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Essential Oil Composition of Four Endemic *Tanacetum* L. (Asteraceae) Taxa from Turkey and a Chemotaxonomic Approach

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Abstract: In this study the essential oil components aerial parts of *Tanacetum heterotomum* (Bornm.) Grierson, *T. zahlbruckneri* (Nab.) Griersson, *T. densum* (Lab.) Schultz Bip. subsp. *amani* Heywood and *T. cadmeum* (Boiss.) Heywood subsp. *orientale* were examined by HS-SPME/GC-MS technique. Thirty six, thirty nine, forty and forty five constituents were determined representing 88.9%, 90.1%, 90.8% and 91.5% of the oil, respectively. The main compounds of studied *Tanacetum* L. taxa; borneol, α-pinene, 1,8-cineole, β-pinene, camphor, germacrene D, spathulenol are determined. Studied *Tanacetum* taxa showed congruency with the discription in Flora of Turkey as morphological properties; on the contrary essential oil composition were detected very quiet diverse infrageneric level. Chemotypes of *Tanacetum* L. taxa were reported as borneol, germacrene D, spathulenol, α-pinene, 1,8-cineole, β-pinene and camphor. The results obtained from this study were discussed in terms of chemotaxonomy and natural products.

Key words: *Tanacetum* L., essential oil, chemotaxonomy, natural products.

1. Introduction

The genus *Tanacetum* L. which is an important member of the Asteraceae or Compositae family, is spreaded in Europe and West Asia throughout the northern temperate areas [1]. *Tanacetum* contains several annual and perennial taxa and represented in Turkey by 45 species, 18 of them are endemic and endemism rate 40% [2, 3].

Tanacetum have not seperated any sections but have placed three groups (A, B and C) based largely on capitula and flower characters, in Flora of Turkey. *T. heterotomum* and *T. zahlbruckneri* are belong to group A; *T. densum* subsp. *amani* and *T. cadmeum* subsp. *orientale* are belong to group B. *T. heterotomum*, *T. zahlbruckneri*, *T. cadmeum* subsp. *orientale* and *T. densum* subsp. *amani* are endemic taxa in Flora of Turkey [2].

Tanacetum taxa are known in Turkey as "pireotu" and their essential oils are used as repellent against insects [4]. *Tanacetum* spp. are rich in essential oils, sesquiterpene lactones and bitter substances and they have antiinflammatory, antibacterial and antihistaminic activities; in moderate doses, tansy essential oils are stomachic, cordial effect and used as a food additive [5]. Various extracts of plants materials and essential oil of plants have agitated interest as sources of natural products. The essential oils and seconder metabolites of plant samples have been investigated for their potential uses as alternative remedies for the treatment of many diseases. Especially antioxidant, antimicrobial and antibacterial activities of plants essential oils and various extracts of plant samples have formed the basis of many applications, including pharmaceuticals, alternative medicine, natural and aroma therapies [6].

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Some earlier works have been reported on the essential oils of various Asteraceae taxa [7-10]. Some *Tanacetum* taxa have been cultured in gardens [11] and used in salads, omelets, cakes, dyes, medicines, cosmetics and preservatives as herbal cure [12]. Some members of *Tanacetum* have also been used as anti-helmintic for migraine, neuralgia, rheumatism, loss of appetite [13], antiinflammatory [14], antibacterial and antifungal [15] activities.

The objectives of this research were: (1) to reach chemotaxonomic results from obtained data; (2) to obtain the chemical constituents isolated from the east part of Anatolian region taxa of the *Tanacetum* genus; (3) to discuss the phytochemical relations and usefulness of the studied taxa. For purposes of this, the essential oil composition of four endemic *Tanacetum* taxa (*T. heterotomum*, *T. zahlbruckneri*, *T. densum* subsp. *amani*, *T. cadmeum* subsp. *orientale*) from eastern part of Turkey is reported.

2. Materials and Methods

2.1 Plant Materials

T. heterotomum was collected from north of Dikme village (Bingol), stony slopes, 1,550-1,600 m, 20.VI.2013, Kiliç 4690. *T. zahlbruckneri* was collected from North of Dikme upland from vicinity of Yelesen village (Bingol), slopes, 1,450-1,500 m., 20.VI.2013, Kiliç 4801. *T. densum* subsp. *amani* was collected from West of Mandıra district (Elazığ), slopes, 1,200-1,300 m, 20.VI.2012, Kiliç 4564. *T. cadmeum* subsp. *orientale* was collected from vicinity of Aslankaşı village (Elaziğ), steppe, 960-1,000 m, 20.VI.2012, Kiliç 4563. The voucher specimens have been deposited at the Herbarium of Biology Department, Bingol University (BIN).

2.2 HS-SPME Procedure

The dried aerial part of 5 g plant samples were powdered with a liquidizer and was filled a 40 mL vial. The vials were equipped with a "mininert" valve and were carried out by a HS-SPME (headspace solid phase microextraction) method using a DVB/CAR/PDMS fiber, with 50/30 lm film thickness; before the analysis the fiber was preconditioned in the injection port of the GC as indicated by the manufacturer. The vials was kept at 35 °C with continuous internal stirring and the sample was left to equilibrate for 30 min; then, the SPME fiber was exposed for 40 min to the headspace while maintaining the sample at 35 °C. After sampling the SPME fiber was introduced into the GC injector, and was left for 3 min to allow the analytes thermal desorption. In order to improve the technique, sample volume, sample headspace volume, sample heating temperature and extraction time, were studied on the extraction efficiency as previously reported by Verzera et al. [16].

2.3 GC-MS Analysis

A Varian 3800 gas chromatograph interfaced with a Varian 2000 ion trap mass spectrometer (Varian Spa, Milan, Italy) was used. Injector temperature, 260 °C; injection mode, splitless; column, 60 m, CP-Wax 52 CB 0.25 mm i.d., 0.25 lm film thickness (Chrompack Italy s.r.l., Milan, Italy). The oven temperature was programmed 45 °C held for 5 min, then increased to 80 °C at a rate of 10 °C/min, and to 240 °C at 2 °C/min. Helium used as carrier gas was at a constant pressure of 10 psi; the transfer line temperature 250 °C; the ionisation mode, electron impact (EI); acquisition range, 40-200 m/z; scan rate, 1 us^{-1}. The compounds were identified using the NIST (National Institute of Standards and Technology) library, mass spectral library and verified by the retention indices, which were calculated as described by Van den Dool and Kratz [17]. The relative retention indexes were calculated on the basis of peak-area ratios. The essential oil compositions of studied samples were showed in Table 1.

3. Results and Discussion

In this study the essential oil composition aerial parts of *T. heterotomum*, *T. zahlbruckneri*, *T. densum*

Table 1 Essential oil composition of studied *Tanacetum* taxa.

Compounds	*RRI	*T. heterotomum*	*T. zahlbrucknei*	*T. densum* subsp. *amani*	*T. cadmeum* subsp. *orientale*
Santolinatriene	998	-	0.6	0.4	-
Tricyclene	1012	0.1	-	-	0.4
α-thujene	1016	-	1.2	0.1	-
α-pinene	1023	3.4	1.0	6.7	7.6
Camphene	1035	1.2	2.3	1.5	5.4
Sabinene	1054	-	0.6	-	0.2
β-pinene	1059	4.5	-	8.9	1.8
Bicyclo (3.1.1) heptane	1065	-	0.4	0.1	0.8
Benzene	1071	-	0.2	-	-
α-phellandrene	1082	0.1	-	0.2	1.1
γ-terpinene	1085	0.2	0.8	-	0.5
Benzene, 1-methyl-4	1090	-	0.2	0.3	-
Limonene	1094	-	0.4	-	1.2
1,8-cineole	1101	17.9	1.3	16.7	19.6
Trans-sabinenehydrate	1124	0.6	-	0.1	0.1
α-terpinolene	1135	1.2	0.5	-	-
Cyclohexene	1145	-	-	1.2	0.7
Cis-sabinenehydrate	1151	1.7	-	1.3	-
Bicyclo (3.1.0) hexan-3-one	1165	-	2.1	-	0.8
Trans-chrysanthemol	1168	-	1.7	0.7	3.1
4-acetyl-1-methylcyclohexan	1171	0.3	-	1.2	0.6
Trans-pinocarveol	1178	-	0.3	-	-
Camphor	1182	22.4	3.8	26.8	17.2
Pinocarvone	1190	1.2	-	2.4	1.8
Cis-chrysanthemol	1195	-	0.5	1.3	-
2-cyclohexen-1-ol	1203	0.5	-	0.5	1.7
Borneol	1208	18.8	21.3	3.8	5.3
3-cyclohexen-1-ol	1211	0.7	2.4	-	0.4
α-terpineol	1218	1.3	1.9	-	-
Myrtenol	1222	-	-	0.4	0.8
Trans-carveol	1231	0.6	0.1	0.7	0.4
Propanoic acid	1246	-	0.2	-	-
Trans-geraniol	1256	0.4	-	-	0.5
Bicyclo (2.2.1) heptan-2-ol	1282	0.2	1.1	0.4	-
Thymol	1285	-	2.7	0.3	0.2
Phenol	1291	0.3	-	-	0.5
α-terpinene	1332	-	0.6	0.2	-
Cis-verbenol	1353	-	0.1	-	0.4
α-copaene	1360	1.3	-	2.6	2.8
β-bourbenene	1371	0.4	0.1	1.4	-
β-elemene	1374	-	-	-	1.9
Trans-caryophyllene	1385	0.3	-	0.2	0.7
β-cubebene	1396	-	0.2	0.4	1.3
Trans-β-farnesene	1412	0.9	-	1.2	0.3
Isoledene	1420	-	0.2	-	1.5
Germacrene D	1432	0.8	21.4	3.9	-
β-selinene	1442	1.4	0.1	0.3	0.1
Naphthalene	1453	-	-	0.8	0.4

(Table 1 continue)

Compounds	*RRI	*T. heterotomum*	*T. zahlbrucknei*	*T. densum* subsp. *amani*	*T. cadmeum* subsp. *orientale*
δ-cadinene	1460	0.4	-	-	0.3
Spathulenol	1495	0.6	16.2	1.4	-
Caryophylleneoxide	1500	1.1	0.2	-	0.2
Muurolene	1518	-	-	0.2	1.6
Epi-bicyclosesquiphellandrene	1532	0.8	-	-	1.7
Copaene	1539	-	0.4	0.3	-
α-cadinol	1541	0.4	0.1	-	1.3
β-bisabolene	1551	-	-	1.1	0.8
Aromadendrene	1558	0.3	1.2	-	1.3
2-pentadecanone	1625	-	0.4	0.2	-
Hexadecanoic acid	1685	1.6	-	0.3	0.7
Carene	1741	0.3	0.2	-	0.4
Octadecanal	1862	-	-	0.1	0.5
Tricosane	1902	0.7	0.5	-	-
Eicosane	1935	-	0.6	0.2	0.6
Total		88.9	90.1	90.8	91.5

*RRI: relative retention index.

subsp. *amani* and *T. cadmeum* subsp. *orientale* were investigated by HS-SPME/GC-MStechnique. Germacrene D (22.4%), borneol (18.8%) and spathulenol (17.9%) were detected the main constituents of *T. heterotomum*. Germacrene D (21.4%), borneol (21.3%) and spathulenol (16.2%) were determined the main components of *T. zahlbruckneri*. Camphor (26.8%), 1,8-cineole (16.7%), β-pinene (18.8%) and α-pinene (6.7%) were found to be the main constituents of *T. densum* subsp. *amani*. 1,8-cineole (19.6%), camphor (17.2%) and α-pinene (18.8%) were reported the major constituents of *T. cadmeum* subsp. *Orientale* (Table 1).

1,8-cineole was found to be the main compounds of *T. densum* subsp. *amani* (16.7%) and *T. cadmeum* subsp. *orientale* (19.6%); whereas this compound was reported low amounts in the esential oil of *T. heterotomum* (0.8%) and *T. zahlbruckneri* (1.3%) (Table 1). Like our study 1,8-cineole was characterized the leaf (31%) and herb (11%) oils of *T. armenum* [4]. Camphor was detected the main compounds of *T. densum* subsp. *amani* (26.8%) and *T. cadmeum* subsp. *orientale* (17.2%); whereas this compound was detected low amounts in the esential oil of *T. heterotomum* (0.8%) and *T. zahlbruckneri* (3.8%) (Table 1). Camhor also has been detected the main compounds of *T. chiliophyllum* var. *chiliophyllum* (17%) and *T. haradjani* (16%) [4]; *T. parthenium* (56.9%) [18] and *T. chiliophyllum* var. *chiliophyllum* (28.5%) [19]. The essential oils of Turkish *T. aucheranum* and *T. chiliophyllum* var. *chiliophyllum* were analyzed by GC-MS and the major components of *T. aucheranum* oil were 1,8-cineole (23.8%), camphor (11.6%), terpinen-4-ol (7.2%) and α-terpineol (6.5%); on the other hand camphor (17.9%), 1,8-cineole (16.6%) and borneol (15.4%) were detected the main constituents in the oil of *T. chiliophyllum* [20]. Borneol was obtained high amounts in *T. heterotomum* (18.8%), *T. cadmeum* subsp. *orientale* (5.3%); and *T. zahlbruckneri* (21.3%) oils; whereas borneol was detected only low amount in the esential oil of *T. densum* subsp. *amani* (3.8%) (Table 1).

α-thujone was found to be the major constituent of *T. argyrophyllum* var. *argyrophyllum* leaf (52%) and flower (63%) oils; this compound also has been reported in the *T. argenteum* subsp. *canum* var. *canum* (12%) and *T. praeteritum* subsp. *massicyticum* (51%) essential oils [21] whereas in our study α-thujene was found to be very low amount in the essential oils of *T.*

densum subsp. *amani* (0.1%) and *T. zahlbruckneri* (1.2%) (Table 1). In another study, the main compounds of *T. nitens* were 1,8-cineole (27.57%), α-pinene (4.62%) and spathulenol (4.14%), whereas α-pinene (27.86%), santolinatriene (8.82%) and 1,8-cineole (6.82%), were detected the major constituents of *T. argenteum* subsp. *Argenteum* [22] similarly α-pinenecontained high concentrations of *T. densum* subsp. *amani* (6.7%) and *T. cadmeum* subsp. *orientale* (7.6%) (Table 1). Germacrene D and spathulenol was determined the major components of *T. heterotomum* (22.4%, 17.9%) and *T. zahlbruckneri* (21.4%, 16.2%) respectively; it is noteworthy that Germacrene D and spathulenol detected only low amount in the esential oil of *T. densum* subsp. *amani* (3.9%, 1.4%) respectively and no percentages in the essential oil of *T. cadmeum* subsp. *orientale* (Table 1).

4. Conclusions

It is possible to conclude from the results of this study that germacrene D/borneol/spathulenol are the most probable chemotypes of the essential oil in *T. heterotomum* and *T. zahlbruckneri* which were in the same group (A group) in Flora of Turkey. In additioncamphor/1,8-cineole/β-pinene and 1,8-cineole /camphor/α-pinene are the most probable chemotypes of the essential oil in *T. densum* subsp. *amani* and *T. cadmeum* subsp. *orientale*, respectively, which were in the same group (B group) in Flora of Turkey. So chemical findings of studied *Tanacetum* taxa are overlapping with morphological results from Flora of Turkey. The results showed that the genus *Tanacetum* had a considerable changing in essential oil composition and our study shows the occurrence of germacrene D/borneol chemotypes of *T. heterotomum* and *T. zahlbruckneri*; camphor/1,8-cineole chemotypes of *T. densum* subsp. *amani* and *T. zahlbruckneri* in Eastern Anatolian region of Turkey. Besides, the results of essential oil compositions of four endemic *Tanacetum* taxa have demostrated that studied taxa can be used for medicinal, agricultural and pharmaceutical purposes.

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References

[1] K. Bremer, Molecular phylogenetic dating of asteroid flowering plants shows early cretaceous diversification, Timb. Port 10 (2004) 295.

[2] P.H. Davis, Flora of Turkey and the East Aegean Islands, University Press, Edinburgh, 1982, pp. 64-268.

[3] S. Erik, B. Tarikahya, Türkiye florası üzerine, Hacettepe Ün. Yayınları, Ankara, Kebikeç. 17 (2004) 139-162.

[4] K.H.C. Baser, B. Demirci, N. Tabanca, T. Ozek, N. Goren, Composition of the essential oils of *Tanacetum armenum* (DC.) Schultz Bip., *T. balsamita* L., *T. chiliophyllum* (Fisch. & Mey.) Schultz Bip. var. *chiliophyllum* and *T. haradjani* (Rech. fil.) Grierson and the enantiomeric distribution of camphor and carvone, Flavour Fragr. J. 16 (2001) 195-200.

[5] D. Bown, Encyclopedia of Herbs and Their Uses, Dorling Kindersley, London, 1995, pp. 208-209.

[6] M. Lis-Balchin, S.G. Deans, Bioactivity of selected plant essential oils against *Listeria monocytogenes,* J. of Appl. Bac. 82 (1997) 759-762.

[7] O. Kilic, A. Kocak, E. Bagci. Composition of the volatile oils of two *Anthemis* L. taxa from Turkey, ZnC. 66 (2011) 535-540.

[8] E. Bagci, O. Kilic, Chemical Composition of essential oil of *Senecio vernalis* Waldst. Et Kit. (Asteraceae) from Turkey, Jeobp. 15 (2012) 399-404.

[9] O. Kilic, E. Bagci, Chemical composition of essential oil of *Tripleurospermum parviflorum* (Willd.) Pobed (Asteraceae) from Turkey, Asian J. of Chem. 24 (2012) 1319-1321.

[10] O. Kilic, E. Bagci, Chemical composition of endemic *Inula macrocephala* Boiss. and Kotschy ex Boiss. from Turkey, Asian J. of Chem. 25 (2013) 7952-7954.

[11] L.W. Mitich, Intriguing world of weeds—Tansy, Weed Technol. 6 (1992) 242-244.

[12] M. Grieve, Tansy, in: C.F. Leyel (Ed.), A Modern Herbal, Penguin Books Ltd., Middlesex, Great Britain, 1984, pp. 789-790.

[13] M. Blumenthal, The complete german commission e monographs: Therapeutic guide to herbal medicines, Tansy Flower and Herb, Unapproved Herbs, American Botanical Council/Integrative Medicine Communications, Austin, TX/Boston, MA, 1998, pp. 379-380.

[14] A.M.G. Brown, C.M. Edwards, M.R. Davey, J.B. Power, K.C. Lowe, Effects of extracts of *Tanacetum* species on human polymorphonuclear leucocyte activity *in vitro*, Phytother. Res. 11 (1997) 479-484.

[15] A. Neszmelyi, G.W.A. Milne, E. Hethelyi, Composition of the essential oil of clone 409 of *Tanacetum vulgare* and 2D NMR investigation of trans-chrysanthenyl acetate, J. Essent. Oil Res. 4 (1992) 243-250.

[16] A. Verzera, M. Zino, C. Condurso, V. Romeo, M. Zappala, Solid-phase microextraction and gas chromatography/mass spectrometry for the rapid characterisation of semi-hard cheeses, Anal. Bioanal. Chem. 380 (2004) 930-936.

[17] H. Van Den Dool, P.D. Kratz, A generalization of the retention index system including linear temperature programmed gas-liquid partition chromatography, J. of Chromatography 11 (1963) 463-471.

[18] H.A. Akpulat, B. Tepea, A. Sokmen, D. Daferera, M. Polissiou, Composition of the essential oils of *Tanacetum argyrophyllum* (C. Koch) Tvzel. var. *argyrophyllum* and *Tanacetum parthenium* (L.) Schultz Bip. (Asteraceae) from Turkey, Biochem. Syst. Ecol. 33 (2005) 511-516.

[19] E. Bagci, M. Kursat, A. Kocak, S. Gur, Composition and antimicrobial activity of the essential oils of *Tanacetum balsamita* L. subsp. *balsamita* and *T. chiliophyllum* (Fisch. et Mey.) Schultz Bip. var. *chiliophyllum* (Asteraceae) from Turkey, JEOBP 11 (2008) 476-484.

[20] E. Salamci, S. Kordali, R. Kotan, A. Cakir, Y. Kaya, Chemical compositions, antimicrobial and herbicidal effects of essential oils isolated from Turkish *Tanacetum aucheranum* and *Tanacetum chiliophyllum* var. *chiliophyllum*, Biochem. Syst. Ecol. 35 (2007) 569-581.

[21] N. Gören, B. Demirci, K.H.C. Başer, Composition of the essential oils of *Tanacetum* spp. from Turkey, Flav. Frag. J. 16 (2001) 191-194.

[22] E. Bagci, A. Kocak, Essential oil composition of two endemic *Tanacetum* (*T. nitens* (Boiss. & Noe) Grierson and *T. argenteum* (Lam.) Willd. subsp. *argenteum*) (Asteraceae) taxa, growing wild in Turkey, Indust. Crops Prod. 31 (2010) 542-545.