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Original article

COMPARATIVE ANALYSES OF THE ESSENTIAL OILS FROM *TORDYLIUM* L. SPECIES GROWING IN TURKEY

Alev TOSUN

Ankara University, Faculty of Pharmacy, Department of Pharmacognosy, 06100 Tandoğan, Ankara, TURKEY

Abstract

Tordylium L. belonging to the Apiaceae family consists of annual Mediterranean plants which have been known to be used as spice in some countries. The essential oil compositions from the aerial parts of Tordylium L. species were analyzed by GC and GC/MS to identify the major components. In total, 16 components characterized, representing 83 % in T. trachycarpum, 28 components representing 53.4 % in T. lanatum, 24 components representing 51.6 % in T. aegyptiacum, 46 components representing 55.1 % in T. syriacum, 35 components representing 68.3 % in T. pustulosum. The main constituents were determined as β-caryophyllene, α-bisabolene, caryphyllene-oxyde and octyl 2-methyl butyrate in the profile of the oils analyzed in this study. In the present study, compositions of the essential oils obtained from the aerial parts of Tordylium species were discussed and compared with the previous relevant works.

Key words: *Apiaceae, Essential oil, Tordylium L., GC/MS.*

Türkiye'de Yetişen *Tordylium* L. Türlerinin Uçucu Yağlarının Karşılaştırmalı Analizleri

Apiaceae familyasına ait olan ve bazı ülkelerde baharat olarak kullanılan, Tordylium L., tek yıllık Akdeniz bitkilerindendir. Tordylium L. türlerinin toprak üstü kısımlarından elde edilen uçucu yağ bileşimi, ana bileşiklerini teşhis etmek amacı ile GC ve GC/MS ile analiz edilmiştir. Toplam olarak, 16 bileşik T. trachycarpum'da %83 oranında, 28 bileşik %53,4 T. lanatum'da, 24 bileşik %51.6 oranında T. aegyptiacum'da, 46 bileşik %55.1 oranında T. syriacum'da, 35 bileşik %68.3 oranında T. pustulosum'da tanımlanmıştır. Başlıca bileşikler β-karyofillen, α-bizabolen, karyofillen-oksit ve oktil 2-metil butirat olarak bu çalışmada incelenen yağlarda tayin edilmiştir. Bu çalışmada, Tordylium türlerinin toprak üstü kısımlarından elde edilen uçucu yağ bileşimleri tartışılmış ve daha önceki ilgili çalışmalar ile karşılaştırılmıştır.

Anahtar kelimeler: *Apiaceae, Uçucu yağ, Tordylium L., GC/MS.*

Correspondence: E-mail: alevtosun@yahoo.com
Tel: +90 312 203 30 89

INTRODUCTION

Apiaceae is a well known family having aromatic and economically important plants, composed of more than 2500-3000 species in the world (1-3). The genus *Tordylium* L. belongs to Apiaceae family, and is represented by 16 species including 6 species endemic in Turkey. The genus *Tordylium* L. *(Syn.: Hasselquistia* L., *Condylocarpus* Hoffm., *Ainsworthia* Boiss., *Synelcosciadium* Boiss.) is described as branching annual plants with scabrous to villous, with simple basal and lower cauline leaves. Umbels are terminal, 5-40 rayed, petals are white to yellow. Mericarps are ovate-elliptic to suborbicular; either all of them in the same umbellule strongly compressed, or the ones in the centre of umbellule hemispherical and unicarpellate, peripheral ones compressed (4-6).

Some of the phytochemical and biological activity studies regarding *Tordylium* species are limitedly present (7-11). Some flavonoids and bioactive coumarins were isolated from the aerial parts of *T. apulum* (7). In the another study, some coumarins were isolated from *T. apulum* and tested *in vitro* for their cytotoxic activity against two cell line systems, *T. apulum* is widely used in Greece as a spice with the common name "kafkalithra" (8). The essential oil of the fruits from *T. apulum* were examined chemically and then for the antibacterial activity by Kofinas et al. in 1993 (9). In addition, the leaves of *T. apulum* showed a notable activity in lipid peroxidation assay (10). By the way, a few essential oil studies exist on *Tordylium* species in literature.

Recently, the studies on the chemistry of the essential oils obtained from fruits have been effectively continued on Turkish *Tordylium* species (12-16). For the first time, the aerial parts of *Tordylium* species collected during flowering times are examined concerning their essential oil composition and compared for their major components in the present study.

EXPERIMENTAL

Plant materials

The aerial parts of *Tordylium* species were collected from different localities in Turkey. The collection sites, dates, herbarium numbers, and essential oil percentages were shown as below (Table 1). All the species were identified by Prof. H. Duman. Voucher specimens have been deposited at the Herbarium of the Faculty of Pharmacy of Ankara University (AEF), Ankara, Turkey.

Table 1. *Tordylium* L. species collected from different localities.

Plant name	Collection site	Herbarium No	Essential oil (v/w%)
T. aegyptiacum (L.) Lam.	Adana-İskenderun highway, 2004	AEF 23141	0.15
T. lanatum (Boiss.) Boiss.	Antalya-Korkuteli-Elmalı, 2003	AEF 22991	0.1
T. pustulosum Boiss.	Antalya-Alanya, Hacımehmetli Village, 2003	AEF 22990	0.25
T. syriacum L.	Antakya-Belen, near the side of road, 2004	AEF 23145	0.08
T. trachycarpum (Boiss.) Al-Eisawi & Jury	Antakya-around St. Peters Church, 2004	AEF 23142 AEF 23143	0.1

Isolation of the essential oils

The aerial parts were subjected to hydrodistillation to obtain the oils for 3 h using a Clevenger-type apparatus. The yields of the oils obtained from *T. aegytiacum*, *T. lanatum*, *T. pustulosum*, *T. syriacum* and *T. trachycarpum* were 0.15 %, 0.1 %, 0.25 %, 0.08 % and 0.1 % on dry weight basis (v/w), respectively as shown in Table 1.

Analysis of the oils

Gas chromatography and gas chromatography/mass spectroscopy

GC and GC/MS analyses were carried out using an Agilent 6890 N gas chromatograph apparatus equipped with a flame ionization detector (FID) and coupled to a quadrupole Agilent 5973 Network mass selective detector working in electron impact (EI) mode at 70 eV (scanning over 35-350 amu range). The gas chromatograph was equipped with two fused silica capillary column HP-1 (PDMS, 50 m × 0.2 mm i.d., film thickness = 0.33 μm). The analytical parameters were as follows: The carrier gas was helium at a flow rate of 1 mL/min (head pressure for both columns=25 psi); oven temperature was programmed from 60 to 250°C at 2°C/min and held isothermal for 40 min. The injector (split mode, ratio 1/100) temperature was 250°C. FID temperature was set at 250°C and in the GC/MS analyses, the temperatures of the ion source and the transfer line were 170 and 280°C, respectively.

Identification of the constituents

The constituents of the essential oil were identified by comparison of their mass spectral pattern and relative retention indices (RRI) with those of pure compounds registered in commercial libraries (Wiley 6N and NIST 98) and literature data, or laboratory-made database build up from authentic compounds.

RESULTS AND DISCUSSION

In flowering periods, several *Tordylium* species of Turkish origin were investigated by GC and GC/MS regarding major components of the essential oils obtained from the aerial parts. The compounds found in the oils were characterized as shown in Table 2, and the ratio of the total identified compounds were calculated as 51.7 %, 53.1 %, 82.87 %, 68.3 %, 55. 1% in the oil of *T. aegyptiacum, T. lanatum, T. trachycarpum, T. pustulosum* and *T. syriacum,* respectively. The list of the compounds identified in the hydrodistilled oils with their relative percentages and relative retention indices are given in Table 2.

Table 2. The composition of the essential oils from the aerial parts of *Tordylium* species.

RRI	Compound	A%	B%	C%	D%	E%
823	(E)-2-Hexenal	-	-	-	tr	-
846	Hexanol	-	0.2	-	-	-
922	α-Thujene	-	-	-	0.1	-
930	α-Pinene	-	0.1	tr	0.1	-
962	Hexanoic acid		-	-	-	0.3
964	Sabinene	-	-	-	4.2	-
969	β-Pinene	1.5	-	0.2	0.2	-
977	2-Pentylfuran	-	-	-	0.1	-
981	Myrcene	1.5	0.3	0.2	0.1	-
1000	Decane	4.6	-	-	-	-
1009	α-Terpinene	-	-	-	0.2	-
1011	*p*-Cymene	-	0.1	-	0.3	-
1019	β-Phellandrene	-		0.3	tr	-
1020	Limonene	3.9	0.4	0.1	0.1	-
1036	*trans*-β-Ocimene	-	-	-	0.2	-
1047	γ-Terpinene	-	-	-	0.5	-
1052	Octan-1-ol	5.4	3.4	1.0	0.7	**8.8**
1077	Terpinolene	-	-	-	0.2	-
1083	Linalool	-	-	-	0.2	0.1
1157	Octanoic acid		-	-	-	0.2
1159	Terpinen-4-ol	-	-	-	0.2	-
1170	α-Terpineol	-	-	-	Tr	0.2
1193	Octyl acetate	-	-	-	-	0.1
1221	Hexyl-2-methylbutyrate	-	-	-	-	0.1
1245	Phellandral	-	-	0.2	-	-
1255	Decanol	-	-	-	-	0.5
1266	Bornylacetate	-	-	-	-	0.1
1267	Thymol	-	-	tr	0.1	0.1
1272	2-Undecanone	-	0.5	-	-	-
1276	Carvacrol	-		-	0.1	0.1
1285	2-Undecanol	-	0.3	-	-	-
1301	*Z*-3-Hexenyl tiglate	-	-	-	0.1	-
1330	Octyl isobutyrate	-	-	-	-	1.8
1358	*(E)*-β-Damascenone	-	-	0.2	-	0.1
1371	α-Ylangene	-	-	0.1	-	-

1372	Octyl butyrate	-	-	-	-	0.1
1373	2-Dodecanone	-	0.2	-	-	-
1379	β-Bourbonene	-	0.6	0.1	0.2	-
1412	β-Caryophyllene	**19.5**	3.9	**8.1**	1.0	1.7
1416	β-Gurjunene	-	-	-	tr	-
1419	γ-Decalactone	-	-	-	0.1	-
1421	Octyl 2-methylbutyrate	-	-	-	-	**19.7**
1427	Geranylacetone	-	0.5	-	0.1	0.1
1429	*trans*-α-Bergamotene	-	-	1.8	1.3	-
1437	α-Cadinene	-	-	-	0.5	-
1445	α-Humulene	1.1	0.6	1.4	**5.7**	0.2
1450	Unknown	-	-	-	1.2	-
1467	α-Curcumene	-	1.5	0.5	0.6	0.2
1469	γ-Curcumene	-	0.2	0.1	-	-
1470	Germacrene-D	1.3	-	-	0.4	0.2
1475	2-Tridecanone	-	**11.3**	-	-	-
1483	α-Zingiberene	-	-	-	0.2	-
1485	α-Selinene	-	-	0.5	-	-
1487	2-Tridecanol	-	4.9	-	-	-
1492	Unknown	4.8	-	-	-	-
1494	α-Farnesene	-	-	-	-	0.1
1499	α-Bisabolene	**13.1**	0.1	**20.6**	**13.5**	1.7
1505	Calamenene	3.4	-	-	**9.1**	1.4
1510	λ-Cadinene	-	-	-	-	1.1
1511	β-Sesquiphellandrene	4.9	1.7	0.9	1.1	-
1514	trans-Calamenene	-	0.1	-	-	-
1523	α-Calacorene	-	-	-	0.3	-
1532	Selina-3,7(11)diene	0.7	-	-	-	-
1540	*cis*-3-Hexenyl benzoate	-	-	-	0.2	-
1545	*E*-Nerolidol	-	0.1	-	0.2	0.6
1557	Spathulenol	1.5	2.4	1.4	1.6	2.7
1559	Unknown	1.2	-	-	-	-
1562	Caryophyllene oxyde	**18.3**	**10.0**	**6.8**	2.0	3.5
1565	Unknown	-	1.8	-	1.8	-
1567	Octyl hexanoate	-	-	-	-	**16.6**
1576	2-Tetradecanone	-	0.4	-	-	-
1577	Unknown	-	-	-	1.2	-
1581	Carotol	-	-	-	-	0.9
1587	α-Humulene epoxyde II	1.0	-	-	4.4	-
1604	Unknown	-	-	-	1.1	1.1

1614	Caryophylla-4(12), 8(13)-dien	-	1.2	1.3	-	-
1619	Unknown	-	-	-	3.5	1.6
1630	Unknown	-	-	-	1.4	-
1635	Unknown	-	-	1.2	-	-
1649	Unknown	-	1.7	1.7	-	-
1652	Unknown	-	-	1.1	1.0	-
1654	Unknown	-	-	-	2.9	-
1661	Unknown	-	-	-	1.0	2.5
1664	Unknown	-	-	-	1.2	-
1667	Unknown	-	-	-	1.4	-
1678	2-Pentadecanone	-	1.5	-	-	-
1683	Unknown	-	-	-	1.1	-
1695	Unknown	-	-	1.2	1.5	-
1760	Octyl octanoate	-	-	0.7	-	0.4
1772	5-Hydroxycalamenene	-	-	-	1.5	-
1827	Trimethylpentadecanone	1.3	4.2	3.7	1.5	1.6
1889	Farnesylacetone	-	-	0.6	0.1	0.2
1907	Methyl palmitate	-	-	-	-	0.4
1909	Unknown	-	-	-	1.1	-
1993	Unknown	-	-	1.4	-	-
2061	Unknown	-	-	1.1	-	-
2069	Methyl linoleate	-	-	-	-	0.8
2100	Phytol	-	2.7	3.6	1.9	1.7
2111	Unknown	-	3.8	-	-	-
Total		**88.84**	**61.8**	**62.1**	**77.5**	**73.6**
Total identified		**82.87**	**53.1**	**51.7**	**55.1**	**68.3**

RRI: Relative retention Indices calculated against *n*-alkanes, % calculated from FID data
tr: trace amount of component (<0.1 %)
A: *T. trachycarpum*
B: *T. lanatum*
C: *T. aegyptiacum*
D: *T. syriacum*
E: *T. pustulosum*

In previous studies, isolation of some flavonoids and a series of antifungal and cytotoxic coumarins were reported from *T. apulum* L. used as spice in Greece (7, 8). Antibacterial activity of the oil from the aerial parts of *T. apulum* was investigated, and α-humulene (28.7 %), octyl hexanoate (11.7 %) and farnesyl acetone (9.8 %) were found as the main components in the oil (9). Moreover, the leaves of *T. apulum* exhibited a remarkable activity in lipid peroxidation assay (10). Trillini et al (2006) also investigated the essential oil of *T. apulum* from Italy, and (*E*)-β-ocimene (17.3 %), α-humulene (11.4 %) and octyl octanoate (8.8 %) were determined as major constituents (11).

In our previous studies, several *Tordylium* species growing in Turkey, such as *T. apulum* L., *T. pustulosum* Boiss., *T. pestalozzae* Boiss., *T. lanatum* (Boiss.) Boiss.; *T. trachycarpum* (Boiss.) Al-Eisawi et Jury, *T. hasselquistiae* DC., *T. ketenoglui* H. Duman & A. Duran and *T. aegyptiacum* (L.) Lam., were investigated for their fruit essential oils (12-15). The main constituents in the fruit oil of *T. apulum* were found to be octyl hexanoate (44 %), octyl octanoate (34.5 %), octanol (16.5 %), while the octyl hexanoate (73.2 %), octanol (10.4 %), octyl 2-methyl butyrate (5.5 %) were the main components of the oil of *T. pustulosum* (12). On the other hand, octyl hexanoate (56.0 %), octyl octanoate (15.7 %), octanol (14.5 %), hexadecanoic acid (6.0 %) were the main constituents in the fruit oil of *T. pestalozzae,* whereas octyl hexanoate (68.8 %), octyl 2-methylbutyrate (17.8 %), octanol (4.2 %); octyl hexanoate (58.8 %) and octanol (21.5 %) were obtained as main constituents of the oils produced from *T. pustulosum* and *T. lanatum*, respectively (13). In *T. ketenoglui*, the main constituents were octyl octanoate (28.9 %), octanol (11.6 %) and bornyl acetate (7.2 %) (14). Moreover, the fruits of *T. trachycarpum* and *T. hasselquistiae* were analyzed by GC and GC/MS and the main constituents were found as octyl octanoate (79.9 %), octanol (11.0 %) and octanoic acid (2.9 %) in *T. trachycarpum;* and octyl hexanoate (72.7 %), octyl octanoate (12.7 %) and octanol (3.3 %) in the oil of *T. hasselquistiae* (15). In addition, the essential oil obtained by hydrodistillation from the fruits of *T. aegyptiacum* (L.) Lam. was analyzed and the main constituents were determined as hexadecanoic acid (40.1%), β-caryophyllene (10.6 %), octyl octanoate (8.8 %) and caryophyllene oxyde (8.5 %) (16).

In the present study, the aerial parts of the some *Tordylium* species growing in Turkey were examined and their major constituents were determined as β-caryophyllene (19.5 %), caryophyllene oxyde (18.3 %), α-bisabolene (13.1%) in the oil of *T. trachycarpum;* 2-tridecanone (11.3 %), caryophyllene oxyde (10.0 %) in the oil of *T. lanatum;* α-bisabolene (20.6%), β-caryophyllene (8.1%), caryophyllene oxyde (6.8%) in the oil of *T. aegyptiacum*; α-bisabolene (13.5 %), calamenene (9.1 %), α-humulene (5.7 %) in the oil of *T. syriacum*; octyl 2-methylbutyrate (19.7 %), octyl hexanoate (16.6 %), 1-octanol (8.8 %) in the oil of *T. pustulosum.*

The present work is the first report on the composition of essential oils obtained from the aerial parts of above-mentioned *Tordylium* species. While the octanol and octyl esters appear to be predominant components in the fruit oils; the sesquiterpenes such as, caryophyllene oxyde, β-caryophyllene and bisabolene are the most common constituents in the oils obtained from aerial parts of the species. However, it is obvious that the aerial part of *T. pustulosum* contains high amount of octanol and its esters as well as its fruits. So, the other constituents observed in the other oils are not prominent in the aerial parts of *T. pustulosum.*

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