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Chemical Composition of the Essential Oil of the Subterranean Parts of *Valeriana alliariifolia*

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Abstract: The subterranean parts of *Valeriana alliariifolia* Adams were subjected to hydrodistillation and trace amount of essential oil was obtained. The chemical composition of the oil was identified by using capillary Gas Chromatography (GC) and GC/MS simultaneously. In total 68 constituents were identified, representing 87.6 % of the total oil. The essential oil was dominated by isovaleric acid (28.6%), which is followed by δ-guaiane (7.2%), α-humulene (4.7%), hexadecanoic acid (4.3%), valeric acid (3.7%) and humulene epoxide-II (3.6%) as the major components.

Keywords: *Valeriana alliariifolia;* essential oil; isovaleric acid; delta-guaiane; GC/MS.

1. Plant Source

The genus *Valeriana* L. (Valerianaceae) comprises more than 350 species throughout the world and represented by 12 species in the flora of Turkey [1,2]. The name *Valeriana* comes from the Latin "valere" meaning a state of being well or happy [3]. The roots of some *Valeriana* species comprise the drug "valerian" that has been used for sedative purposes since it was described by the ancient Greek and Roman physicians [4]. The therapeutic indication stated in ESCOP monograph for valerian is "relief of temporary mild nervous tension and/ or difficulty in falling asleep" [5]. Although most popularly *Valeriana officinalis* is used for those therapeutic purposes, *Valeriana alliariifolia* is also utilized as spasmolytic agent in some folkloric medicine, particularly in Turkey [6]. *V. alliariifolia* is a large shrub 1-5 m tall, perennial, glabrous plant with cylindrical and branched rhizome, simple leaves and white to pink flowers with 5-50 cm long petioles [2].

Underground parts of the plant material were collected from Uludağ, Bursa, Turkey in July 2009. The plant was identified by Dr. Galip Akaydın (Department of Biology Education, Hacettepe University, Ankara, Turkey). A voucher specimen (Akaydın, 12491) was kept at the Herbarium of the Department of Biology Education, Hacettepe University, Ankara, Turkey.

2. Previous Studies

There are few researches on *V. alliariifolia* about its biological activity and chemical composition. The neurotropic activity of a natural mixture of valepotriates (valiracyl), obtained from

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V.alliariifolia was investigated. Valiracyl, which is composed of 11 compounds; four of them accounted for 98% of the content and were identified as valtrate, isovaleroxyvaltrate hydrin, acetoxyvaltrate hydrin, and isovaleroxyhydroxydihydrovaltrate, was found to possess strong sedative effect on animals and it was thought that the neurotropic effects of it was apperantly related to the increased levels of GABA and decreased energy metabolism in the brain [7,8].

The iridoid composition of the roots of *V. alliariifolia* was well established [9,10]. Regarding the volatile principles, there exist two works in the literature reporting the chemical compositions of the essential oils isolated from both aerial and underground parts of the title plant collected from different locations [1,11]. The essential oil, obtained from the aerial parts of *V. alliarifolia* collected from Iran, is found to be dominated by *trans*-caryophyllene (38.9%), β-pinene (12.1%), α-pinene (9.9%), α-terpinene (9.5%), isoterpinolene (7.1%), 1,8-cineole (6.76%), 1-borneol (3.27%) and calarene (2.3%) [1]. According to the results of a very recent research conducted on the roots of the plant which is provided from Azerbaijan province, Iran, the major compounds are listed as (*Z*/*E*)-farnesyl acetate (9.3%), limonene (3.5%), neryl acetate (2.8%) and ar-turmerone (2.2%) [11]. Interestingly, the reported compounds of the oils, particularly of the roots, were quite distinct from any *Valeriana* species. These conflicting data prompted us to reinvestigate the chemical composition of *V. alliariifolia* collected from Turkey.

3. Present Study

The air-dried underground parts of the plant material were hydrodistilled for 3h using a Clevenger-type apparatus to produce a trace amount of essential oil which was trapped in *n*-hexane. The oil was analyzed subsequently by capillary GC and GC/MS. The individual components characterized are given in Table 1.

The GC-MS analysis was carried out with an Agilent 5975 GC-MSD system. Innowax FSC column (60 m x 0.25 mm, 0.25 μm film thickness) was used with helium as a carrier gas (0.8 ml/min). GC oven temperature was kept at 60°C for 10 min and programmed to 220°C at a rate of 4°C/min, and kept constant at 220°C for 10 min and then programmed to 240°C at a rate of 1°C/min. Split ratio was adjusted at 40:1. The injector temperature was set at 250°C. Mass spectra were recorded at 70 eV. Mass range was from *m/z* 35 to 450.

The GC analysis was carried out using an Agilent 6890N GC system. FID detector temperature was 300°C. To obtain the same elution order with GC-MS, simultaneous auto-injection was done on a duplicate of the same column applying the same operational conditions. Relative percentage amounts of the separated compounds were calculated from FID chromatograms. The analysis results are given in Table 1.

Identification of the essential oil components were carried out by comparison of their relative retention times with those of authentic samples or by comparison of their relative retention index (RRI) to series of *n*-alkanes. Computer matching against commercial (Wiley GC/MS Library, Adams Library, MassFinder 3 Library) and in-house "Başer Library of Essential Oil Constituents" built up by genuine compounds and components of known oils, as well as MS literature data was used for the identification [12-15].

This paper describes the chemical composition of the essential oil obtained from the underground parts of *V. alliariifolia* Adams growing wild in Turkey. Essential oil was obtained by hydrodistillation from the air-dried underground parts of *V. alliariifolia.* The drug contains trace amount of volatile oil obtained by hydrodistillation. In total 68 constituents were identified, representing 87.6 % of the total oil. The major constituents of the oil were determined as isovaleric acid (28.6%), δ-guaiane (7.2%), α-humulene (4.7%), hexadecanoic acid (4.3%), valeric acid (3.7%) and humulene epoxide-II (3.6%). Isovaleric acid is the compound responsible for the foul odour of the fermented *Valeriana* root.

Recently Samaneh et al. reported the volatile composition of the subterranean parts of *V. alliariifolia* which was collected from Azerbaijan province, Iran [15]. Totally 11 components were identified in the essential oil of *V. alliarifolia* root by them whereas 68 components were identified in Turkish *V. alliariifolia* by this work. Moreover significant differences were seen in the chemical compositions of two oils. The major element of Iranian *V. alliariifolia* essential oil was *(Z/E)*- farnesyl acetate (9.3%),

Table 1. The volatile oil composition of *Valeriana alliariifolia*

RRI	Compound	%	RRI	Compound	%
1000	Decane	0.7	1786	*ar*-Curcumene	0.1
1058	3-Hexanone	0.5	1808	2-Methl-2-butenoic acid	0.2
1087	2-Hexanone	0.9	**1815**	**Valeric acid**	**3.7**
1202	3-Hexanol	0.1	1827	(*E,E*)-2,4-Decadienal	2.5
	2-Hexanol	0.6	1849	Dihydro-β-ionone	0.6
1244	2-Pentyl furan	0.7	1849	Calamenene	0.7
1299	2-Methylbutyl isovalerate	0.6	1973	1-Dodecanol	0.1
1400	Nonanal	0.3	1977	Dihydro-β-ionol	0.1
1457	Hexyl isovalerate	0.2	2008	Caryophyllene oxide	1.0
1493	α-Ylangene	0.3	2041	Pentadecanal	0.4
1497	α-Copaene	0.4	2045	Humulene epoxide-I	0.4
1506	Decanal	0.1	2050	(*E*)-Nerolidol	0.2
1516	Theaspirane A	0.7	**2071**	**Humulene epoxide-II**	**3.6**
1535	β-Bourbonene	0.2	2077	1-Tridecanol	0.1
1544	α-Gurjunene	0.2	2081	Humulene epoxide-III	0.5
1553	Theaspiran B	0.5	2131	Hexahydrofarnesyl acetone	0.4
1596	α-Guaiene	2.0	2144	Spathulenol	0.6
1600	β-Elemene	1.0	2179	1-Tetradecanol	0.1
1612	β-Caryophyllene	1.0	2192	Nonanoic acid	0.2
1658	α-Patchoulene	0.4	2198	Thymol	0.2
1664	γ-Patchoulene	0.4	2239	Carvacrol	0.9
1684	**Isovaleric acid**	**28.6**	2256	Cadalene	0.8
1687	**α-Humulene**	**4.7**	2273	Selin-11-en-4α-ol	0.2
1688	Selina-4,11-diene	2.3	2298	Decanoic acid	0.1
1704	γ-Muurolene	0.7	2345	Galaxolide-I	0.1
1730	**δ-Guaiene**	**7.2**	2353	Galaxolide-II	t
1740	α-Muurolene	0.6	2503	Dodecanoic acid	0.5
1744	α-Selinene	1.1	2607	1-Octadecanol	0.1
1745	Selina-4(15),7(11)-diene	0.5	2622	Phytol	0.9
1766	1-Decanol	t	2670	Tetradecanoic acid	0.5
1773	δ-Cadinene	T	2700	Heptacosane	0.2
1776	γ-Cadinene	0.6	2822	Pentadecanoic acid	0.5
1779	(*E,Z*)-2,4-Decadienal	1.5	2900	Nonacosane	0.6
1785	7-*epi*-α-Selinene	2.6	**2931**	**Hexadecanoic acid**	**4.3**
				Total	**87.6**

RRI: Relative retention indices calculated against n-alkanes; %: calculated from FID data t: Trace (< 0.1 %)

which is followed by limonene (3.5%) neryl acetate (2.8%) and ar-turmerone (2.2%) and α-longipinene (2.1%) while none of these principles were detected in Turkish *V. alliariifolia* essential oil. When compared Iranian *V. alliariifolia* (I) and Turkish *V. alliariifolia* (T) essential oils in terms of all the components, it is clear that there is no any resemblance of their components except spathulenol (I: 0.7%, T: 0.6) and α-gurjunene (I: 1.3%, T: 0.2%).

In 2010, Taherpour et al. reported the volatile oil composition of the aerial parts of *V. alliariifolia* which was collected from Iran [1]. It is clearly evident that the chemical compositions of the essential oils obtained from the underground and the aerial parts were significantly different, if results of both studies were compared. The Iranian *V. alliariifolia* essential oil was dominated by β-caryophyllene (38.9%) while β-caryophyllene was detected in trace amounts (1.0%) in Turkish *V. alliariifolia*. On the other hand, isovaleric acid (28.6%), the main component of the Turkish *V. alliariifolia* essential oil, was almost undetectable in Iranian *V. alliariifolia* [1]. Furthermore none of the major components of *V. alliariifolia* from Iran and V. *alliariifolia* from Turkey resemble.

Notable differences were also observed between the essential oils obtained from the roots of *V. alliariifolia* and *V. officinalis* [16]. Thus, *V. officinalis* roots was reported to contain bornyl acetate (11.6%) as the chief constituent whereas this compound was not a component of *V. alliariifolia* essential oil. The noticeable compounds of *V. officinalis* essential oil such as valerenic acid (8.0%), *(Z)*-valernyl acetate (7.9%), acetoxyvaleranone (7.6%), (*E*)-caryophyllene (5.1%), spathulenol (4.7%), *allo*-aromadendrene (4.1%), kessane (3.3%) e*pi*-α-cadinol (2.8%) and *dehydro*-aromadendrene (2.7%)

were not present among the major components of the *V. alliarifolia* essential oil except for spathulenol (0.6%). Other than isovaleric acid (0.9%) and α-humulene (0.7%), the major components of *V. aliariifolia* root essential oil were not present in *V. officinalis* root essential oil.

These significant differences between the volatile principles of *V. alliariifolia* roots might arise from the different collection areas, the differences in collection seasons and misidentification of these volatile principles.

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References

[1] A.A. Taherpour, H. Maroofi, O. Bajelani, K. Larijani (2010). Chemical composition of the essential oil of *Valeriana alliariifolia* Adams of Iran, *Nat. Prod. Re*. **24**, 973-978.
[2] B.K. Richardson (1972). *Valeriana* L., In: Flora of Turkey and East Aegean Islands, ed: P.H. Davis Vol 4. Universtity Press, Edinburgh, pp. 550-558.
[3] E.A. Carlini (2003). Plants and the central nervous system, *Pharmacol. Biochem. Behav*. **75**, 501-512.
[4] X.Q. Gao, L. Björk (2000). Valerenic acid derivatives and valepotriates among individuals, varieties and species of *Valeriana*, *Fitoterapia*. **71**, 19-24.
[5] Kemper FH (ed) (2003). Valerian Root, In: E/S/C/O/P Monograph, European Scientific Cooperative on Phytotherapy. Thieme, New York p 539-546.
[6] F. Ozgokce, H. Ozcelik (2004). Ethnobotanical aspects of some taxa in East Anatolia, Turkey, *Econ. Bot,* **58** (4), 697-704.
[7] S. D. Trzhetsinkii, V. V. Dunaev, V. S. Tishkin, N. S. Fursa (1987). Neurotropic activity of *Valeriana alliarifolia*-derived valepotriates, *Khim. Farm. Zh,* **21** (11), 1344-1348.
[8] V. V. Dunaev, S. D. Trzhetsinskii, V. S. Tishkin, N. S. Fursa, V. I. Linenko, V. R. Stets (1987). Biological activity of the valepotriates isolated from *Valeriana alliariifolia* Adams, *Farmakol. Toksikol*. **50** (6), 33-37.
[9] H. Ebrahimzadeh, T. Radjabian, A. E. Tousi, V. Nikham, V. Mozaffarian (2008). Evaluation of some Iranian wild species from *Valerianaceae* as commercial sources of valepotriates, *J. Biol. Sci* **8** (3), 549-555.
[10] J. Hoelzl, U. Koch (1984). Constituents of *Valeriana alliariifolia*, *Planta Med*. **50** (5), 458.
[11] E.T. Samaneh, R. Tayebeh, E. Hassan, N. Vahid (2010). Composition of essential oils in subterranean organs of three species of *Valeriana* L., *Nat. Prod. Res*. **24** (19), 1834-1842.
[12] F. McLafferty, D. Stauffer (1989). The Wiley/NBS Registry of Mass Spectral Data, J Wiley and Sons. New York.
[13] W.A. Koenig, D. Joulain, D.H. Hochmuth (2004). Terpenoids and Related Constituents of Essential Oils. MassFinder 3, In: Convenient and Rapid Analysis of GCMS, ed: D.H. Hochmuth, Hamburg, Germany.
[14] D. Joulain, W.A. Koenig (1998). The Atlas of Spectra Data of Sesquiterpene Hydrocarbons, EB-Verlag, Hamburg.
[15] ESO 2000 (1999). The Complete Database of Essential Oils, Boelens Aroma Chemical Information Service. The Netherlands.
[16] A. Safaralie, S. Fatemi, F. Sefidkon (2008). Essential oil composition of *Valeriana officinalis* L. roots cultivated in Iran Comparative analysis between supercritical CO_2 extraction and hydrodistillation, *J. Chromatogr. A*. **1180**, 159-164.