Nat. Volatiles & Essent. Oils, 2021; 8(2): 1-6
DOI: 10.37929/nveo.825372

NVEO Natural Volatiles & Essential Oils

RESEARCH ARTICLE

Chemical profile of the volatile compounds from *Marrubium cuneatum* Banks & Sol.

Mehmet Sina İçen[1,*], Betül Demirci[2], Fatih Demirci[2,3] and İlhan Gürbüz[4]

[1]Department of Pharmacognosy, Faculty of Pharmacy, İnönü University, 44280 Malatya, TURKEY
[2]Department of Pharmacognosy, Faculty of Pharmacy, Anadolu University, 26470 Eskişehir, TURKEY
[3]Faculty of Pharmacy, Eastern Mediterranean University, 99628 Famagusta, N. Cyprus, Mersin 10, TURKEY
[4]Department of Pharmacognosy, Faculty of Pharmacy, Gazi University, 06330 Ankara, TURKEY

*Corresponding author. Email: sina.icen@inonu.edu.tr

Submitted: 13.11.2020; Accepted: 05.04.2021

Abstract

Marrubium cuneatum Banks & Sol. is a perennial plant belonging to the Iran-Turan phytogeographical region, which is distributed in a limited region in the Middle East (Lebanon, Syria, Palestine, Turkey, Iraq and Iran). The chemical composition of the essential oil of *Marrubium cuneatum* Banks & Sol. (Lamiaceae) from Turkey was characterized. Hydro-distilled essential oil was analysed simultaneously by gas chromatography (GC) and gas chromatography-mass spectrometry (GC/MS), respectively. A total of 75 components representing 94.7% of the oil were determined; linaool (29.7%), caryophyllene oxide (9.8%), and β-caryophyllene (9.0%) were identified as the major compounds, to the best of our knowledge for the first time from Turkey.

Keywords: Lamiaceae, *Marrubium cuneatum*, volatiles, chemical composition

Introduction

The genus *Marrubium* (Lamiaceae) comprises about 40 species native to Europe, Asia and the Mediterranean region (Akgül et al., 2008). The genus is represented by 27 taxa in Turkey, including 17 endemic (Celep & Dirmenci, 2017). The *Marrubium* species, which are generally named as 'bozot' or 'bozotu' in Turkey, has been observed to be used for inflammation, diabetes, hypertension, intestinal pain, dyspepsia and haemorrhoids in the traditional medicine (Naghibi et al., 2005; El-Hilaly et al., 2003; Özüdoğru et al., 2011). As for the chemical composition of *Marrubium* species, they produce a large variation of flavonoids, polyphenols, steroids, diterpenoids and phenylpropanoids (Meyre-silva & Cechinel-Filho, 2010). Important biological activities are due to the presence of phytochemicals mentioned above, such as antioxidant, wound healing (Amri et al., 2017), antimicrobial and cytotoxic activity (Hayet et al., 2007), antidiabetic (Boudjelal et al., 2012), anti-inflammatory activity (Sahpaz et al., 2002), antiprotozoal activity (Kırmızıbekmez et al., 2011) among others.

M. cuneatum is native to Iran, Turkey, Iraq, Lebanon-Syria and Palestine. Due to the fact that it spreads in a limited geography, studies are very limited. However, some traditional uses have been recorded in the literature. The flowering part of the plant was used to treat haemorrhoids by compressing the decoction (El Beyrouthy et al., 2012) in Lebanon. In Turkey an infusion that prepared from the leaves of *M. cuneatum* were used to treat abdominal pain (Tetik et al., 2013). The only reports on the essential oils, from plants collected from Iran and Lebanon have been published (Baher Nik et al., 2004; Grassia et al., 2006).

In the present study, composition of essential oil of *M. cuneatum* from Turkey was evaluated, and was compared with the previous results from Iran and Lebanon. To the best of our knowledge, this study is the first report on the *M. cuneatum* Banks & Sol. volatiles from Turkish specimens.

DOI: 10.37929/nveo.825372

Materials and Methods

Plant material and isolation of essential oil

The aerial parts of *Marrubium cuneatum* were collected at the flowering stage from Malatya, Turkey and identified by Prof. Dr. Turan Arabacı. A voucher specimen with the deposition number SI 1001 is stored in the Faculty of Pharmacy Herbarium, İnönü University. The air-dried aerial parts of the plant were hydro-distilled for over 3 h using Clevenger-type apparatus to give a small amount of essential oil, which was trapped in *n*-hexane. The volatiles of the essential oil were analysed both by GC-FID, and GC/MS.

Chromatospectral analyses

The analysis conditions were as previously reported (Demirci et al., 2017). The analyses were performed using an Agilent 5975 GC/MSD system. The analysis results are listed in Table 1.

Determination of the volatile components were performed by comparison of their relative retention times (RRT) with those of original samples or by comparison of their relative retention index (RRI) to series of *n*-alkanes. Computer matching using Wiley GC/MS Library, MassFinder 3 Library among others were performed (McLafferty & Stauffer, 1989; Koenig et al., 2004) and *in-house* "Başer Library of Essential Oil Constituents" built up by authentic compounds of oils, also MS literature data (Joulain & Koenig, 1998; ESO, 2000), was used for the characterization.

Results and Discussion

Due to a relatively low yield, the volatiles were trapped in *n*-hexane. Seventy-five components representing 94.7% of the essential oil were identified and characterized in the present study. Linaool (29.7%), caryophyllene oxide (9.8%) and β-caryophyllene (9.0%) were determined as major components.

In recent studies on *M. cuneatum* essential oil, Germacrene D (15.6%), spathulenol (6.5%) and hexadecanoic acid (6.5%) were determined as major components from Lebanon (Grassia et al., 2006) while bicyclogermacrene (39.7%) and germacrene D (24.1%) were determined as major components of the essential oil obtained from Iran (Baher Nik et al., 2004).

Table 1. The Composition of *Marrubium cuneatum* volatiles

RRI	Compound	%
1174	Myrcene	0.5
1203	Limonene	0.1
1225	(*Z*)-3-Hexenal	0.1
1244	2-Pentyl furan	0.1
1266	(*E*)-β-Ocimene	0.2
1280	*p*-Cymene	0.1
1304	1-octen-3-one	0.1
1393	3-Octanol	0.1
1400	Nonanal	0.1
1452	1-Octen-3-ol	0.5
1492	Cyclosativene	0.1
1495	Bicycloelemene	0.5
1497	α-Copaene	0.1
1506	Decanal	0.2

DOI: 10.37929/nveo.825372

1535	β-Bourbonene	0.8
1538	7,8-Dihydrolinalool	0.3
1553	Linalool	29.7
1565	Linalyl acetate	8.2
1589	β-Ylangene	0.3
1597	β-Copaene	0.3
1600	β-Elemene	0.3
1612	β-Caryophyllene	9.0
1631	Hexyl tiglate	0.1
1659	γ-Gurjunene	0.1
1668	(*Z*)-β-Farnesene	0.5
1669	Sesquisabinene	0.3
1687	α-Humulene	0.7
1704	γ-Muurolene	0.2
1706	α-Terpineol	0.1
1719	Borneol	0.1
1726	Germacrene D	3.9
1742	β-Selinene	0.4
1755	Bicyclogermacrene	1.4
1765	Geranyl acetate	0.2
1773	δ-Cadinene	0.3
1776	γ-Cadinene	0.1
1798	Methyl salicylate	0.1
1808	Nerol	0.2
1838	(*E*)-β-Damascenone	tr
1849	Calamenene	0.1
1857	Geraniol	0.2
1868	(*E*)-Geranyl acetone	0.6
1958	(*E*)-β-Ionone	0.6
1973	1-Dodecanol	0.2
2008	Caryophyllene oxide	9.8
2030	Methyl eugenol	2.0
2046	Norbourbonone	0.4
2071	Humulene epoxide-II	0.4
2095	Hexyl benzoate	0.2
2131	Hexahydrofarnesyl acetone	6.4
2144	Spathulenol	0.6
2148	(*Z*)-3-Hexen-1-yl benzoate	0.2
2156	α-Bisabolol oxide B	0.3
2170	(*E*)-2-Hexenyl benzoate	0.3
2179	3,4-Dimethyl-5-pentylidene-2(5H)-furanone	0.3
2200	3,4-Dimetil-5-pentyl-5H-furan-2-one	0.5
2226	Methyl hexadecanoate (=*Methyl palmitate*)	0.2
2232	α-Bisabolol	0.4
2255	α-Cadinol	0.2
2298	Decanoic acid	0.1

DOI: 10.37929/nveo.825372

2300	Tricosane	0.5
2316	Caryophylla-2(12),6(13)-dien-5β-ol (=*Caryophylladienol I*)	0.2
2324	Caryophylla-2(12),6(13)-dien-5α-ol (=*Caryophylladienol II*)	0.7
2325	Octyl benzoate	0.2
2384	Farnesyl acetone	tr
2384	1-Hexadecanol	0.3
2389	Caryophylla-2(12),6-dien-5α-ol (=*Caryophyllenol I*)	1.0
2392	Caryophylla-2(12),6-dien-5β-ol (=*Caryophyllenol II*)	1.8
2456	(*Z*)-9-Methyl octadecanoate (=*Methyl oleate*)	0.1
2503	Dodecanoic acid	0.2
2622	Phytol	0.4
2670	Tetradecanoic acid	1.1
2700	Heptacosane	0.3
2822	Pentadecanoic acid	0.1
2931	Hexadecanoic acid	3.4
	Total	94.7

RRI: Relative retention indices calculated against *n*-alkanes. % calculated from FID data. tr Trace (< 0.1 %)

According to the literature survey, the major components were spathulenol (15.8%) and β-caryophyllene (9.0%) for *M. globosum* subsp. *globosum* oil (Sarıkürkçü et al., 2008), β-caryophyllene (23.2%) and (*Z*)-β-farnesene (13.5%) for *M. bourgaei* ssp. *caricum* oil (Demirci et al., 2004), hexadecanoic acid (15.4%) and germacrene D (11.1%) for *M*. *parviflorum* subsp. *oligodon* oil (Bal et al., 1997), hexadecanoic acid (33.3%) and hexahydrofarnesyl acetone (6.4%) for *M*. *bourgaei* ssp. *bourgaei* oil (Kürkçüoğlu et al., 2007), (Z)-β- farnesene (20.2 %) and nonacosane (18.5%) for *M. anisodon* oil (Kırımer et al., 2015). Also 9 species of *Marrubium* genus collected from the Aegean province were evaluated for their essential oil chemistry, where the major constituents were determined as (*Z*)-β-farnesene, germacrene D, β-caryophyllene, caryophyllene oxide and bicyclogermacrene with variable percentages (Akbulut et al., 2020). When the major components of the essential oils were compared to other *Marrubium* species from Turkey, the content of linalool in our sample is remarkable.

Linalool showed anti-inflammatory, antinociceptive and antihyperalgesic activities in different animal models, and also its spasmolytic effect and antioxidant properties were reported (Peana et al., 2008). Intraperitoneal administration of caryophyllene oxide at the doses of 12.5 and 25 mg/kg showed significant peripheral analgesic, along with anti-inflammatory, activity on experimental animal model (Chavan et al., 2010). β-Caryophyllene showed significant therapeutic potential in several assays such as antioxidant, anti-inflammatory, antimicrobial and anticancer (Sharma et. al., 2016). The biological activity of *M. cuneatum* essential oil was previously reported, where the antimicrobial activity of essential oil was evaluated against eight selected Gram-positive and Gram-negative bacteria by *in vitro* paper-disc diffusion method, where the activity results in active when compared with antimicrobial standards (Grassia et al., 2006).

Conclusion

The volatile composition was compared with the previous results obtained from other localities, new components were added to the current knowledge. Further detailed studies are needed to evaluate the biological and medicinal properties of *M. cuneatum*.

DOI: 10.37929/nveo.825372

ACKNOWLEDGEMENT

This work was presented at the "International Symposium on Advances in Lamiaceae Science", April 26-29, 2017 Antalya, Turkey (İçen et al., 2017).

CONFLICTS OF INTEREST

The authors have no conflicts of interest to declare.

REFERENCES

Akgül, G., Ketenoğlu, O., Pınar, N.M. Kurt, L. (2008). Pollen and seed morphology of the genus *Marrubium* (Lamiaceae) in Turkey*. Annales Botanici Fennici*, *45*(1), 1-10.

Amri, B., Martino, E., Vitulo, F., Corana, F., Kaâb, L.B.B., Rui, M., Rossi, D., Mori, M., Rossi, S., Collina, S. (2017). *Marrubium vulgare* L. leave extract: Phytochemical composition, antioxidant and wound healing properties. *Molecules*, *22*(11), 1851-1869.

Baher Nik, Z., Mirza, M., Shahmir, F. (2004). Essential oil of *Marrubium cuneatum* Russell and its secretory elements. *Flavour and Fragrance Journal*, *19*(3), 233-235.

Bal, Y., Kaban, S., Kırımer, N., Başer, K.H.C. (1999). Composition of the essential oil of *Marrubium parviflorum* fisch. et mey. subsp. *oligodon* (boiss.) seybold. *Journal of Essential Oil Research*, *11*(3), 300-302.

Boudjelal, A., Henchiri, C., Siracusa, L., Sari, M., Ruberto, G. (2012). Compositional analysis and in vivo anti-diabetic activity of wild Algerian *Marrubium vulgare* L. infusion. *Fitoterapia*, *83*(2), 286-292.

Celep, F., Dirmenci, T. (2017). Systematic and Biogeographic overview of Lamiaceae in Turkey. *Natural Volatiles and Essential Oils*, *4*(4), 14-27.

Chavan, M.J., Wakte, P.S., Shinde, D.B. (2010). Analgesic and anti-inflammatory activity of Caryophyllene oxide from *Annona squamosa* L. bark. *Phytomedicine*, *17*(2), 149-151.

Demirci, B., Başer, K.H.C., Kırımer, N. (2004). Composition of the essential oil of *Marrubium bourgaei* ssp. *caricum* PH Davis. *Journal of Essential Oil Research*, *16*(2), 133-134.

Demirci, B., Yusufoğlu, H.S., Tabanca, N., Temel, H.E., Bernier, U.R., Agramonte, N.M., Alqasoumi, S.I., Al-Rehaily, A.J., Başer, K.H.C., Demirci, F. (2017). *Rhanterium epapposum* Oliv. essential oil: Chemical composition and antimicrobial, insect-repellent and anticholinesterase activities*, Saudi Pharmaceutical Journal*, *25*, 703-708.

Demiröz Akbulut, T., Demirci, B., Baykan, S. (2020). Essential oils of *Marrubium* L. taxa from aegian province of Turkey. *Journal of Essential Oil Research*, *32*(6), 485-493.

El-Hilaly, J., Hmammouchi, M., Lyoussi, B. (2003). Ethnobotanical studies and economic evaluation of medicinal plants in Taounate province (Northern Morocco). *Journal of Ethnopharmacology*, *86*(2-3), 149-158.

El Beyrouthy, M., Dhifi, W., Arnold-Apostolides, N. (2012). Ethnopharmacological survey of the indigenous Lamiaceae from Lebanon. In: *International Symposium on Medicinal and Aromatic Plants*, *997*, 257-276.

ESO (2000). The Complete Database of Essential Oils, Boelens Aroma Chemical Information Service, The Netherlands.

Grassia, A., Senatore, F., Arnold, N. A., Bruno, M., Piozzi, F., Rigano, D.,Formisano, C. (2006). Chemical composition and antimicrobial activity of the essential oils from aerial parts of two *Marrubium* sp. (Lamiaceae) growing wild in Lebanon. *Polish Journal of Chemistry*, *80*(4), 623-628.

Hayet, E., Samia, A., Patrick, G., Ali, M.M., Maha, M., Laurent, G., Mighri, Z., Mahjoub, L. (2007). Antimicrobial and cytotoxic activity of *Marrubium alysson* and *Retama raetam* grown in Tunisia. *Pakistan Journal of Biological Sciences*, *10*(10), 1759-1762.

DOI: 10.37929/nveo.825372

İçen, M.S., Demirci, B., Demirci, F., Gürbüz, İ. (2017). The volatile components of *Marrubium cuneatum* Banks & Sol. From Turkey. In: *International Symposium on Advances in Lamiaceae Science*, *4*, 112.

Joulain, D., Koenig, W.A. (1998). The Atlas of Spectra Data of Sesquiterpene Hydrocarbons, EB-Verlag, Hamburg.

Kırımer, N., Kürkçüoğlu, M., Akgül, G., Başer, K.H.C., Mahmoud, A.A. (2015). Composition of the Essential Oil of *Marrubium anisodon* C. Koch of Turkish Origin. *Records of Natural Products*, *9*(2), 234-236.

Kırmızıbekmez, H., Atay, İ., Kaiser, M, Yeşilada, E., Taşdemir, D. (2011). In vitro antiprotozoal activity of extracts of five Turkish Lamiaceae species. *Natural Product Communications*, *6*(11), 1697-1700.

Koenig, W.A., Joulain, D., Hochmuth, D.H. (2004). Terpenoids and Related Constituents of Essential Oils, MassFinder 3, Hamburg, Germany.

Kürkçüoglu, M., Başer, K.H.C., Tosun, A., Doğan, E., Duman, H. (2007). Essential oil composition of an endemic species of Turkey: *Marrubium bourgaei* Boiss. ssp. *bourgaei* (Labiatae). *Journal of Essential Oil Research*, *19*(1), 34-36.

McLafferty, F.W., Stauffer, D.B. (1989). The Wiley/NBS Registry of Mass Spectral Data, John Wiley and Sons, New York 1989.

Meyre-Silva, C., Cechinel-Filho, V. (2010). A review of the chemical and pharmacological aspects of the genus *Marrubium*. *Current Pharmaceutical Design*, *16*(31), 3503-3518.

Naghibi, F., Mosadegh, M., Mohammadi, M.S., Ghorbani, A. (2005). Labiatae family in folk medicine in Iran: from ethnobotany to pharmacology. *Iranian Journal of Pharmaceutical Research*, *2*, 63-79.

Özüdoğru, B., Akaydın, G., Erik, S., Yeşilada, E. (2011). Inferences from an ethnobotanical field expedition in the selected locations of Sivas and Yozgat provinces (Turkey). *Journal of Ethnopharmacology*, *137*(1), 85-98.

Peana, A.T., Moretti, M.D., Watson, R., Preedy, V. (2008). Linalool in essential plant oils: pharmacological effects. *Botanical Medicine in Clinical Practice*, *10*(55), 716-724.

Sahpaz, S., Garbacki, N., Tits, M., Bailleul, F. (2002). Isolation and pharmacological activity of phenylpropanoid esters from *Marrubium vulgare*. *Journal of Ethnopharmacology*, *79*(3), 389-392.

Sarıkürkçü, C., Tepe, B., Daferera, D., Polissiou, M., Harmandar, M. (2008). Studies on the antioxidant activity of the essential oil and methanol extract of *Marrubium globosum* subsp. *globosum* (Lamiaceae) by three different chemical assays. *Bioresource Technology*, *99*(10), 4239-4246.

Sharma, C., Al Kaabi, J.M., Nurulain, S.M., Goyal, S.N., Amjad Kamal, M., Ojha, S. (2016). Polypharmacological properties and therapeutic potential of β-caryophyllene: a dietary phytocannabinoid of pharmaceutical promise. *Current Pharmaceutical Design*, *22*(21), 3237-3264.

Tetik, F., Civelek, S., Çakılcıoğlu, U. (2013). Traditional uses of some medicinal plants in Malatya (Turkey). *Journal of Ethnopharmacology*, *146*(1), 331-346.