area normalization. 6374 Usta et al.

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ACKNOWLEDGEMENTS

This study was supported by grants from Karadeniz Technical University Research Fund and State Planning Agency (DPT) of Turkey.

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(*Received*: 26 December 2008; *Accepted*: 1 June 2009) AJC-7620