The Effect of Helichrysum pallasii on Essential Oil Composition of Ontogenetic Variability

EMİNE YURTERİ *[1]

[1] *Recep Tayyip Erdoğan University, Faculty of Agriculture, Department of Field Crops, Rize, Türkiye*

Abstract: Since the earliest times of human history, medicinal plants have been used and continue to be used in many areas such as disease prevention, treatment and food additives. Species belonging to the *Helichrysum* genus have many important properties such as antimicrobial, antibacterial, antiviral, antifungal, antioxidant and anti-inflammatory thanks to the components they contain, which vary depending on many factors such as location, climate and soil conditions. For this reason, in this study, the stem, leaf and flower parts of *Helichrysum pallasii* plant collected during the full bloom period from its natural habitat in Köse district of Gümüşhane province of Türkiye were used as plant material. The aromatic components in the essential oil of the plant were determined using the SPME (Solid Phase Microextraction) method in Gas Chromatography (GC-MS) device. 58 different components were found as a result of the analysis. The prominent components are; Methyl butyl phenyl acetate (16.04%), phtyone (11.05%), β-caryophyllene (10.47%), undecly alcohol (7.57%), δ-cadinene (%7.36), γ-cadinene (5.32%), hexadecane (5.24%) and tetradecane (4.51%).

Keywords: *Helichrysum*, aroma component, GC-MS, immortal flowers

***Helichrysum pallasii*'nin Ontogenetik Varyabilitenin Uçucu Yağ Kompozisyonu Üzerine Etkisi**

Öz: *İnsanlık tarihinin en eski zamanlarından beri tıbbi bitkiler hastalığı önleyici, tedavi edici ve gıda katkı maddesi gibi birçok alanda kullanılmıştır ve kullanılmaya da devam etmektedir. Helichrysum cinsi türleri bulunduğu konum, iklim ve toprak koşulu gibi birçok etkene bağlı olarak değişiklik gösteren, içerisinde barındırdığı bileşenler sayesinde antimikrobiyal, antibakteriyel, antiviral, antifungal, antioksidan ve antiinflamatuar gibi birçok önemli özelliğe sahiptirler. Bu sebeple de bu çalışmada, Türkiye'nin Gümüşhane iline bağlı Köse ilçesinde doğal habitatından tam çiçeklenme döneminde toplanan Helichrysum pallasii bitkisinin; sap, yaprak ve çiçek kısımları bitki materyali olarak kullanılmıştır. Bitkinin uçucu yağındaki aromatik bileşenler Gaz Kromatografisi (GC-MS) cihazında SPME (Katı Faz Mikroekstraksiyon) yöntemi kullanılarak belirlenmiştir. Analiz sonucunda 58 farklı bileşen bulunmuştur. Öne çıkan bileşenler; Methyl butyl phenyl acetate (% 16.04), phtyone (% 11.05), ß-caryophyllene (% 10.47) , undecly alcohol (% 7.57), δ-cadinene (% 7.36), γ-cadinene (% 5.32), hexadecane (% 5.24) ve tetradecane (% 4.51) olmuştur.*

Anahtar kelimeler: Helichrysum, aroma bileşeni, GC-MS, ölmez çiçek

INTRODUCTION

Asteraceae is one of the largest families in the plant kingdom and also the family that contains the most endemic species. The endemism rate of the Asteraceae family, which contains a total of 489 endemic species, is 36.3% (Güner, 2013). Members of the Asteraceae family are distributed almost everywhere on earth. It is especially found in the southwest of America, Mexico, the south of Brazil, the Mediterranean Region, southwest Asia, Central Asia, South Africa and Australia (Bremer, 1994). While the genus *Helichrysum* in the Asteraceae family is represented by 600 species in the world, this species is represented by 27 taxa in the Flora of Türkiye, 15 of which are endemic. (Davis et al., 1975; Davis et al., 1988; Güner et al., 2000; Bayer et al., 2007; Şenol et al., 2011). Some *Helichrysum* species are also found in Southwest Asia, southern India, Sri Lanka and Australia (Lourens et al.,2008). *Helichrysum* (Asteraceae) members of the genus are usually aromatic herbs or dwarf perennial shrubs, (Van Vuuren et al., 2006) grown in a wide elevation range from sea level to 1700 m, preferably on sandy or loamy soils (Perrini et al., 2009 ; Mancini et al., 2011 ; Leonardi et al., 2013).

It has been widely used as herbal tea and medicinal plant in folk medicine in Anatolia from past to present. *Helichrysum* species are commonly known as 'immortal flower' or 'golden herb' in Turkish and are widely used as herbal teas in Türkiye. Herbal teas are consumed in Türkiye and around the world for their various biological properties such as anti-inflammatory, antioxidant and antimicrobial activity (Albayrak et al., 2010). These effects of *Helichrysum* species, which are mostly used as diuretics and to eliminate kidney stones in our country, are due to the flavonoids they contain. *Helichrysum* species also have antimicrobial (Sezik et al., 2001; Fujita et al., 1995), antibacterial, antiviral, antifungal (Aslana et al., 2006), antioxidant (Schinella et al., 2002 ; Apak, 2006), anti-inflammatory (Sezik et al., 2001; Fujita et al., 1995; Schinella et al., 2002) and larvicidal (Amer et al., 2006) effects on the health and safety of the population.

Secondary metabolites are of great importance in medicinal plants. Depending on the type of plant, growing conditions, collection times and many other internal or external factors, differences in the active substance may be observed. Secondary metabolites are divided into three main

***Sorumlu Yazar:** emine.yurteri@erdogan.edu.tr*

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categories: volatile oils, glycosides and alkaloids. Of these, volatile oils are formed by the combination of terpenoids and are used mainly as solvents, flavourings and perfumes. (Shuler, 1981). The genus *Helichrysum* is a unique source of a broad spectrum of secondary metabolites (Powell et al., 1965; Manitto et al., 1972; Lawrence, 1998; Appendino et al., 2007). According to studies, the flower petals, sepals, bracts and also the glandular trichomes on the stem leaves are the parts of the plant where essential oils are produced (Charles and Simon, 1991; Roussis et al., 2000; Bianchini et al., 2001; Angioni et al., 2003; Paolini et al., 2006).

In this study, the effects of ontogenetic variability on the essential oil composition of *H. pallasii* plants collected from its natural habitat in Köse district of Gümüşhane province during the flowering period were investigated.

MATERIAL AND METHODS

This study was conducted at the Department of Field Crops, Faculty of Agriculture, Recep Tayyip Erdoğan University in 2023. Voucher number; PZF1/1 *Helichrysum pallasii* was collected from the natural habitat of Kabaktepede village at an altitude of 1680 m in Köse district of Gümüşhane province of Türkiye. Stems, leaves and flower parts of the plants collected at the full bloom period were used as plant material (Figure 1).

Figure 1. *Helichrysum pallasii* Stem, Leaf and Flower appearance

Figure 2. *View of the preparation of Helichrysum pallasii plants for analysis*

The plants were dried in the shade and stored at +4 °C for analysis. Leaves, stems and flowers of the plant were ground separately in a coffee grinder, weighed 0.2 g before analysis, placed in GC tubes and read in the device (Figure 2).

Essential oil components were determined using Shimadzu model GC-MS (2010 Plus) in the Plant Analysis Laboratory of Recep Tayyip Erdoğan University, Faculty of Agriculture. SPME (Solid Phase Microextraction) method used by Yurteri

et al. (2021) was modified and used to determine essential oil components.

RESULTS AND DISCUSSION

As a result of the analysis of *Helichrysum pallasii*, a total of 58 components were detected in different parts of the plant (stem, leaf and flower). When these components were analyzed, the main components were methyl butyl phenyl acetate (16.04%), phtyone (11.05%), β-caryophyllene (10.47%), undecly alcohol (7.57%), δ-cadinene (7.36%), γ-cadinene (5.32%), hexadecane (5.24%), tetradecane (4.51%) (Table.1).

Table 1. Amounts of volatile components in different parts of *Helichrysum pallasii* (%)

Compounds	**R.I***	**Flower**	**Leaf**	**Stem**
Eucalyptol	1026	-	1.92	1.07
Camphor	1138	-	0.97	-
İsoborneol	1161	-	1.39	1.04
Dihydrocitronellol	1186	2.34	2.83	2.79
Dodecane	1195	0.57	0.74	-
Fenchyl acetate <-endo->	1215	-	1.08	-
Pentyallyl butyrate	1275	0.7	-	-
Bornly acetate	1281	-	4.42	3.82
Tridecane	1294	1.42	1.65	1.63
α-Copaene	1372	0.94	1.1	1.59
Undecly alcohol	1386	7.57	6.35	6.68
Tetradecane	1394	3.92	4.51	4.27
α-Gurjunene	1401	0.56	-	-
β-Caryophyllene	1416	10.47	2.94	4.5
Aromadendrene	1436	-	-	1.48
Geranly acetone	1448	-	4.01	4.46
α-Humulene	1450	1.14	-	3.44
γ-Declactone	1456	-	-	1.01
Alloaromadendrene	1458	1.38	1.13	0.89
Lauryl alcohol	1456	1.04	1.64	-
Germancrene D	1473	1.1	-	-
α-Patchoulene	1475	-	-	2.26
(E) -,β-Lonone	1482	-	1.74	-
Pentadecane	1493	2.16	2.26	2.22
α-Muurolene	1497	1.71	0.95	1.42
Methyl butyl phenyl acetate	1508	16.04	11.69	10.89
γ-Cadinene	1510	5.32	3.53	4.79
δ-Cadinene	1520	7.36	3.12	5.5
β-Sesquiphellandrene	1535	1.8	1.35	1.63
Nonaonate <isoamyl->	1540	0.68	-	0.68
Citronellyl butyrate	1545	0.65	1.06	1.12
γ-Undecalactone	1564	-	-	0.77
Caryophyllene oxide	1582	0.36	-	-

Continuation of Table 1

Compounds	R.I*	Flower	Leaf	Stem
Tridecyl alcohol	1586	3.3	2.16	2.15
Hexadecane	1593	3.69	5.24	4.27
Tetradecanal	1606	1.34	1.48	-
α-Acorenol	1616	0.7	-	-
α-,epi-Muurolol	1639	3.57	2.62	3.39
Furan-2- carboxylic acid <octyl-> ester	1656	1.03	1.09	1.32
α-Bisabolol oxide B	1664	-	0.73	-
β-Eudesmol	1649	1.89	-	-
Dihydrojasmonate < methyl - >	1648	-	-	0.39
γ-Eudesmol	1652	1.5	-	0.59
γ-Dodecalactone	1663	-	0.8	-
Heptadecane	1692	-	4.25	2.66
α-Bisabolol	1707	-	0.87	-
Farnesol <-cis,cis->	1723	-	0.8	0.47
Farnesal	1744	0.67	0.96	-
Caprylate <-octyl->	1763	-	0.75	-
Pentadecanol	1784	0.48	-	-
Octadecane	1792	1.74	2.57	1.72
Phtyone	1838	6.3	11.05	7.18
Nonadecane	1890	0.47	-	1.13
Hexadec-6-enoic acid - <16-hydroxy - >	1912	-	1.44	1.33
Palmitate <-methyl->	1918	0.48	-	0.73
Geranly benzoate	1962	-	0.8	-
Phtyol acetate	2214	-	-	1.14

* Kovats Retention Index (R.I).

As can be seen in Table 1, when the different parts of the plant were considered separately, 36 components were detected in the flower, 39 in the leaf and 38 in the stem. The prominent constituents in the flower, leaf and stem parts of the plant, respectively; Undecly alcohol (7.57% - 6.35% - 6.68%), tetradecane (3.92% - 4.51% - 4.27%), β-caryophyllene (10.47% - 2.94% - 4.5%), methyl butyl phenyl acetate (16.04% - 11.69% - 10. 89%), γ-cadinene (5.32% - 3.53% - 4.79%), δ-cadinene (7.36% - 3.12% - 5.5%), tridecyl alcohol (3.30% - 2.16% - 2. 15%), hexadecane (3.69% - 5.24% - 4.27%), α-,epi-muurolol (3.57% - 2.62% - 3.39%) and phtyone (6.30% - 11.05% - 7.18%) (Table 1.). When we examined the components that are not common in the stem, leaf and flower parts of the plant, but are specific to the plant part; the components that are not found in the leaf and stem but only in the flower; β-Eudesmol (1.89%), germancrene d (1.1%), pentyallyl butyrate (0.7%), α-acorenol (0.7%), α-gurjunene (0.7%). 89%), germancrene d (1.1%), pentyallyl butyrate (0.7%), α-acorenol (0.7%), α-gurjunene (0.56%), pentadecanol (0.48%), caryophyllene oxide (0.36%). The constituents found only in the leaves and not in the flowers and stems were (e)-,β-lonone (1.74 %), fenchyl acetate <-endo-> (1.08 %), camphor (0. 97%), α-bisabolol (0.87%), γ-dodecalactone (0.8%), geranly benzoate (0.8%), caprylate <-octyl-> (0.75%), α-bisabolol oxide b (0.73%). The compounds present only in the stem part and not in the flower and leaf part were α-patchoulene (2.26%), aromadendrene (1.48%), phtyol acetate (1.14%), γ-declactone (1.01%), γ-undecalactone (0.77%), dihydrojasmonate < methyl - > (0.39%). When we look at the other components that are not common, the components that are not found in the stem part of the plant but found in the flower and leaf part of the plant are; Tetradecanal (1.34% - 1.48%), lauryl alcohol (1.04% - 1.64%), farnesal (0.67% - 0.96%), dodecane (0.57% - 0.74%), respectively. The constituents not found in the flower part of the plant but found in the leaves and stems

were geranly acetone (4.01% - 4.46%), bornly acetate (4.42% - 3.82%), heptadecane (4.25% - 2. 66 %), eucalyptol (1.92 % - 1.07 %), hexadec-6-enoic acid - <16-hydroxy - > omega lactone (1.44 % - 1.33 %), ısoborneol (1.39 % - 1.04 %), farnesol <-cis,cis-> (0.8 % - 0.47 %). The components not found in the leaf part of the plant but found in the flower and stem parts of the plant were; α-humulene (1.14 % - 3.44 %), γ-eudesmol (1.5 % - 0.59 %), nonaonate <isoamyl-> (0.68 % - 0.68 %), nonadecane (0.47 % - 1.13 %), palmitate <-methyl-> (0.48 % - 0.73 %), respectively. Formisano et al., (2009), In their study on leaves and flowers of *Helichrysum pallasii* in Lebanon, hexadecanoic acid (16.2%), (Z,Z)-9,12-octadecadienoic acid (6.8%), tetradecanoic acid (2.6%) and (Z)-caryophyllene (4. 2%) were the main components of the oil obtained from the leaves, while hexadecanoic acid (14.7%), (Z,Z)-9,12-octadecadienoic acid (14.2%), (Z)-caryophyllene (3.6%) and *∂*-cadinene (3.1%) dominated in the oil obtained from the flowers. The other compounds obtained were γ-cadinene 0.5 % - 3.5 %, *δ*-cadinene 2.5 % - 3.1 %, α-humulene 2.9 % - 2.1 %, α-muurolene 0.3 % - 0.5 %, alloaromadendrene 0.6 % - 0 % in leaves and flowers respectively.

The main components obtained from the flowers of *H. pallasii* collected in Armutlu district of Bayburt province were α-springene (34.89%), (-)-ısoledene (7.11%), δ-selinene (5.79%), aristolene (5.09%), β-caryophy (4.76%) and α-patchoulene (4.74%) (Yurteri et al., 2021). When the obtained results are compared with the study conducted by Formisano et al. (2009), they are different from the main components we found in our study, but when we look at the other components they found, the values are close to each other, although there are proportional differences in γ-cadinene, *δ*-cadinene, α-humulene, α-muurolene, alloaromadendrene. When compared with the study conducted by Yurteri et al. (2021), it was observed that they contained relatively different components. These differences may arise due to the variety and amount of bioactive substances found in medicinal and aromatic plants, the part of the plant used, post-harvest processing, and the methods used to obtain and analyze essential oils (Kaytanlıoğlu et al., 2021).

4. CONCLUSION

Helichrysum pallasii has been widely used as herbal tea and medicinal plant in folk medicine in Anatolia from past to present. *Helichrysum* species are commonly known as 'immortal flower' or 'golden herb' in Turkish and are among the plants commonly used as herbal tea in our country. It is possible to say that it is widely used in the treatment of many diseases today due to its many biological properties (anti-inflammatory, antioxidant and antimicrobial) due to the many components found in its essential oil. In our study, in which we aimed to investigate the effect of ontogeneti variability on the essential oil composition of *Helichrysum pallasii* collected from the natural habitat of Kabaktepede village at an altitude of 1680 m in Köse district of Gümüşhane province of Türkiye, it was revealed that there were differences in the components and their amounts in different parts of the plant (stem, leaf and flower). The prominent components were methyl butyl phenyl acetate (16.04%), phtyone (11.05%), β-caryophyllene (10.47%), undecly alcohol (7.57%), *δ*-cadinene (7.36%), γ-cadinene (5.32%), hexadecane (5.24%) and tetradecane (4.51%). There are very few studies on the volatile components of immortal species, which are very common in our natural flora. Our study will be an important scientific material for researchers working on this subject.

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