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ESSENTIAL OIL COMPOSITION OF *Valeriana officinalis* SSP. *officinalis* GROWN IN LITHUANIA

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The application of valerian for its healthy properties is well documented [1–6]. Although the active components have not been fully characterized, they are generally believed to be the essential oil, the valepotriates and valerenic acid and its derivatives. The root and rhizome oil contents and composition of *V. officinalis* ssp. o*fficinalis* collected from Apuan Alps and Yugoslavian Karst [7], Bulgaria [8] or collected from different botanical gardens in Europe [3] have been reported. We studied the essential oil profile from roots and rhizomes of *Valeriana officinalis* cultivated in the experimental garden of the Lithuanian Institute of Horticulture in Babtai, Lithuania, and collected after flowering in October 2004. The roots and rhizomes were separated from the herb and dried at 40°C in the dark. Hydrodistillation in a Clevenger-type apparatus was used for the complete isolation of volatile compounds from fresh and dried comminuted valerian roots and rhizomes [9]. The oils were analyzed by a *Fisons 8000* GC apparatus. A DB-5 fused silica capillary column (50 m × 0.32 mm i.d., 0.25 μm film thickness) was used with helium as carrier gas at linear flow velocity of 40 cm/s at 50°C. The detector temperature was 320°C, and the oven temperature was programmed from 50°C (for 2 min) to 280°C (hold 10 min) at the rate of 5°C min^{-1}. A split/splitless injector was used at 250°C in the split mode at a ratio of 1:5. The content of the eluted compounds was expressed as a GC peak area percent; mean values were calculated from triplicate injections. GC-MS analyses were performed using a Perkin Elmer Clarus 500 system in the electron impact ionization mode at 70 eV; the mass range was *m/z* 29–550 using an Elite-5 MS column (30 m × 0.25 mm i.d., 0.25 μm film thickness). The oven temperature was programmed as described above. The carrier gas was helium, adjusted to a linear velocity of 36 cm/s at 50°C. Split mode was used at a ratio of 1:20 and an injector temperature of 250°C.

The identity of the components was assigned by comparison of their Kovats retention indices (KI) relative to C_8–$C_{30,32}$ *n*-alkanes (Sigma Chemical Co., St. Louis, MO), obtained on a nonpolar DB-5 column with those reported by Adams [10] and by comparison of their mass spectra with the data provided by the NIST (vers.1.7), NBS 75K/WILEY 275 and EPA/NIH mass spectral libraries and mass spectra with corresponding data of components of reference oils. Positive identification was assumed when a good match of mass spectrum and KI was achieved.

It was determined that total essential oil content was 0.20% (v/w) and 0.55% (v/w) on a fresh and dried weight basic, respectively. Most pharmacopoeia standards require that valerian must contain a minimum of 0.5% essential oil based on dry weight and a valerian acid and derivatives content not less than 0.17% (calculated as valerenic acid) [11]. High quality material was reported to contain 1.0–1.5% essential oil and ≥ 0.5% valerenic acid [2, 6]. Only few studies have been conducted on fresh material, with the most recent published report finding approx. 0.25% essential oil [12]. In total, 93 constituents were identified in valerian essential oil by capillary GC and GC–MS (Table 1). The compounds are listed in order of their elution time on a DB-5 column, which accounted for 96.4% (fresh) and 95.9% (dried) of the total peak area of the chromatographic profiles in the examined samples. The major constituents in the volatile oils were characteristic for the widespread *V. officinalis* species; however, their percentages were quite different as compared with published results [2, 3, 5–8]. The *Valeriana officinalis* analyzed in the present study depends on the bornyl acetate chemotype, which constituted 15.6% and 15.4% in fresh and dried herb, respectively. Other quantitatively important components are camphene (8.6%; 6.9%), α-fenchene (8.2%; 5.6%), myrtenyl acetate (2.7%; 4.1%), δ-elemene (3.4%; 2.9%), β-phellandrene (3.5%; 1.9%), hinesol (2.9%; 3.1%), valerianol (2.3%; 2.6%), valeranone (0.4%; 7.1%), valerenal (5.6%; 7.3%), α-kessyl acetate (2.1%; 2.1%), and hexadecanoic acid (1.6%; 3.9%). Some changes in the percentage composition of volatile constituents were detected after drying.

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TABLE 1. Composition of Essential Oil Isolated from Roots and Rhizomes of *Valeriana officinalis* Grown in Lithuania

Constituent	KI on DB5[c]	GC peak area[a], %		Constituent	KI on DB5[c]	GC peak area[a], %	
		fresh	dried			fresh	dried
Tricyclene	927	0.1	Tr.[d]	α-Humulene[b]	1473	1.0	1.2
α-Thujene[b]	929	0.1	0.1	*allo*-Aromadendrene	1478	0.1	0.3
α-Pinene[b]	938	5.2	2.8	γ-Muurolene	1481	0.2	0.2
α-Fenchene[b]	953	8.2	5.6	*ar*-Curcumene*	1485	0.2	0.1
Camphene[b]	953	8.6	6.9	Germacrene D	1490	1.1	0.8
Sabinene[b]	974	0.3	0.1	(*Z*)-β-Guaiene	1492	0.5	0.5
β-Pinene[b]	980	1.5	1.2	α-Zingiberene	1499	1.1	1.0
Myrcene	992	0.1	Tr.	α-Farnesene	1506	0.1	0.2
α-Phellandrene[b]	1006	0.1	Tr.	(*E*)-β-Guaiene	1508	0.2	0.2
α-Terpinene[b]	1019	0.1	0.1	β-Bisabolene	1516	0.1	0.1
p-Cymene[b]	1027	0.1	0.1	α-Bulnesene	1524	0.3	0.2
d-Limonene[b]	1031	1.5	0.5	Bornyl isovalerate	1529	0.1	0.1
β-Phellandrene[b]	1032	3.5	1.9	δ-Cadinene	1534	1.0	1.2
1,8-Cineole[b]	1033	Tr.	Tr.	α-Cadinene	1541	0.2	0.1
γ-Terpinene[b]	1062	0.6	0.2	(-)-Pacifigorgiol*	1544	0.4	0.3
Terpinolene[b]	1090	0.1	0.1	Kessane	1546	1.3	1.3
Linalool[b]	1104	0.1	N.d.[e]	Elemol	1551	0.7	0.5
Terpinen-1-ol	1137	Tr.	N.d.	Myrthenyl isovalerate	1558	0.3	0.7
Camphor[b]	1146	Tr.	N.d.	Faurinone*	1569	0.1	0.3
Isoborneol[b]	1153	0.1	Tr.	Maaliol*	1571	0.7	0.6
Borneol[b]	1170	0.5	0.2	Ledol	1574	0.6	0.4
Terpinen-4-ol[b]	1181	0.5	0.3	Spathulenol	1584	1.1	1.6
α-Terpineol[b]	1193	0.1	0.1	Hinesol	1635	2.9	3.1
Myrtenol[b]	1198	0.1	0.1	β-Eudesmol	1646	0.8	0.8
(*Z*)-Carveol	1231	0.1	0.05	α-Eudesmol	1651	1.0	0.3
Thymol methyl ether	1236	0.1	0.1	Valerianol	1657	2.3	2.6
Carvacrol methyl ether	1246	0.1	0.1	Valeranone	1684	0.4	7.4
(*Z*)-Anethole*	1258	Tr.	N.d.	α-Bisabolol	1694	0.7	0.1
Bornyl acetate[b]	1293	15.6	15.4	α-Kessyl alcohol	1703	0.1	0.1
Thymol[b]	1298	0.2	0.3	Valerenal	1727	5.6	7.3
(*E*)-Sabinyl acetate	1319	0.1	0.1	Valerenol	1734	0.9	0.6
Myrtenyl acetate[b]	1329	2.7	4.1	Eugenyl isovalerate	1750	0.1	0.1
δ-Elemene	1344	3.4	2.9	Benzyl benzoate	1763	0.1	0.1
α-Terpinyl acetate[b]	1352	0.4	0.3	Drimenol*	1773	0.1	0.1
Eugenol[b]	1357	0.1	0.1	(*E*)-Valerenyl acetate	1808	1.6	1.4
α-Ylangene	1369	Tr.	0.1	α-Kessyl acetate	1817	2.1	2.1
α-Copaene[b]	1378	0.1	N.d.	(*Z*)-Valerenyl acetate	1831	0.8	1.0
β-Patchoulene*	1386	0.2	0.2	Isoeugenyl isovalerate	1863	0.5	0.1
β-Elemene	1393	0.4	0.3	Valerenic acid	1871	0.9	1.6
Eudesma-2,6,8-triene	1403	0.1	0.2	Kessanyl acetate*	1882	1.1	0.1
α-Gurjunene	1410	0.3	0.4	Hexadecanoic acid	1913	1.6	3.9
2,5-Dimethoxy-*p*-cymene	1414	0.4	0.5	(*Z*)-Valerenyl isovalerate	2042	Tr.	Tr.
β-Caryophyllene[b]	1419	0.3	0.2	(*E*)-Valerenyl isovalerate	2056	0.2	0.5
γ-Elemene	1424	1.1	0.7	Monoterpene hydrocarbons		30.1	19.6
α-Guaiene	1435	1.1	0.8	Oxygenated monoterpenes		22.3	23.0
β-Gurjunene	1438	0.1	Tr.	Sesquiterpene hydrocarbons		15.7	15.3
γ-Patchoulene*	1449	Tr.	Tr.	Oxygenated sesquiterpenes		26.8	33.9
(*Z*)-β-Farnesene	1453	0.1	0.1	Others		1.6	3.9
α-Pathoulene*	1460	0.1	0.1	Total identified, %		96.4	95.9
γ-Gurjunene	1466	2.3	3.1	%RSD[f]		8.1	8.7

[a]Average GC peak area percentage of three replicates; [b]Identification confirmed by co-injection of reference compound; [c]Relative to C_8-$C_{30,32}$ *n*-alkanes on the DB5 column; [d]Tr.: ≤0.04%; [e]N.d.: not determined; [f]%RSD, average coefficient of variance of individual compounds from three replicate injections; *Tentative identification.

It was quite unexpected that cyclopentanoid sesquiterpene valeranone constituted only 0.6% of fresh valerian root, while in the dried valerian its content increased significantly and composed 7.4% of the whole collected oil. A decrease in the content of monoterpene hydrocarbons (the most volatile compounds) and an increase in some oxygenated sesquiterpene hydrocarbons (possibly due to oxidation) can be observed after drying.

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