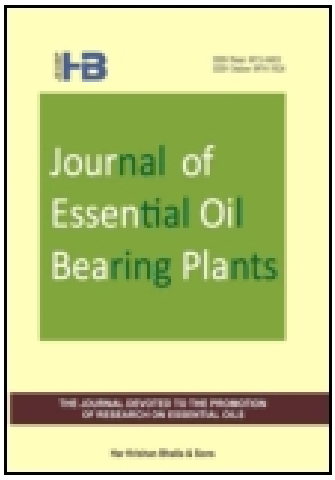

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Essential Oil Composition of Wiedemannia Fisch. & C.A. Mey. Genus from Turkey: A Chemotaxonomic Approach

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Essential Oil Composition of *Wiedemannia* Fisch. & C.A. Mey. Genus from Turkey: A Chemotaxonomic Approach

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Abstract: The essential oils water distilled aerial parts of *Wiedemannia orientalis* Fisch. & C.A.Mey. and *Wiedemannia multifida* (L.) Benth. (Lamiaceae) were investigated by GC and GC-MS. Thirty seven and thirty six compounds were identified comprising representing 93.4 % and 94.9 % of the total components in the oils, respectively. Germacrene D (23.3 %), thymol (16.4 %) and carvacrol (12.3 %) in *W. orientalis*; germacrene D (29.8 %), thymol (19.3 %) and β-caryophyllene (13.9 %) were identified as major components in *W. multifida.* The chemical distribution of the essential oil compounds in the genus pattern were discussed in means of chemotaxonomy and natural products.

Key words: *Wiedemannia*; Lamiaceae, Essential oil; Germacrene D; Thymol.

Introduction

Many taxa of Lamiaceae are aromatic and often used as herbs, spices, folk medicines and a source of fragrance [1]. The Lamiaceae is a large family. Most of the species have great importance due to their economic values. Lamiaceae is represented by about 258 genera and 3500 species in the world [2] and it is represented by 46 genera and 571 species of which 44.2 % are endemic, and with subspecies, varieties and hybrids altogether 763 taxa exists in the flora of Turkey. The usefulness of the structure of the vascular bundles in petioles for species identification in the family Lamiaceae has been demonstrated [3]. The taxonomic significance of the structure of glandular hairs is well known in the Lamiaceae and related families [4,5]. The morphology, distribution and frequency of glandular trichomes are used as discriminative characters at subfamiliar level in the Lamiaceae [6,7]. Pollen morphology has been pointed to be useful in systematics of the Lamiaceae [8]. Some petiole anatomic characters are determined in designated taxonomical structures of some species [9-11]. Most of the taxonomic problems in the genus arise from its unique biological characteristics. *Lamium multifidum* L. which was transferred by Bentham (1848) to *Wiedemannia*, described in 1837 by Fisch & C.A. Mey. [12].

The genus *Wiedemannia* Fisch. & C.A.Mey. (Lamiaeae) is represented by 2 species (*W. orientalis* and *W. multifida*) in the flora of Turkey which are annual herbs, differing from *Lamium* principally by the bilabiate 10-veined calyx, with upper leaves lanceolate, lower bifid. Corolla mauve, purple or pink, with densely villous to tomentose hood; tube with ring of hairs near base. Nutlets trigonous. *W. orientalis* and *W. multifida* differing from bracts structure and the species

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grows steppe, fields, roadsides, on light soils and hedgerows. *W. orientalis* is an endemic species and is widespread throughout Anatolia. *W. orientalis* is very variable in density of indumentum. Although usually saringly pilose, some examples are subglabrous, while others (B3 Afyon: Bolvadin, N.&M. Tanker ISTE 8141) have densely villous stems and leaves. *W. multifida* rather variable in the degree of division of the bracts; where the range overlaps with that of *W. orientalis*, intermediates with only deeply dentate bracts ocur. These may be of hybrid origin; futher studies are needed [13].

Typical secondary metabolites of Lamiaceae include various terpenoids, especially mono-, sesqui-, di- and tri-terpenes. Few genera produce sesquiterpenes; furthermore, biologically active diterpenes have been found in some members of the Nepetoideae. Diterpene are a class of secondary metabolites with a large variety of structures; the interest in the isolation of these compounds is due to their biological activity, ecological and taxonomic function and use as templates for synthesis [14]. Iridoid glycosides, which derive from monoterpenes have been regarded as good taxonomic marker in Labiatae, very common in members of the subfamily Lamioideae. Fatty acids also has chemotaxonomic importance in the some genus patterns in Labiatae [15]. Secondary metabolites apparently act as defence against herbivores, microbes, viruses or competing plants and as signal compounds to attract pollinating or seed dispersing animals; they are thus important for plant survival and reproductive fitness. Secondary metabolites therefore represent adaptive characters that have been subjected to natural selection during evolution [16]. Many species of family are aromatic and often used as herb species, folk medicines and fragrances [17,18].

Genus *Wiedemannia* lacks detailed phytochemical investigation. A research was made about *W. orientalis* as regards its iridoid, flavonoid and phenylethanoid glycosides contents [19]. Therefore, the aim of this study is to provide chemical data that might be helpful in potential usefulness and chemotaxonomic significance of *Wiedemannia* taxa growing in Turkey.

Materials and methods

Plant material

The aerial part of samples were collected from their natural habitats by Kilic. *W. orientalis* (Kilic-1825) was collected from Elazig-Keban, Aslankasi village, road side, in May 2010 at an altitude of 850-950 m. *W. multifida* (Kilic-2605) was collected from Elazig-Keban, around the Geyiktas village, on slopes, in June 2010, at an altitude of 950-1000 m. Plant materials were identified with Flora of Turkey and East Aegean Islands, vol. 7 [13] and deposited in the Firat University Herbarium (FUH).

Isolation of the essential oil

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)

The oils were analysed by GC-FID-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°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). Mass spectra 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 *Wiedemannia* species are listed in Table 1.

Results and discussion

The essential oil components of aerial parts of *W. orientalis* and *W. multifida* were investigated by GC and GC-MS. The yield of oils are ca. 0.50 and 0.60 mL/100 g respectively. Thirty seven and thirty six compounds were identified representing 93.4 % and 94.9 % of the oil, respectively. Germacrene D (23.3 %), thymol (16.4 %) and carvacrol (12.3 %) in *W. orientalis*; germacrene D (29.8 %), thymol (19.3 %) and β-caryophyllene (13.9 %) were identified as major components in *W. multifida* (Table 1). Water distilled essential oil from fresh aerial parts of *W. orientalis* was analyzed by GC and GC-MS, and 31 compounds were identified with germacrene D (38.94 %), geijerene (14.60 %), and pregeijerene (12.90 %) as the major constituents [24]. In the present study, germacrene D (23.3 % - 29.8 %) was also determined major compounds of *W. orientalis* and *W. multifida* respectively (Table 1).

Carvacrol (12.3 %) reported as major component in *W. orientalis* oil. However this compound determined minor in *W. multifida* (2.1 %) (Table 1). While β-caryophyllene (13.9 %) was a major component in *W. multifida*, it was not among the major components of *W. orientalis* (3.1 %) oil. The major monoterpenes of *W. orientalis* were thymol (16.4 %), carvacrol (12.3 %) and γ-terpinene (5.4 %) (Table 1). The major monoterpenes of *W. multifida* were thymol (19.3 %) and γ-terpinene (4.3 %). So, monoterpene contents of *W. orientalis* oil were found at higher levels than in *W. multifida* oil (Table 1). However, sesquiterpene contents [germacrene-D (29.8 %), β-caryophylene (13.9 %), α-humulene (3.6 %)] of *W. multifida* oil were found at higher levels than in *W. orientalis* [germacrene-D (23.3%), β-caryophylene (3.1 %), α-humulene (3.4 %)] oil. In the other hand oils of two taxa contained less oxygenated monoterpenes such as linalool, *trans*-pinocarveol and α-terpinolene (Table 1). It is noteworthy that high percentages of β-caryophyllene (13.9 %) in *W. multifida* was distinctive from *W. orientalis* (3.1 %). Likewise

Table 1. Chemical profiles of *Wiedemannia* species

Compounds	RRI	*W. orientalis*	*W. multifida*
Santolina triene	998	0.5	-
α-Thujene	1016	1.5	1.4
α-Pinene	1022	3.4	1.5
Camphene	1034	-	0.2
Sabinene	1052	0.6	0.7
β-Pinene	1056	0.1	-
β-Mrycene	1064	2.2	1.2
α-Terpinene	1085	1.0	1.6
Benzene, 1-methyl-2	1090	0.6	-
Limonene	1096	3.1	0.7
1,8-Cineole	1098	1.6	1.2
cis-Ocimene	1100	-	0.6
1,3,6-Octatriene	1108	0.8	-
γ-Terpinene	1117	5.4	4.3
trans-Sabinene hydrate	1126	-	0.4
Filifolene	1128	0.5	-
Linalool	1148	-	0.4
2-Cyclohekzen-1-ol	1166	0.4	-
trans-Pinocarveol	1178	-	0.3

table 1. (continued).

Compounds	RRI	*W. orientalis*	*W. multifida*
Camphor	1182	1.4	0.4
Borneol	1200	0.6	0.3
3-Cyclohexen-1-ol	1205	0.5	1.1
α-Terpinolene	1220	2.5	2.1
Thymol	1295	16.4	19.3
Carvacrol	1300	12.3	2.1
α-Copaene	1350	0.2	0.6
β-Caryophyllene	1382	3.1	13.9
trans-b-Farnesene	1360	0.6	-
β-Cubebene	1400	0.3	0.2
Aromadendrene	1406	-	0.1
α-Humulene	1418	3.4	3.6
Napthalene	1430	0.2	0.2
Germacrene D	1435	23.3	29.8
β-Selinene	1441	0.8	0.4
Ledene	1445	-	0.1
β-Bisabolene	1450	0.6	0.2
α-Amorphene	1455	0.8	-
δ-Cadinene	1462	-	1.6
Spathulenol	1495	0.2	-
Caryophyllene oxide	1497	-	0.8
Muurolene	1520	2.1	0.5
Izoaromadendrene epoxide	1545	0.3	-
Tetradecanal	1562	0.1	-
Azulene	1572	-	0.3
β-Farnesene	1576	-	0.5
2-Pentadecanone	1650	0.1	-
Hexadecanoic acide	1702	0.4	-
Ericosane	1901	1.5	2.1
Tricosane	1935	-	0.2
Total		93.4	94.9

high percentages of carvacrol (12.3 %) in *W. orientalis* was distinctive from *W. multifida* (2.1 %) (Table 1). Monoterpene and sesquiterpene derivatives are characteristic for *Wiedemannia* taxa and they represent excellent chemo-taxonomical markers.

Upper lip of corolla clearly falcate in the genus *Wiedemannia* and *Lamium* L. [13]. *Lamium multifidum* L. which was transferred by Bentham (1848) to *Wiedemannia*, described in 1837 by Fisch & C.A. Mey. *Lamium* L. is composed of nearly 40 species distributed extensively in Europe, eastern Asia, northern Africa, north of the Atlas mountains and Macaronesia. Its diversity centre lies in the Irano-Turanian and the Mediterranean phytogeographic regions [12]. *Lamium* species are used in official and traditional medicines in Anatolia, Europe and China, possessing antioxidant, anti-inflammatory, blood tonic, uterotonic, antiplasmodic, antiseptic, uterotonic, trauma, hypertension, chronic bronchitis, pharyngitis and other properties [19-20]. Chelsea *et al.*, [21] reported that *L. amplexicaule* essential oil was composed largely of α-pinene,

β-pinene, 1-octen-3-ol, (*E*)-caryophyllene, and germacrene D, while *L. purpureum* oil was dominated by α-pinene, β-pinene, 1-octen-3-ol, β-elemene, and germacrene D [21]. There are number of studies on chemical composition of Lamiaceae genus [22,28].

This study showed that the genus *Wiedemannia* had a considerable variation in essential oil composition and this study demonstrates the occurrence of the Germacrene D (23.3 %), thymol (16.4 %), carvacrol (12.3 %) chemotype of *W. orientalis* and Germacrene D (29.8 %), thymol (19.3 %), β-caryophyllene (13.9 %) chemotype of *W. multifida* in the eastern Anatolian region of Turkey (Table-1).

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