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Essential Oil Compounds of two Centaurea L. taxa From Turkey. A Preliminary Evaluation of their Use in Chemotaxonomy by Cluster Analysis

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ABSTRACT

In this study, chemotaxonomical relationships between two species (Centaurea balsamita and C. Behen) belongs to the genus Centaurea were investigated. The essential oil yields of these species were found as 0.4 and 0.3% v/w, respectively. The essential oils were analysed by gas chromatography and gas chromatography/mass spectrometry. A total of sixty three components have been identified constituting 90.6% and 87.5% of the oil, respectively. Butanoic acid (16.3%), spathulenol (15.5%), α-terpinolene (10.2%) and caryophyllene oxide (4.6%) were detected main compounds of C. balsamita, however caryophyllene oxide (15.9%), spathulenol (11.4%), germacrene D (6.6%) and allo-aromadendrene (6.1%) were detected major constituents of C. behen. The compositions of the oils were subjected to a hierarchical cluster analysis by application of the SPSS, with a view to test their use in chemotaxonomy.

Keywords: Centaurea, Butanoic acid, Caryophyllene oxide, Essential oil, Chemotaxonomy

INTRODUCTION

Centaurea genus is one of the largest genera and the genus has about 500 species herbaceous thistle-like flowering plants from Asteraceae family with wide distribution mostly in Europe and Mediterranean. Common names for different species are star-thistle, cornflower, and knapweed. Centaurea species represented with approximately 179 species in Turkey [1]. Turkey is one of the main centers of diversity for this group [2]. Because Centaurea s.l. is considered a taxonomically unnatural grouping, recent approaches have split this taxon into several, more natural genera: Centaure as. str., Cyanus Miller, Psephellus Cassini and Rhaponticoides Vaillant [3,4].

Centaurea balsamita is annual and stem erect, 30-80 cm, with several long one-capitulate branches in upper part, rarely simple. Leaves scabrous with very short hairs, entire to denticulate or rarely lower with few coarse teeth at base and flowers yellow, marginal scarcely radiant which belongs to sect. Stizolophus (Cass.) DC. *C. balsamita* is growing wild in Turkey. This species grows on steppe, fallow fields [5]. *Centaurea behen* is perennial with erect glabrous stem, 60-150 cm, branched above with several capitula. Leaves firm, with elevated nerves, appearing glabrous, usually lyrate and flowers yellow which belongs to sect. Microlophus (Cass.) *C. behen* is growing wild in Turkey. This species grows on rocky slopes, fallow fields [5].

Its medicinal importance, as antidiabetic, antidiarrhoeal, antirheumatic, antiinflammatory, colagog, choleretic, digestive, stomachic, diuretic, menstrual, astringent, hypotensive, antipyretic, sitotoxic, antibacterial, has been widely emphasized by several workers [6-8].

In the context of essential oil study in our laboratuary in the same Centaurea genus [9-11] it is aimed that to evaluate the composition of the essential oils obtained from the aerial parts of *C. balsamita* and *C. behen* from Turkey. The results were discussed with the *Centaurea* genus pattern in means of chemotaxonomy, natural products and renewable resources.

MATERIALS AND METHODS

Plant materials

C. balsamita (Hayta 2887) and *C. behen* (Hayta 2879) specimens were collected during to flowering stage from Harput (Elazig-Turkey) an altitude of 1200-1250 m., in June, 2010. Voucher specimens are kept at the Firat University Herbarium (FUH).

Isolation of the essential oils

Air-dried aerial parts of the plant materials (100 g) were subjected to hydrodistillation using a Clevenger-type apparatus for 3 h to yield.

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-MS, using a Hewlett Packard system. HP- Agilent 5973 N GC-MS system with 6890 GC in Plant Products and Biotechnology Res. Lab. (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°C, split flow was 1 ml/min. The GC oven temperature was kept at 70°C for 2 min. and programmed to 150°C at a rate of 10°C/min and then kept constant at 150°C for 15 min to 240°C at a rate of 5°C/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.

Table 1: Identified components of Centaurea taxa (%)

No.	Compounds	RRI	*C. balsamita*	*C. behen*
1	Hexenal	936	0.5	0.7
2	2-hexenal	964	--	0.8
3	2,4-octadiyne	970	0.3	--
4	1-hexanol	974	--	0.3
5	Heptanal	997	--	0.2
6	α-pinene	1022	0.6	1.6
7	2-heptanal	1039	--	0.2
8	Benzaldehyde	1043	--	0.4
9	β-pinene	1055	--	1.8
10	1-octen-3-ol	1057	--	0.9
11	2-pentyl-furan	1065	0.5	1.2
12	3 octanol	1070	--	0.2
13	Octanal	1075	--	0.2
14	2,4-heptadienal	1081	--	0.3
15	dl-limonene	1095	--	0.7
16	*β*-phellandrene	1096	--	0.2
17	1,8-cineole	1098	0.3	--
18	3,5-octadien-2-ol	1101	--	0.1
19	Benzenacetaldehyde	1106	--	0.2
20	Tolualdehyde	1125	--	0.7
21	3,5-octadien-2-one	1143	--	0.2
22	Nonanal	1151	1.2	1.8
23	Camphor	1182	0.4	--
24	Iso-menthone	1189	0.2	--

25	Safranal	1218	--	0.3
26	Decanal	1221	0.8	0.5
27	Piperitone	1257	0.3	--
28	α-ıonone	1262	--	0.5
29	Theaspirane B	1296	--	1.6
30	2,4-decadienal	1312	--	0.3
31	α-terpinolene	1337	**10.2**	**--**
32	Butanoic acid	1357	**16.3**	0.3
33	α-copaene	1360	--	1.9
34	β-bourbonene	1366	--	0.6
35	Methyl, 2,4-decadienoate	1375	0.9	--
36	Trans-caryophyllene	1393	0.8	3.8
37	β-caryophyllene	1418	--	2.4
38	β-ıonone	1433	--	0.4
39	Germacrene D	1435	**3.5**	**5.6**
40	Bicyclogermacrene	1445	1.8	2.1
41	α-muurolene	1446	2.1	2.2
42	γ-cadinene	1454	1.1	--
43	D-cadinene	1458	0.4	--
44	1,5-epoxysalvial-4[14] ene	1490	0.7	1.8
45	Spathulenol	1495	**15.5**	**11.4**
46	Caryophyllene oxide	1498	**4.6**	**15.9**
47	Salvial-4[14]-en-1-one	1504	--	2.8
48	Veridiflorol	1506	1.9	--
49	Longiborneol	1510	1.5	3.2
50	Humulene epoxide II	1514	3.1	1.2
51	Isolongifolene	1521	--	0.5
52	t-muurolol	1532	1.3	--
53	Allo-aromadendrene	1539	**4.4**	**7.1**
54	Neo-intermedol	1542	3.1	--
55	Limonene-oxide	1547	1.4	--
56	α-bisabolol	1555	4.1	--
57	Tetradecanoic acid	1591	--	0.9
58	Benzyl benzoate	1596	0.4	--
59	2-pentadecanone,6,10,14 trimethyl	1631	0.9	3.5
60	Hexadecanoic acid	1692	3.3	3.1
61	Abietetrane	1756	--	2.2
62	Abietal, dehydro	1883	--	0.4
63	Tricosane	1902	2.2	0.3
Total			**90.6**	**87.5**

*RRI: Relative Retention Index

Statistical analysis

The Cluster Analysis was applied to the data set on statistical software SPSS 21. The Cluster Analysis is a statistical method to group objects within the data. The main idea of the Cluster Analysis is to create groups (clusters) in which the association between two objects is maximal if they belong to the same cluster and minimal otherwise [12]. In this study, the species that are similar to each other were identified using the Cluster Analysis.

RESULTS AND DISCUSSION

The chemical composition essential oil of dried aerial parts of *C. balsamita* and *C. behen* were analyzed by GC and GC-MS. The relative concentrations of the volatile components identified are presented in Table 1, according to their retention indices on a HB-5 column. 34 and 48 compounds were identified in *C. balsamita* and *C. Behen,* respectively, accounting from 90.6% to 87.5% of the whole oil. The yield of oils are ca. 0.4 and 0.3 mL/100 g, respectively. Butanoic acid (16.3%), spathulenol (15.5%), α-terpinolene (10.2%) and caryophyllene oxide (4.6%) were detected main compounds of *C. balsamita*, however caryophyllene oxide (15.9%), spathulenol (11.4%), germacrene D (6.6%) and allo-aromadendrene (6.1%) were detected major constituents of *C. behen*. The essential oils of *C. balsamita* and *C. behen* were characterized, either numerically or quantitatively, by sesquiterpenes. Total sixty three compounds have been determined. *C. balsamita* and *C. behen* oils are characterized by the presence of sesquiterpenes; mainly hydrocarbon derivatives and in small amounts oxygenated ones.

Among the sesquiterpenes, spathulenol was found principal constituents of *C. balsamita* (15.5%), *C. behen* (11.4%) (Table 1), this compound also principal constituents of *C. cuneifolia* (6.3%) and *C. euxina* (10.8%) [13]. It is interesting that spathulenol was not detected in *C. napifolia* and detected in trace amounts in *C. cineraria* [14].

Caryophyllene oxide was found as principal constituents of *C. balsamita* (4.6%) and in *C. behen* (15.9%) (Table 1). Like our results, this compound also has been detected as a principal constituent in *C. chrysantha* (9.5%) [15], *C. euxina* (6.2%) [13], *C. helenioides* (18.2%) [16], *C. amanicola* Hub.-Mor. (12.0%), *C. consanguinea* DC. (7.3%), *C. ptosimopappa* (4.3%) Hayek. [17], *C. iberica* (10.7%), *C. virgata* (9.5%) and in *C. solstitialis* subsp. *solstitialis* (5.2%) [9]. On the other hand, this compound was not a principal constituent in *C. cuneifolia* Sibth. [13] and was of low amounts in *C. pseudoscabiosa* subsp. *pseudoscabiosa* Boiss. et Buhse (4.4%) and in *C. hadimensis* Wagenitz (3.1%) [18].

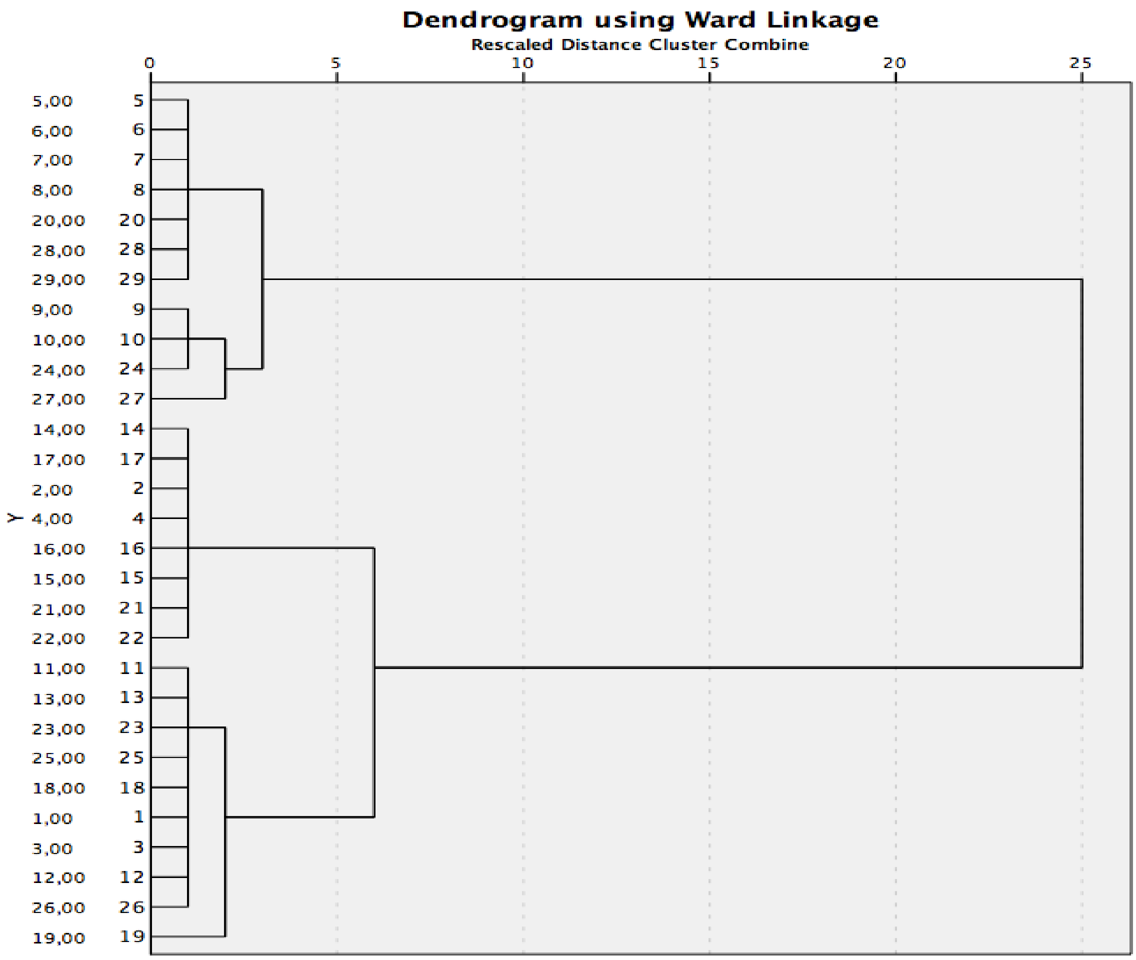
In accordance with the results obtained in previous studies on volatile oils from other *Centaurea* sp. endemic to Turkey [18,19], the oils were characterized by a higher content of sesquiterpenes. In this study, sesquiterpenes were the main content in this Centaurea species like in *C. pseudoscabiosa* subsp*. pseudoscabiosa*, *C. hadimensis*, *C. kotschyi* var. *kotschyi*, *C. kotschyi* var. *decumbens* and *C. solstitialis* [18,20-22].

In *Centaurea pelia, C. thessala* subsp*. drakiensis* and *C. zuccariniana*, *C. raphanina* subsp. *mixta*, monoterpene hydrocarbons and alcohols are completely absent; the main volatiles are caryophyllene oxide, β-elemene, dodecanoic, tetradecanoic and hexadecanoic acids, and the n-hydrocarbons hexacosane and heptacosane [23,24]. Our analysis results has shown some similarities with this study pattern in means of the low contents of monoterpenes in the oil.

Previous chemical studies on the genus Centaurea seem to indicate that the sesquiterpene lactones are the most characteristic constituents and systematically important [25,26]. These findings have also chemotaxonomical and economic significance for utilization of the species in the pharmaceutical, cosmetic and chemical industries.

The essential oils of two endemic Centaurea species from Turkey, *C. mucronifera* and *C. chrysantha.* The main compounds of the former were germacrene D (29.3%), β-eudesmol (17.4%) and β-caryophyllene (7.3%), while in the latter germacrene D (27.4%), caryophyllene oxide (9.5%) and bicyclogermacrene (5.4%) were detected among its major constituents [15]. While germacrene D and bicyclogermacrene were identified in trace amount for the essential oils of *C. balsamita* and *C. behen.* It is interesting that β-eudesmol was not detected in our analysis result.

To appraise whether the reported essential oil compounds could be useful in reflecting the taxonomic relationships among the different Centaurea taxa, the components of all the essential oils were subjected to hierarchical cluster analysis (HCA). In this study, the chemotaxonomic importance and essential oil compounds in this genus was confirmed particularly with regard to the studied and taxa from literature. Results of cluster analysis (Figure 1) based on the distribution of essential oil show two main big groups. One of them is a big group including (5-10, 20, 24, 27-29) samples. The other big group includes (1-4, 11-19, 21-26) samples. We can say that the first and second big group are divided into two small groups according to this dendogram.



1. C. pseudoscabiosa subsp. *pseudoscabiosa,* 2. *C. hadimensis* [18], 3. *C. kotschyi* var. *Decumbens,* 4. *C. kotschyi* var. *kotschyi*, 5. *C. thessala* subsp. *drakiensis,* 6. *C. zuccariniana* [24], 7. *C. raphanina* subsp. *mixta*, 8. *C. spruneri* [23], 9. *C. sessilis,* 10. *C. armena* [16], 11. *C. mucronifera,* 12. *C. chrysantha* [15], 13. *C. aladaghensis,* 14. *C. antiochia* var. *Prealta,* 15. *C. antitauri,* 16. *C. babylonica,* 17. *C. balsamita,* 18. *C. cheirolepidoides,* 19. *C. deflexa,* 20. *C. iconiensis,* 21. *C. lanigera*, 22. *C. ptosimopappoides* [18], 23. *C. iberica*, 24. *C. solstitialis* subsp. *Solstitialis,* 25. *C. virgata* [9], 26. *C. kurdica*, 27. *C. saligna* [10], 28. *C. balsamita*, 29. *C. behen* (Studied samples)

Figure 1: Hierarchical cluster analysis of twenty nine Centaurea taxa

Table 2: Agglomeration schedule

Agglomeration Schedule						
Stage	**Cluster Combined**		**Coefficients**	**Stage Cluster First Appears**		**Next Stage**
	Cluster 1	**Cluster 2**		**Cluster 1**	**Cluster 2**	
1	5	6	3,785	0	0	11
2	8	20	11,425	0	0	18
3	2	4	23,440	0	0	4
4	2	16	37,285	3	0	6
5	14	17	55,180	0	0	17
6	2	15	73,960	4	0	8
7	23	25	99,220	0	0	10
8	2	21	126,188	6	0	17
9	1	3	157,003	0	0	15
10	18	23	201,350	0	7	21
11	5	7	247,758	1	0	18

12	12	26	299,458	0	0	15
13	9	10	351,658	0	0	20
14	28	29	430,863	0	0	22
15	1	12	539,781	9	12	21
16	11	13	659,476	0	0	23
17	2	14	780,813	8	5	19
18	5	8	923,639	11	2	22
19	2	22	1114,057	17	0	27
20	9	24	1311,650	13	0	24
21	1	18	1537,922	15	10	23
22	5	28	1789,134	18	14	26
23	1	11	2056,248	21	16	25
24	9	27	2381,532	20	0	26
25	1	19	2930,995	23	0	27
26	5	9	3560,624	22	24	28
27	1	2	5038,512	25	19	28
28	1	5	12299,961	27	26	0

Table 2 is the Agglomeration Schedule which shows how the cases are clustered together at each stage of the cluster analysis. Clusters are formed by merging cases and clusters a step at a time, until all cases are joined in one big cluster. At each stage, one case or cluster is joined with another case or cluster. For example, *C. thessala* subsp. *drakiensis* (5) and *C. zuccariniana* (6) are joined at stage 1, *C. spruneri* (8) and *C. iconiensis* (20) are joined at stage 2 and so on. In addition, the coefficients column shows the distance (or dissimilarity) between the two clusters (or cases) joined at each stage. For instance, 5 and 6 are closer to each other than 8 and 20.

Butanoic acid/spathulenol chemotype of *C. balsamita* and caryophyllene oxide/spathulenol chemotype of *C. behen* in our analysis results. Some of the *Centaurea* species showed different chemotype of essential oil, like Germacrene D chemotype in *C. pseudoscabiosa* subsp. *pseudoscabiosa, C. hadimensis, C. kotschyi* var. *decumbens, C. kotschyi* var. *kotschyi*, *C. mucronifera*, *C. chrysantha, C. aladaghensis, C. antiochia* var. *prealta, C. antitauri, C. babylonica, C. balsamita, C. cheirolepidoides C. lanigera, C. ptosimopappoides, C. iberica, C. virgata* and *C. kurdica,* β-eudesmol chemotype in *C. sessilis, C. armena*, *C. solstitialis* subsp. *solstitialis* and *C. spruneri,* β-caryophyllene chemotype in *C. deflexa* and *C. iconiensis*, caryophyllene oxide/hexadecanoic acid chemotype in *C. thessala* subsp. *drakiensis, C. zuccariniana* and *C. raphanina* subsp. *mixta,* caryophyllene oxide/β-eudesmol chemotype in *C. saligna* (Table 3).

Table 3: Main constituents of Centaurea taxa from literature and studied samples (%)

Constituents	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28	29
β-caryophyllene	8.1	9.8	11.2	12.1	0.7	0.9	6.0	1.0	1.3	5.4	7.3	4.2	18.3	4.5	13.5	9.9	1.7	14.3	33.9	3.4	13.7	22.5	10.5	5.3	16.5	9.5	3.3	--	2.4
Germacrene D	36.0	44.3	29.4	44.2	--	--	--	--	--	3.3	29.3	27.4	22.7	45.1	40.2	43.0	40.2	21.7	21.1	--	43.1	36.9	20.3	6.3	21.4	28.3	10.2	3.5	5.6
Bicyclogermacrene	4.2	7.9	4.1	5.5	--	--	--	--	--	--	4.8	5.4	3.5	5.5	5.0	3.9	7.1	3.1	2.9	--	6.7	3.5	4.2	14.2	4.8	--	5.2	1.8	2.1
Caryophyllene oxide	4.1	3.1	1.9	3.0	7.8	6.2	10.3	0.3	10.0	4.7	5.2	9.5	7.5	0.8	2.8	0.4	0.4	6.1	12.8	0.5	2.5	1.5	10.7	5.2	9.5	10.5	25.2	4.6	15.9
Hexadecanoic acid	--	--	--	--	7.4	6.5	6.7	0.1	--	--	--	--	--	--	--	--	--	--	--	--	--	--	3.2	4.1	0.6	--	--	3.3	3.1
B-eudesmol	--	--	1.9	--	--	--	5.6	2.9	12.4	19.3	17.4	--	11.8	--	--	--	--	--	--	--	4.7	--	5.3	15.5	4.8	5.3	11.5	--	--
Spathulenol	--	--	--	--	3.8	4.2	3.9	0.9	4.9	3.9	1.5	3.8	0.8	3.3	1.0	--	2.2	2.2	0.7	--	1.8	0.6	5.4	11.3	7.5	5.4	2.3	15.5	11.4
Tricosane	0.3	--	0.3	3.6	0.3	2.3	0.8	0.1	--	--	1.2	3.7	7.2	0.8	--	--	0.9	--	1.5	0.6	2.4	--	--	0.4	0.3	--	0.5	2.2	0.3

1. C. pseudoscabiosa subsp. *pseudoscabiosa*, 2. *C. hadimensis* [18], 3. *C. kotschyi* var. *decumbens*, 4. *C. kotschyi* var. *kotschyi,* 5. *C. thessala* subsp. *drakiensis,* 6. *C. zuccariniana* [24], 7. *C. raphanina* subsp. *mixta*, 8. *C. spruneri* [23], 9. *C. sessilis* and 10. *C. armena* [16], 11. *C. mucronifera*, 12. *C. chrysantha* [15], 13. *C. aladaghensis,* 14. *C. antiochia* var. *prealta,* 15. *C. antitauri,* 16. *C. babylonica,* 17. *C. balsamita* 18-*C. cheirolepidoides* 19- *C. deflexa* 20- *C. iconiensis* 21- *C. lanigera* and 22- *C. ptosimopappoides* (Flamini et al., 2006) 23. *C. iberica*, 24. *C. solstitialis* subsp. *solstitialis*, 25. *C. virgata* [9], 26. *C. kurdica*, 27. *C. saligna* [10], 28. *C. balsamita*, 29. *C. behen* (Studied samples)

CONCLUSION

The main constituents of the essential oil of Centaurea taxa from literature and studied samples showed differences, similarities and different qualitative and quantitative profiles. We can say that these differences could be due to the ecological conditions of their habitat like soil properties, climatic and seasonal factors. However, taking into account the differences referred to some constituents, also the taxonomic distance of these species could be confirmed by our chemical data. In addition to the essential oil results have given some clues on the chemotaxonomy of the genus patterns and usability of the oils as natural product and oil resource plant.

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