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ESSENTIAL OIL COMPOSITION OF *SENECIO DESFONTAINEI* DRUCE (COMPOSITAE)

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ABSTRACT

The essential oil of *Senecio desfontainei* Druce was analyzed by GC and GC - MS. A total of 41 compounds were identified. Oil profiles and contents of the flowers, leaves, stems and roots were determined. In the flowers, β-myrcene (38.1%), Cymene (19.7%), phellandrene (9.8%) and dehydrofukinone (10.1%) are the major constituents. In the leaves and stems dehydrofukinone is the major component constituting 42.8% and 77.6%, of the oil respectively. The major components of the root oil were, eremophilane (dehydrofukinone 46.9% and euparin 20.9%), caryophyllene 8.5% and farnesene (Z) β (3.7%). The antimicrobial activity of the oils was evaluated and showed broad and powerful activity aganist two Gram - positive, two Gram - negative and two fungi.

INTRODUCTION

Senecio is the largest genus in the family Compositae. It comprises from 1500 to 2000 species distributed all over the world [1]. Pyrrolizidine alkaloids [2], eremophilanes, furanoeremophilanes, benzofurans, oplopanes and other terpenes (di-and sesqueterpenes), flavonoids and polyacetylens have been isolated from several *Senecio* species [3]. Only few reports have appeared concerning the volatile oil chemistry of this genus. Some of the relevant reports on *Senecio* species come from Japan, Netherlands and India [4-6]. In Egypt, the genus is represented by about 7 species [7]. Eremophilanes, benzofurans have been previonsly identified in a solvent extract of the aerial parts of *Senecio desfontainei* Druce *(S. coronopifolius* Desf.) species [8-12]. Reviewing current literature, nothing was reported about the volatile oil of *S. desfontainei* Druce. In this paper the essential oil constituents of *S. desfontainei* Druce growing in Egypt was described as well as the antimicrobial activity of the oil was reported.

EXPERIMENTAL

Plant material : Plant material was collected in the flowering stage during April 1998 from the Bilbeis area in the southern of Zagazig. The plant identity was kindly verified by Dr. H. Abdel Baset, Lecturer of Plant Taxonomy, Faculty of Science, University of Zagazig. Voucher specimens have been deposited in the Herbarium of the Pharmacognosy Department, Faculty of Pharmacy, University of Zagazig.

^{1}H- and ^{13}C NMR spectra were recorded on AC Bruker. Instrument in $CDCl_3$ at 300 and 75 MHz, respectively. MS was carried out on Varian/MAT 311A mass spectrometer U.S.A. Melting point was determined on STUART SMP1 (U.K.) apparatus and was uncorrected.

Essential oil isolation : Fresh flowers, leaves, stem and root samples were hydrodistilled and the percentage of the oil for each plant organ was determined (0.22, 0.23, 0.05 and 0.04% V/W yield, respectively) following the E.P. method [13]. The oils were dried with anhydrous sodium sulphate and kept at 4°C in sealed vials for analysis.

Essential oil analysis : The oil samples (2mg each) were dissolved in 1 ml CH_2Cl_2 and 2μl was injected to gas chromatography (Carlo Erba Miga 5160) under the following conditions : column, DB1 fused silica capillary (30m x 0.25 mm i.d.), carrier gas He (2 ml min^{-1}); detector, FID., temp. 300°C, inj. temp. 250°C; split 1:10; oven temp. program : initial temp. 50°C 4 min. isothermal, 50-90°C at 4°C min^{-1}, 90-300°C at 10°C min^{-1} then 10 min. isothermal. Percentage of the identified compounds were computed from GC peak area.

Capillary GC-MS was performed on OV1 (30m x 0.25 mm i.d.) column coupled directly to a quadrupole Finnigan MAT 4500 mass spectrometer. EI-MS were recorded at 45 eV. Condition : Carrier gas He (50 Kpa), split ratio 1:20; inj. temp. 250°C; oven temp. Program: initial temp. 46°C 4 min isothermal, 46-100°C at 4°C min^{-1} 100-300°C at 8°C min^{-1}, then 10 min. isothermal. Kovats retention indices (RI) were calculated using co-chromatographed standard hydrocarbons (C-9 to C-24). Identification of the constituents was performed by comparing their retention indices and mass fragmentation patterns with the published data [14-19] and also by the aid of the computer library search (NBS). Results are recorded in Tables 1 and 2 and the compounds are listed in order of elution from a DB1 and OV1 capillary columns.

Chromatographic trials were carried out to isolate any of the major components in the oils of different organs. The oil of the root (2 ml) was chromatographed on silica gel column (2 x 50 cm x 200) and eluted with light petrolum (40 - 60)/ benzene in a gradient elution technique. Yellow crystalline needles (50 mg) were successfully isolated from the

fraction eluted with light peterolum / benzene 9:1. The isolated compound has a m.p. 118-119°C, R_f 0.85 (solvent system benzene : ethyle acetate 8.5 : 1.5) and shows the following spectral data:

EI-MS, m/z (rel. int. %) [M$^+$] 216 (90), 202 (13), 201 (100), 198 (9), 173 (20), 116 (5), 115 (18), 108 (4), 100 (6), 91 (9), 77 (5), 69 (10), 65 (4), 57 (3), 51 (4), 43 (12). **^{1}H NMR** ($CDCl_3$, 300 MH_Z), 2.08 (3H, s, H-12), 2.66 (3H, s, H-14), 5.17 (1H, br s, H-11), 5.74 (1H, br s, H-11), 6.53 (1H, s, H-3), 6.96 (1H, s, H-7), 7.89 (1H, S, H-4), 12.84 (OH). **^{13}C-NMR** ($CDCl_3$, 75 MH_Z), 19.2 (q, C-12), 26.6 (q, C-14), 99.4 (d, C-7), 102.4 (d, C-3), 113.7 (t, C-11), 116.8 (s, C-5), 121.9 (s, C-9), 123.5 (d, C-4), 132.1 (s, C-10), 157.9 (s, C-6), 159.7 (s, C-2), 161.6 (s, C-8), 203.9 (s, C-13).

Comparison of the obtained results with those in the literature supports this structure **(46)** [10, 12].

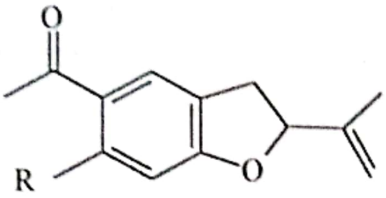
Biological assays :

The *in vitro* antimicrobial studies were carried out by agar diffusion (cup plate) method. Each cup was filled accurately with 50µl of 20% oil in dimethylformamide (DMF) for each oil (flowers and leaves). The sensitivity of the oils was tested against two Gram - positive bacteria : *Staphylococcus aureus*; *Bacillus subtilis* and two Gram - negative bacteria : *Escherichia coli* and *Klebsiella pneumoniae* and two fungi : *Candida albicans* and *Aspergillus flavus*, all of them are standard strains obtained from stock cultures of the Department of Microbiology, Faculty of Pharmacy, University of Zagazig. The plates were incubated over night at 37°C in case of bacteria and 30°C for fungi. The diameters of inhibition zones were measured (in mm) using tetracycline, gramicidine, penicillin, and chloramphenicol as a standard antibiotics and nystatin as standard antifungal in order to control the sensitivity of the test organisms.

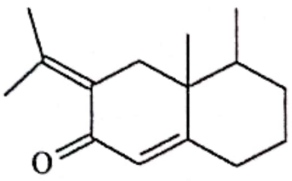
RESULTS AND DISCUSSION

Quantitative and qualitative variation between the 4 oils were evident. Table 1 shows the identification of the oil components while table 2 represents the percentage of different constituents in different plant organs.

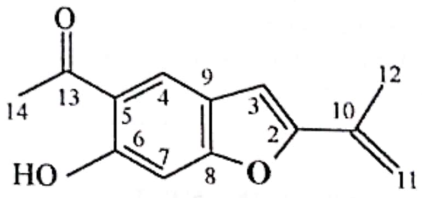
The oil from the flowers was characterized by a high content of β-myrcene (38.1%), o-cymene (19.7%), dehydro fukinone (10.2%) and β-phellandrene (9.8%). Leaves oil contained a high percentage of dehydrofukinone (42.8%), β-myrcene (28.5%) and 5-hepten-2-one (4.8%). Stem oil possessed the highest content of dehydrofukinene (77.6%). It is worth noting that monoterpens (hydrocarbons and oxygenated) which are by far the major components in the other organs, could not be detected in the oil of the root. The most characteristic difference in the composition of the root oil was the dominance of euparin (20.9%). The contribution of sesquiterpene hydrocarbons and oxygenated sesquiterpene was also significant for all examined organs. Although euparin **(46)** and dehydrofukinone **(44)** have been previously identified in a solvent extract of the aerial parts of *Senecio desfontainei* [10], the obtained result confirm the presence of these substances in the oil as well as tremetone **(42)** and dihydroeuparin **(45)** as volatile constituents for the first time.



R = H **(42)**
R = OH **(45)**



(44)



(46)

Fig. 1: Eremophilanes identified in the volatile oil of *Senecio desfontainei*.

The antimicrobial activities of the flowers and leaves oils obtained from the two investigated organs were also evaluated (see Table 3). Both oils exhibited significant levels of activity against the tested microorganisms.

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Table (1): Volatile components identified in the oils of *Senecio desfontainei* [14-19].

No.	Compound	RI*	M^+	B.P.	Major Peaks	Identification method
1	α-Pinene	924	136	93	121, 105, 92, 91, 79, 77	GC-MS, RI
2	Sabinene	960	136	93	121, 107, 91, 79, 77, 41	"
3	β-Pinene	961	136	93	121, 107, 91, 79, 77, 69	"
4	5-Hepten-2-one	976	126	43	111, 97, 83, 69, 55	"
5	β-Myrcene	982	136	41	121, 107, 93, 91, 77, 69	"
6	α-Phellandrene	991	136	93	92, 91, 79, 77, 65, 41	"
7	o-Cymene	1008	134	119	117, 91, 77, 65, 41	"
8	β-Phellandrene	1014	136	93	121, 107, 91, 79, 77, 41	"
9	Limonene	1017	136	68	121, 107, 93, 79, 67, 53	"
10	(Z) β-Ocimene	1030	136	93	121, 105, 92, 91, 79, 77	"
11	(E) β-Ocimene	1041	136	93	121, 105, 92, 91, 80, 79, 41	"
12	α-Terpinene	1048	136	93	121, 105, 91, 79, 77, 43	"
13	Cis-Sabinene hydrate	1053	n.d.	43	121, 111, 93, 81, 71, 69	"
14	Terpinolene	1077	136	121	105, 93, 92, 79, 67, 41	"
15	Terpin-4-ol	1156	154	71	136, 111, 93, 86, 55, 43	"
16	α-Terpineol	1168	n.d.	59	136, 121, 93, 81, 67, 43	"
17	Octanol acetate	1193	172	43	142, 113, 99, 82, 67, 54	"
18	Carvone	1222	150	82	85, 67, 57, 55, 41	"
19	Carvacrol	1283	150	135	121, 115, 105, 91, 79, 43	"
20	Methyl decanoate	1314	186	74	143, 87, 55, 43	"
21	*trans*-Carvyl acetate	1331	n.d.	43	134, 119, 105, 93, 77, 67	"
22	Unidentified (A)**	1340	204	204	189, 146, 147, 122, 121, 107	"
23	Cyperene	1371	204	204	189, 175, 161, 147, 122, 105	"
24	β-Cedrene	1383	204	161	147, 133, 119, 105, 91, 81	"
25	α-cis-Bergamotene	1385	204	93	161, 147, 133, 119, 105, 81	"

Table (1): Continue

No.	Compound	RI*	M+	B.P	Major Peaks	Identification method.
26	(E) Caryophyllene	1411	204	41	133, 120, 105, 93, 91, 79, 69, 55	GC-MS, RI
27	(Z) β-Farnesene	1434	204	69	161, 133, 120, 105, 93, 79, 69, 55	"
28	∝-Humulene	1445	204	93	147, 121, 107, 80, 67, 55	"
29	(E)- β-Farnesnre	1450	204	69	161, 133, 120, 93, 79, 55	"
30	(γ)-Curcumene	1472	204	119	161, 121, 105, 93, 79, 41	"
31	Valencene	1479	204	161	189, 133, 119, 107, 93, 79, 41	"
32	Bicyclogermacrene	1489	204	93	161, 136, 121, 119, 107, 41	"
33	*delta*-Cadinene	1513	204	161	189, 134, 119, 105, 91, 81	"
34	Unidentified (B)**	1563	-	69	207, 204, 161, 121, 119, 95	"
35	Unidentified (C)**	1566	222	69	207, 189, 121, 93, 85, 80	"
36	Unidentified (D)**	1578	-	93	205, 138, 121, 67, 57, 43	"
37	(β)-Oplopenone	1584	220	69	177, 136, 121, 93, 80, 57, 43	"
38	Geranyl-n-propanoate	1589	210	69	136, 121, 93, 85, 80, 68, 57	"
39	Cubenol	1614	222	119	179, 161, 109, 105, 95, 82, 69, 55, 43	"
40	Anhydrooploanone	1658	220	43	204, 161, 105, 69, 55, 43	GC-MS, Ref (5)
41	(∝)-Bisabolol	1672	222	137	177, 159, 133, 132, 121, 93, 95, 81	GC-MS., RI
42	Tremetone	1690	202	43	187, 159, 144, 131, 115, 91	GC-MS, (Ref (20)
43	Unidentified (E)**	1722	218	135	218, 150, 135, 68, 67, 55, 43	GC-MS
44	Dehydrofukinone	1778	218	161	203, 189, 175, 147, 133, 121, 105, 91	GC-MS (Ref., 10,21)
45	Dihydroeuparin	1819	218	218	203, 185, 175, 160, 157, 147, 129, 43	
46	Euparin	1852	216	201	see experimental section	GC-MS, ^{1}H-and ^{13}CMR

RI* = retention index, M+, molecular ion peak; B.P., base peak; n.d., not detected.

** = Unidentified compounds.

RI data were measured relative to n-alkanes on a OV1 Column under condition listed in the experimental section.

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Table (2): Percentage composition of the oils from the fresh flowers, leaves, stems and roots of *Senecio desfontainei*.

No.	Compound	Percentage			
		Flowers	Leaves	Stem	Root
1	α-Pinene	tr.	tr.	-	-
2	Sabinene	3.7	1.4	tr.	-
3	β-Pinene	tr.	1.2	tr.	-
4	5-Hepten-2-one	8.2	4.8	2.6	-
5	β-Myrcene	38.1	28.5	6.7	-
6	α-Phellandrene	5.7	1.1	tr.	-
7	o-Cymene	19.7	6.7	0.9	-
8	β-Phellandrene	9.8	5.1	3.0	-
9	Limonene	1.2	0.9	tr.	-
10	(Z) β-Ocimene	tr.	0.2	tr.	-
11	(E) β-Ocimene	tr.	0.2	tr.	-
12	∝-Terpinene	tr.	tr.	tr.	-
13	Cis-Sabinene hydrate	tr.	tr.	tr.	-
14	Terpinolene	0.3	0.2	tr	-
15	Terpin-4-ol	tr.	tr.	tr.	-
16	∝-Terpineol	tr.	tr.	tr.	-
17	Octanol acetate	tr.	tr.	tr.	-
18	Carvone	tr.	tr.	tr.	-
19	Carvacrol	tr.	tr.	tr.	-
20	Methyl decanoate	tr.	tr.	tr.	-
21	*trans*-Carvyl acetate	tr.	tr.	tr.	-
22	Unidentified (A)	tr.	tr.	tr.	tr.
23	Cyperene	tr.	0.4	0.5	1.1
24	β-Cedrene	0.4	0.4	0.7	0.9
25	∝-cis-Bergamotene	tr.	tr.	tr.	tr.

Table (2): Continue

No.	Compound	Percentage			
		Flowers	Leaves	Stem	Root
26	(E) Caryophyllene	0.5	0.6	0.2	8.5
27	(Z) β-Farnesene	0.4	1.0	0.9	7.3
28	∝-Humulene	1.7	1.5	1.1	2.3
29	(E)- β-Farnesene	tr.	0.9	1.8	3.7
30	(γ)-Curcumene	0.1	0.4	0.6	0.5
31	Valencene	tr.	tr.	tr.	tr.
32	Bicyclogermacrene	tr.	tr.	tr.	tr.
33	(delta)-Cadinene	tr.	tr.	tr.	tr.
34	Unidentified (B)	tr.	tr.	tr.	tr.
35	Unidentified (C)	tr.	tr.	tr.	tr.
36	Unidentified (D)	tr.	tr.	tr.	tr.
37	(β)-Oplopenone	tr.	tr.	tr.	tr.
38	Geranyl-n-propanoate	tr.	0.4	0.7	tr.
39	Cubenol	tr.	tr.	tr.	tr.
40	Anhydrooploanone	tr.	tr.	tr.	tr.
41	(∝)-Bisabolol	tr.	tr.	tr.	tr.
42	Tremetone	tr.	tr.	tr.	tr.
43	Unidentified (E)	tr.	tr.	tr.	tr.
44	Dehydrofukinone	10.2	42.8	77.6	46.9
45	Dihydroeuparin	tr.	tr.	tr.	1.4
46	Euparin	tr.	0.3	0.4	20.9
	Total	100%	99%	97.7%	93.5%
	Monoterpene hydrocarbons	78.5 (12 comp)	45.5 (12 comp.)	10.6 (11 comp.)	-
	Oxygen containing monoterpens	traces (6 comp.)	traces (6. comp.)	traces (6 comp.)	-
	Sesquiterpene hydrocarbons	3.1 (11 comp.)	5.2 (11 Comp.)	5.8 (11 Comp.)	24.3 (11. comp.)
	Oxygen containing sesquiterpene	traces (4 comp.)	traces (4 comp.)	traces (4 comp.)	traces (4 comp.)
	Eremophilanes	10.2 (4 comp.)	43.1 (4 comp.)	78 (4 comp.)	69.2 (4 comp).
	Others	8.2 (4 comp.	5.2 (4 comp.)	3.5 (4comp.)	traces (1 comp.)

tr. = traces conc. (< 0.1 %) - = not detected comp. = compound

Table (3): Results of antimicrobial screening of volatile oils (flowers and Leaves) of *Senecio desfontainei* (50 µL were applied in each assay).

Material	Diameter of inhibition zone in mm.					
	Gram. neg. bacteria		Gram-pos. bacteria		Fungi	
	E. coli	*K. pneumoniae*	*S. aureus*	*B. subtilis*	*C. albicans*	*A. Flavus*
Volatile oil of flowers *	8	11	12	17	19	20
Volatile oil of leaves *	12	13	20	10	22	30
Tetracycline 30 µg /disc	-	9	8	16	-	-
Chloramphenicol 30µg / disc	15	15	20	15	-	-
Penicillin 10µg / disc	-	-	5	-	-	-
Gramicidin 10µg / disc	-	18	12	25	-	-
Nystatin 30µg / disc	-	-	-	-	15	10

— = No zone of inhibition

* Concentration : 20% oil in DMF.

REFERENCES

1- Sharma, OP., Plant Taxonomy. Tata McGraw-Hil Publishing Co. Limited. New Delhi, P. 312 (1993).

2- Hartmann, T. and Witte, L., Chemistry, Biology and Chemecology of Pyrrolizidine Alkaloids. In : Alkaloids : Chemical and Biological perspectives (Pelletier S.W., ed.) Pergamon, Oxford, Vol. 9, PP. 155 - 233 (1995) and the references cited in.

3- Rizk, A.M., The Phytochemistry of the Flora of Qatar. Scientific and Applied Research Center University of Qatar. PP. 85 - 90 (1986). and the references cited in.

4- Miyazawa M., Hika, N. and Kameoko H. **Koen Yoshishu - Koryo, Terupen Oyobi Seiyu Kagaku ni Kansuru Toronkai**, 33rd, 51 (1979); C.A. **93**, 22578.

5- Van Dooren, B., Bos, R. and Tattje, D.H.E., **Planta medica** 42, 385 - 389 (1981).

6- Mengi, N., Garg, S.N., Agarwal, S.K. and Mathela, C.S., **J. Essent. Oil Res.** 7, 511-514 (1995).

7- Tackholem, V. "Students Flora of Egypt. "2nd Ed. Cooperative printing Co. Beirut P. 581 (1974).

8- Ghazy, N.M. and El-Masry, S., **Acta Pharm Jugosl .**, 36, 67 - 68 (1986).

9- Metwally, M.A. and Dawidar, A., **Pharmazie** 41, 522 - 523 (1986).

10- Ghazy, N.M. and El-Masry S., **Egypt. J. Pharm. Sci.** 29, 33-37 (1988).

11- Ahmed A.A., **J. Nat.Prod.** 54, 271 - 272 (1991).

12- Hussein, N.S., **Pharmazie** 47, 468 - 469 (1992).

13- Egyptian Pharmacopoeia, General Organization for Governmental Printing Affairs, Cairo, P. 31 (1984).

14- Adams, R.P., Identification of Essential oil Components by Gas Chromatography / Mass Spectrometry. Allured Publ. Corp., Carol Stream, Illinois. (1995).

15- Masada, Y., "Analysis of Essential oils by Gas Chromatography and Mass Spectrometry" John Wiley, New York (1976).
16- Ryhage, R. and Sydow, E.V., **Acta Chem. Scand.**, 17, 2025 - 2035 (1963).
17- Sydow, E.V., **Acta Chem. Scand.**, 17, 2504 - 2512 (1963).
18- Alencar, J.W., Craveiro, A.A. and Matos, F.J.A. **J. Nat. Prod.**, 47, 890 - 892 (1984).
19- Asres, K., Tei, A., Moges, G., Sporer, F. and Wink M., **Planta Med.** 64, 473 - 475 (1998).
20- El-Dahmy, S.I., **Zagazig. J. Pharm. Sci,** 2, 73-80 (1993).
21- Hayashi, K., Nakamura, H. and Mitsuhashi, H., **Phytochemistry** 12, 2931 - 2933 (1973).

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دراسة مكونات الزيت الطيار لنبات سنسيو ديسفونتنيا دريوس

عاصم محمد الشاذلى

قسم العقاقير – كلية الصيدلة – جامعة الزقازيق – مصر

تم تحليل الزيت الطيار المحضر بتقطير الأجزاء المختلفة لنبات سنسيو ديسفونتنيا دريوس الذى ينمو فى مصر بإستعمال تقنية كروماتوجرافيا الغاز الشعرية ومطياف الكتله أمكن التعرف على ٤١ مركب من المونوتربين والسيسكوتربين و أريموفيلان. ووجد أن هناك إختلافاً كمياً وكيفياً بين محتويات كل جزء.

كما تمت دراسة تأثير هذا الزيت على بعض الميكروبات وثبت أن لها تأثيراً قوياً وشاملاً لكل من البكتريا والفطريات المختارة.