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Composition of The Essential Oils of *Tanacetum densum* (Lab.) Schultz Bip. subsp. *amani* and *T. densum* (Lab.) Schultz Bip. subsp. *laxum* (Asteraceae) from Turkey

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The aerial parts of *Tanacetum densum* subsp. *amani* and *T. densum* subsp. *laxum* were hydrodistilled to produce the oils with yields of 0.30 % (v/w) and 0.15 % (v/w), respectively. The oils were analyzed by GC and GC/MS. Seventy three and seventy components were identified representing 92.2 and 80.6 % of the oils, respectively. The main compounds of *T. densum* subsp. *amani* were α-pinene (3.0 %), 1,8-cineole (14.7 %), borneol (31.3 %) and endoborneol (21.0 %). Whereas α-pinene (5.0 %), (+)-epi-bicyclosesquiphellandrene (31.4 %), α-cadinol (7.0 %), 1-heptadecanol (5.6 %) and eicosane (3.2 %) were the major constituents in *T. densum* subsp. *laxum*. Distribution of the predominate compounds in essential oil were discussed among the *Tanacetum* genus patterns.

Key Words: *Tanacetum*, *Tanacetum densum*, Essential oil, Borneol, 1,8-Cineole.

INTRODUCTION

The genus *Tanacetum* (Compositae) is distributed in Europe and West Asia throughout the northern temperate regions[1]. The genus is represented with *ca.* 60 taxa in Flora of Turkey[2,3]. *Tanacetum densum* (Lab.) Schultz Bip. is also represented with four subspecies; subsp. *sivasicum* Hub.-Mor.& Grierson, subsp. *laxum* Grierson, subsp. *amani* Heywood and subsp. *eginense* Heywood[2]. *Tanacetum* spp. are rich in essential oils, bitter substances and sesqui-terpene lactones and aromatic annual and perennial plants[2,4]. *Tanacetum densum* has been shown to produce a variety of sesqui-terpenes and investigations into subsp. *sivasicum* showed a new germacranolide[1] from *T. densum* subsp. *sivasicum*[5]. Both taxa are endemic to Turkey[2]. Some members of Asteraceae family particularly genus *Tanacetum* have traditionally been used in balsams, cosmetics, dyes, insecticides, medicines and preservatives as herbal remedy (for example, *T. vulgare*)[6-8]. They have also been used as anti-helmintic for migraine, neuralgia, rheumatism and loss of appetite[9]. According to recent studies, essential oils and extracts of members of the genus *Tanacetum* exhibit antiinflammatory[10,11], antibacterial[12,13], antifungal[14,15] and insecticidal effects[16,17]. Oil of tansy (*Tanacetum* *vulgare* L.) rubbed on skin is supposed to repel insects. In moderate doses, the plant and its essential oils are stomachic, cordial and used as food additive[18-20]. Some earlier works have been reported on the essential oils of various *Tanacetum* species from all over the world[21] and Turkey[1,8,22]. The volatile compounds from *T. vulgare* have been examined in detail[23-25]. The present work presents the chemical composition of the hydrodistilled oils of *T. densum* subsp. *amani* and *T. densum* subsp. *laxum* of Turkey origin firstly and results are compared to those reported in the other *Tanacetum* genus patterns.

EXPERIMENTAL

Tanacetum densum subsp. *amani* and *T. densum* subsp. *laxum* samples were collected from South-Eastern Anatolian region, in Elazig in July 2006 (Haroglu Mountain 1800m. *Tanacetum densum* subsp. *amani* (Bagci, 1928); *Tanacetum densum* subsp. *laxum* (Bagci-1927). Voucher specimens are kept at the Herbarium of Firat University (FUH) and Plant Products and Biotechnology Research Laboratory.

Isolation of the essential oils: Air-dried aerial parts of the plant materials were subjected to hydrodistillation using a Clevenger-type apparatus for 3 h.

Gas chromatographic (GC) analysis: The essential oil was analyzed using HP 6890 GC equipped with and FID detector and an HP- 5 MS column (30 m × 0.25 mm i.d., film tickness 0.25 µm) capillary column was used. The column and analysis conditions were the same as in GC-MS. The percentage composition of the essential oils was computed from GC-FID peak areas without correction factors.

Gas chromatography/mass spectrometry (GC-MS) analysis: The oils were analyzed by GC, GC-MS, using a Hewlett Packard system. HP-Agilent 5973 N GC-MS system with 6890 GC in Plant Products and Biotechnology Research Laboratory (BUBAL) in Firat University. HP-5 MS column (30 m × 0.25 mm i.d., film tickness 0.25 µm) was used with helium as the carrier gas. Injector temperature was 250 ºC, split flow was 1 mL/min. The GC oven temperature was kept at 70 ºC for 2 min. and programmed to 150 ºC at a rate of 10 ºC/min and then kept constant at 150 ºC for 15 min to 240 ºC at a rate of 5 ºC / min. Alkanes were used as reference points in the calculation of relative retention indices (RRI). MS were taken at 70 eV and a mass range of 35-425. Component identification was carried out using spectrometric electronic libraries (WILEY, NIST). The identified constituents of the essential oils are listed in Table-1.

RESULTS AND DISCUSSION

The essential oil yields (v/w) of *T. densum* subsp. *amani* and *T. densum* var. *laxum* were 0.30 and 0.15 %, respectively with yellowish oil. The result of the analysis of *T. densum* subsp. *amani* and *T. densum* subsp. *laxum* essential oils are present in Table-1.

TABLE-1
CHEMICAL COMPOSITION OF *T. densum* subsp. *amani* AND *T. densum* subsp. *Laxum*

No.	Compounds name	Ref.	RRI	*T. densum* subsp. *amani*	*T. densum* subsp. *laxum*
1	1-Pentanol		951	0.1	–
2	Bicyclo(4,1,0)heptane		994	–	0.2
3	α-Pinene	adf	1019	3.0	5.0
4	Camphene	adf	1032	0.7	–
5	Heptanol		1046	0.1	–
6	Sabinene	adfg	1049	0.2	0.1
7	β-Pinene	adf	1053	0.8	0.1
8	6-methyl-5-heptene-2-one		1057	0.1	–
9	1,2,4,4-tetramethylcyclopentane		1062	0.3	–
10	Benzene, 1-methyl-4		1089	0.5	0.1
11	d-Limonene	cd	1092	0.1	–
12	1,8-Cineole	abcdf	1095	14.7	1.5
13	1-Octanol		1096	0.2	–
14	γ-Terpinene	ad	1114	0.1	–
15	*trans*-Sabinene hydrate	abd	1123	1.0	–
16	α-Terpinolene	adf	1134	0.1	–
17	Fencholenic aldehyde		1137	0.1	–
18	Terpineol	f	1146	0.7	–
19	Nonanal	ad	1148	0.1	–
20	δ-Fenchyl alcohol		1159	0.1	–
21	2-Cyclohexene-1-ol		1162	0.1	–
22	3-Cyclopentene-1-acet-aldehyde		1164	0.2	–
23	+\- 4-acetyl-1-methyl-cyclohexene		1167	0.5	–
24	Isopinocarveol	abcd	1174	3.3	0.8
25	Camphor	acdg	1179	1.2	–
26	Exo-methyl-camphenilol		1185	0.1	–
27	Pinocarvone	abcd	1189	2.0	0.2
28	γ-Campholenol		1192	0.1	–
29	Borneol	abcdef	1198	31.3	1.6
30	3-Cyclohexene-1-ol		1202	1.0	–
31	Cyclohexene		1212		0.2
32	6-Octen-1-ol		1225	0.1	–
33	Cyclooctyl bromide		1226	–	0.1
34	*trans*-(+)-Carveol	abcd	1227	0.6	0.1
35	Phenol		1231	0.1	–
36	*cis*-Carveol	ab	1236	0.3	–
37	2-Cyclohexene-1-one		1245	0.2	–
38	Cyclopentane		1254	0.1	–
39	1-Decenal		1267	0.1	–
40	4-Hydroxy-3-methyl-acetophenone		1271	0.1	–
41	Endoborneol		1279	21.0	–
42	Thymol	b	1283	1.2	0.7
43	Acetic acid		1300	0.1	–

44	2,4-Decadienal		1308	0.1	–
45	Nerylacetate		1334	0.1	–
46	β-Myrcene		1335	–	1.1
47	Endobornylacetate		1355	0.1	–
48	Propanoic acid		1357	–	0.1
49	β-Elemene		1366	0.1	0.1
50	Bornyl ester of isobutanoic acid		1385	0.1	–
51	1,6,10-Dodecatriene		1411	0.1	–
52	1H-Cycloprop(e)azulene		1417	–	0.3
53	Tricyclo(4,3,1,18,8)undecane		1426	0.1	–
54	E-Ocimenone		1427	–	0.1
55	β-Lonone		1428	0.1	0.1
56	Germacrene D	bdf	1431	0.1	0.5
57	δ-Selinene		1435	0.1	–
58	Germacrene B		1440	0.1	0.1
59	β-Bisabolene		1448	0.1	1.6
60	Naphthalene		1452	–	1.3
61	Valencene 1		1453	–	0.1
62	δ-Cadinene		1455	–	1.2
63	Sabinyl acetate	f	1476	–	0.1
64	β-Caryophyllene	f	1478	0.1	–
65	1,3,6-Octatriene		1485	0.1	–
66	2,6-Dimetyloxytoluene		1489	0.1	–
67	α-Copaene-8-ol		1490	0.1	–
68	Ethanone		1494	–	0.8
69	Junipene		1496	–	0.1
70	(-)-Caryophylleneoxide	f	1501	0.1	–
71	Oplopenone		1506	–	0.5
72	Nerolidol	b	1508	–	0.5
73	4,7-Methanoazulene		1513	–	0.8
74	Bicyclo(2,2,1)heptane		1515	–	0.2
75	Azulene		1518	0.1	0.2
76	9-Aristolen-1, alpha-ol		1519	–	1.4
77	Germacrene D		1527	0.2	–
78	(+)-Epi-bicyclosesquiphellandrene		1528	–	31.4
79	Dehydroaromadendrene		1530	–	0.6
80	β-Selinene		1532	–	0.2
81	Pyrene		1535	0.3	–
82	α-Cadinol	bd	1536	–	7.0
83	(+)-Spathulenol		1542	0.3	2.4
84	1(2H)-Naphthalenone		1545	0.3	–
85	Cyclododecane		1546	–	1.7
86	Aromadendreneoxide-(1)		1548	–	0.7
87	Caryopyhllene oxide		1550	0.1	–
88	*trans*-Caryophyllene		1562	–	0.1
89	Farnesol		1565	0.2	–
90	Tetradecenal		1566	–	0.6

91	1,6,10-Dodecatriene-3-ol		1571	–	0.8
92	Benzenepropanoic acid		1581	–	0.2
93	1-Hexadecanol	d	1597	0.1	0.7
94	1,8-Cyclopentadecadyne		1605	–	0.1
95	Pentadecenal		1616	–	0.2
96	2,6,10-Dodecatrien-1-ol		1622	1.0	–
97	Farnesyl acetate 3		1623	–	1.8
98	2-Pentadecanone		1627	0.1	0.6
99	Cyclotetradecane		1628	0.1	–
100	Pyridine		1635	0.1	–
101	Cyclohexadecane		1645	0.4	–
102	1-Heptadecenol		1646	–	5.6
103	Dodecane		1652	–	0.1
104	2-Heptadecanone		1655	0.1	0.6
105	Caryophylla-2(12),6-dien-5-one	ad	1663	–	1.0
106	Di-epi-α-cedrene		1668	0.3	–
107	1,6-Cylodecadiene		1669	–	1.0
108	Hexadecanoic acid	abcd	1679	–	0.4
109	17-Pentatriacontene		1683	–	0.8
110	1-Eicosanol		1700	–	0.4
111	1,3-Dimethyl-3-vinycyclohexene-1		1705	–	0.2
112	Cyclotetradecane		1717	–	0.7
113	Delta-(13)-tetradecenol		1726	–	0.1
114	Phytol isomer		1788	–	0.2
115	9-Octadecanoic acid (Z)		1804	–	1.0
116	Octadecanoic acid		1820	–	0.1
117	Phenol		1953	–	0.1
118	Gibberellin A3		1956	–	0.1
119	Cyclotrisiloxane		1973	–	0.2
120	Pentacosane	ad	1985	–	1.2
121	Eicosane		1987	0.1	3.2
122	Acetamide		2020	–	0.1
	Total			92.2	87.8

RRI = Relative retention indices, a = *Tanacetum armenum* [Ref. 1], b = *T. balsamita* [Ref. 1], c = *T. chiliophyllum* var. *chiliophyllum* [Ref. 1], d = *T. haradjani* [Ref. 1], e = *T. praeteritum* subsp. *praeteritum* [Ref. 22], f = *T. vulgare* L. var. *vulgare* [Ref. 25].

In case of *T. densum* subsp. *amani*, 73 compounds were identified representing 92.2 % of the oils. Borneol was determined to be present at the high percentage (31.3 %). The presence of α-pinene (3.0 %), 1,8-cineole (14.7 %), endoborneol (21.0 %) and *trans*-pinocarveol (3.3 %) are also important for the oil profile. A comparison of the data presented in present studies with the other species of *Tanacetum* show that there are qualitative and quantitative differences in some of the compounds presented. The oil obtained from the leaves of *T. balsamita* L. ssp. *balsamitoides* (Schults-Bip.) and *Tanacetum praeteritum* subsp. *praeteritum* are reported to contain a high percentage of bornyl acetate (47.7 %, 10 %), respectively[22,26].

Camphor (17 %) was the main constituent in the oils of *T. chiliophyllum* var. *chiliophyllum* and *T. haradjani*, respectively[1]. Other species of genus *Tanacetum*, rich in camphor include *T. armenum*[1], *T. lingulatum*[27], *T. khorassanicum*[28] and *T. vulgare*[29]. At the same kind, it also characterizes the essential oils of *T. armenum*, T. *haradjani* (26-16 %)[1] and *T. parthenium* (56.9 %)[8], whereas it ranged between 0.06 and 73.02 %[23] in 20 genotypes of *T. vulgare* collected from different geographical locations in Finland. It is not found at the large percentages (1.2 %) in *T. densum* subsp. *amani* studied in here.

Considerable amounts of 1,8-cineole (14.7-1.5 %) was determined in both oils in present study, have also been found in the essential oil of *T. lingulatum* (18.6 %)[27]. In the case of *T. balsamita* L. ssp. *balsamitoides* (Schults-Bip.) Grierson, bornyl acetate is reported to predominate in its essential oil[26].

In the case of *T. densum* subsp. *laxum*, 70 components were identified representing 87.8 % of the oil (Table-1). (+)-epi-bicyclosesquiphellandrene was the predominant compound (31.4 %) followed by α-cadinol (7.0 %), 1-heptadecanol (5.6 %), α-pinene (5.0 %) and eicosane (3.2 %).

It is surprising that large qualitative and quantitative differences were found between two *Tanacatum* subspecies in view of main compounds. Twenty one compounds are common in both subspecies of *Tanacaetum densum*. Infraspecific variation is also determined in essential oils of *Hypericum capitatum* var. *luteum* and var. *capitatum* (Hyperiaceae) from Turkey[28]. An opposite correlation was noticed for mono and sesquiterpenes hydrocarbons and oxygenated sesquiterpenes between two subspecies. The results showed that *T. densum* subsp. *amani* was rich in mono and sesquiterpene hydrocarbons. On the contrary, *T. densum* var. *laxum* was rich in oxygenated sesquiterpenes as shown in Table-1. At the same time this table shown a small comparison of the major components found in this two *Tanacetum* taxa with the literature review as presence/absence of the essential oils components in other *Tanacetum* species.

Literature review of the *Tanacetum* genus patterns showed that the oils of *Tanacetum* patterns are distributed among three or more chemotypes groups in genus. α-Thujene/β-thujene dominated group; *Tanacetum praeteritum* subsp. *massicyticum* Heywood., *T. argyrophyllum* var. *Argyrophyllum*[22], *T. vulgare* L. var. *vulgare* from Norway[24,29]. 1,8-Cineole dominated group; *T. praeteritum* subsp. *praeteritum* (Horwood) Heywood, *T. armenum*[1], *T. Lingulatum*[27], *T. vulgare* chemotypes from Lithuania[25,29], *T. santolinoides* (DC.) Feinbr.[30], *T. argyrophyllum*[8], *T. chliliophyllum* (Fisch. & Mey.) Schultz Bip. var. *chiliophyllum*[13]. Camphor dominated group comprised to; *T. armenum* and *T. haradjani* (Rech. fil.), *T. chliliophyllum* var. *chiliophyllum*[1,13]; *T. lingulatum*[27], *T. vulgare* chemotypes from Lithuania[25,29], *T. parthenium* (L.) Schultz Bip.[8], *T. balsamita* subsp. *balsamitoides* from Iran (Schultz Bip.) Grierson.[26], *T. balsamita* subsp. *balsamita* from Turkey[13]. The results and the chemical data gives more clues on the chemotaxonomy of genus *Tanacetum.*

It is reported that as with other members of the Compositae family, *T. densum* has been shown to produce a variety sesquiterpenes and investigations into subsp. *sivasicum* have previously yielded eudesmanolides, germacranolides, guaianolides and farnesol derivatives[5]. Chemotypical classification of Norwegian tansy genotypes (*T. vulgare*) was underscored, indicating the genetic uniformity and biochemical stability of the domesticated plants[24].

In conclusion, this study demonstrates the occurrence of 1,8-cineole, borneol/endoborneol chemotype of *T. densum* subsp. *amani* and (+)-epi-bicyclosesquiphellandrene/α-cadinol chemotype of *T. densum* subsp. *laxum* in Eastern Anatolia region of Turkey. However, the absence of (+)-epi-bicyclosesquiphellandrene from *T. densum* subsp. *amani* chemotype and 1,8-cineole and borneol absence from *T. densum* subsp. *laxum* studied in herein are noteworthy.

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