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ESSENTIAL OIL COMPOSITION OF TWO SPECIES OF *SCUTELLARIA* AERIAL PARTS

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The chemical composition of essential oils obtained by hydrodistillation method from two plants of the genus *Scutellaria*, grown in Uzbekistan and used in folk medicine were comparatively investigated by GC/MS and FID. Overall individually thirty three constituents were identified in both of aerial parts of *S. adenostegia* and *S. comosa* essential oils, representing 94.4 and 97.0% of the total, respectively. The main components were determined as acetophenone (24.2%), eugenol (12.3%), caryophyllene oxide (8.9%), and *β*-caryophyllene (7.0%) in the oil of *S. adenostegia*. *β*-Caryophyllene (12.5%), phytol (11.4%), linalool (11.1%), acetophenone (10.4%), caryophyllene oxide (6.6%),1-hexanol (5.3%), and (*E*)-2-hexenal (5.1%) were found as major components in the *S. comosa* oil. The composition of the oils of *S. adenostegia* and *S. comosa* was being reported for the first time. The essential oils of *S. adenostegia* and *S. comosa* showed significant antimicrobial properties against *Bacillus subtilis*, moderate effect against *Salmonella enterica* and *Escherichia coli*.

Keywords: *Scutellaria adenostegia*; *Scutellaria comosa*; essential oil; GC/MS/FID; antibacterial activity.

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Introduction

The genus of *Scutellaria* L., skullcaps, "Ko'kamaron" (local name) which belongs to the family *Lamiaceae*, is represented by 360 species and is widely spread in mild, subtropical, and tropical regions of the world, including Europe, North America, and Eastern Asia [1]. Approximately 120 species and subspecies of the genus grow across the countries of Commonwealth of Independent States (CIS), mainly in the Caucasus Mountains and in Middle Asia [1, 2]. Skullcaps are perennial or, very rarely, annual grasses, rarely subshrubs or half-shrubs. Many of the skullcap species are decorative plants, some are medicinal herbs, but all belong to dyeing plants. In Uzbekistan, there are thirty eight species of the *Scutellaria* L. genus plants. It is used in Uzbekistan in treatment of inflammation, chorea, nervous tension and high-blood pressure [3]. Chemical composition of plants of the *Scutellaria* L. genus is diverse. Earlier, flavonoids, phenylpropanoids, phenolic acids, iridoids, clerodane diterpenoids, steroids, triterpenes, lignans, alkaloids, phytosterols, polysaccharides, tannin substances, essential oils, and other classes of natural compounds have been isolated from different species [1, 2, 4]. *S. adenostegia* Briq. is a perennial native plant growing on rocky and clay mountain slopes, dried up riverbeds and streams, rocky placers and gravels along the banks of the rivers of Tian-Shan, Pamir-AlayMountains (Central Asia). Previous phytochemical studies on this plant reported the isolation and identification of flavonoids [3]. *S. comosa* Juz. mainly occurring in the Tian Shan and Pamir-AlaiMountains, it is a perennial shrub species which endemic to the Central Asia. Flavonoids on this plant species have been extensively studied [3, 5]. Several authors reported on the study of essential oils of plants of *Scutellaria* genus [1, 6–10].

It was previously reported that essential oils isolated from plants of this genus possess antioxidant and antibacterial activities [10–14].In the literature, there is a report on the study of the component composition and antioxidant activity of essential oils of three species of plants of the genus *Scutellaria*, growing in Uzbekistan [10]. But until now, there are no published reports concerning the phytochemistry and biological activities of the essential oils of *S. adenostegia*and *S. comosa*. We have reported here the isolation and characterization of essential oils, which to the best of our knowledge, is the first investigation on volatile compositions of the aerial parts of two *Scutellaria* species.

Experimental

The aerial parts (stems, leaves, flowers) of *S. adenostegia* and *S. comosa* employed in this investigation were collected in the flowering stage (May, 2019) from Chust (41°00′00″ N 71°13′59.88″ E) and Turakurgan District (41°00′00″ N 71°30′56.88″ E) Namangan Region of Uzbekistan respectively. The plants were identified at the Flora of Uzbekistan Department, Institute of Botany (Uzbekistan) by Dr. O.T. Turginov. The voucher specimens of *S. adenostegia* (accession number (A.N.) N20190550) and *S. comosa* (A.N. N20190551) have been deposited at the Flora of Uzbekistan Department.*Isolation of the essential oil.*The air-dried aerial parts (moisture content was 11–13% w.b.) of the *S. adenostegia* and *S. comosa* were hydrodistilled three times (3×100 g each) for 3 h, using a Clevenger-type apparatus. Further hydrodistillation of plant raw materials did not lead to an increase in the yield of essential oil.The obtained essential oils were then dried using anhydrous sodium sulfate and stored at 4 °C in the dark until use. The essential oil content was calculated as a relative percentage (v/w) of the dry plant material.

GC and GC/MS analysis of essential oils.The qualitative and quantitative composition of the essential oils were determined on an Agilent 5977B MSD/8890A GC (Agilent Technologies, USA) gas chromatography-mass spectrometer equipped with flame ionization detector (FID) and an Agilent 7693A ALS autoinjector. The components of the mixture were separated on an Agilent DB-Wax quartz capillary column (30m×250μm×0.25 μm film thickness) in the following temperature mode: 50 °C (1 min) – 4 °C/min to 200 °C (6 min) – 15 °C/min to 250 °C (35 min). The samples were prepared in dichloromethane and 1.0 μL injected in splitting mode (50 : 1). The flow

rate of the mobile phase (H_2) was 1.1 mL/min. The injector temperature was 220 °C. MS conditions were as follows: ionization energy 70 eV, source temperature 230 °C, quadrupole temperature 150 °C. EI-MS spectra were obtained in the *m/z* range of 10–550 a.m.u.

FID was used for the quantification of the volatile compounds. The chromatographic conditions and the column were identical to those used for the GC/MS analysis. The injector temperature was 250 °C and the carrier gas was H_2at 1.1 mL/min.

Components of essential oils were identified by comparison of the chromatographic peaks retention times with those of authentic compounds analyzed under the same conditions, and by comparison of retention indices (as Kovats indices) with literature data [15].

Comparisons of MS fragmentation patterns with mass spectrum database search were performed using the Wiley Registry of Mass Spectral Data-9th Ed., NIST Mass Spectral Library (2011) and the Automated Mass Spectral Deconvolution and Identification System (AMDIS, Version 2.72) containing NIST14 Library. A C_9–C_{32}*n*-alkane standard solution (Agilent Technoligies, USA) was used for the determination of chromatographic retention indices (RI). Percent composition was obtained for each constituent on the basis of flame ionization detection analyses of the essential oils.

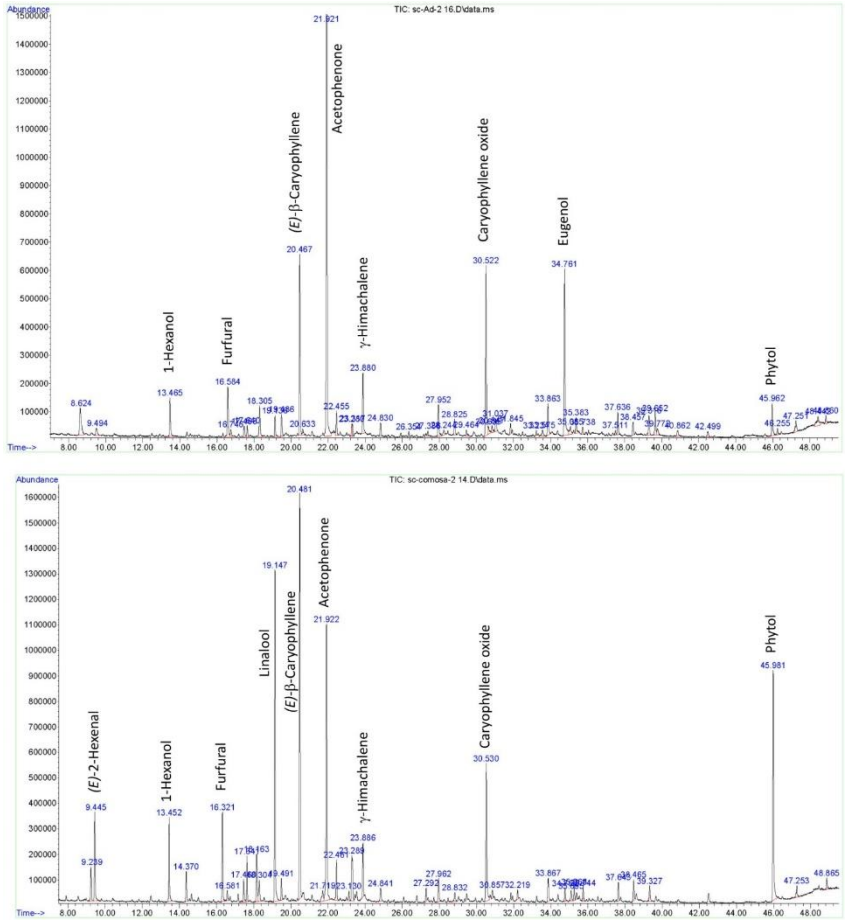
*Antimicrobial activity.*The essential oils antimicrobial activities were assessed against four pathogenic bacterial strains, two Gram-positive *Staphylococcus aureus* (MTCC 737) and *Bacillus subtilis* (NK-1, isolated from Natto) and two Gram-negative *Salmonella enteric* (ATCC 14028) and *Escherichia coli* (MTCC 1302). The above microorganisms were obtained from the Department of Microbiology of the Medical Institute of Surgut State University. The assay was performed using a 96-well microliter plate-based method with resazurin as a cell growth indicator following a previously used method with minor adjustments [16].

Statistical analysis. Results were expressed as mean ± standard deviation. Statistical comparisons were performed with Student's *t*-test using GraphPad Prism version 7.00. Differences were considered significant at $p < 0.05$.

Results and discussion

Chemical composition of essential oils. The average yields of essential oils obtained from three independent determinations by the hydrodistillation method were 0.19% (v/w; *S. adenostegia*; light yellow), and 0.17% (v/w; *S. comosa;* yellow) on a dry weight. The chemical compositions of the essential oils isolated from the air-dried aerial parts of plants were investigated by GC/MS/FID. Chromatographic profile of the volatiles from two *Scutellaria* species on the DB-Wax column is presented on Figure and Table 1 show the composition of compounds identified from the studied oil samples. Totally thirty three compounds representing 94.4% of the total oil were characterized in essential oil of *S. adenostegia*. The classes of compounds present in *S. adenostegia* were aldehydes and ketones (35.2%), phenols (16.0%), alcohols (12.4%), sesquiterpene hydrocarbons (12.3%) and oxygenated sesquiterpenes (11.0%).

The main compounds of *S. adenostegia* were acetophenone (24.2%), eugenol (12.3%), caryophyllene oxide (8.9%), and *β*-caryophyllene (7.0%). Moreover, high amount of 1-hexanol (3.8%), furfural (3.3%) and *γ*-himachalene (2.7%) were also observed in essential oil. It should be noted that acetophenone was also the main component of the essential oils of *S. immaculate* and *S. schachristanica* [10]. The total phenolic compounds content in essential oil of this plant was 13.3%, of which 11.8% was eugenol. *S. adenostegia* essential oil were rather poor in content of oxygenated monoterpenes (3.0%).



Chromatographic profile of the volatiles from essential oils of *Scutellaria adenostegia* Briq. (upper) and *Scutellaria comosa* Juz. (lower)

Table 1. Essential oil composition of two *Scutellaria* species

No	Compounds	RT, min	LRI*	*S.adenostegia*, (Conc., %)	*S. comosa*, (Conc., %)
1	1,8-Cineol	9.231	1192	–	0.9
2	(*E*)-2-Hexenal	9.495	1202	1.6	5.1
3	1-Hexanol	13.466	1341	3.8	5.3
4	(*Z*)-3-Hexen-1-ol,	14.364	1369	–	2.0
5	1-Octen-3-ol	16.315	1433	–	3.9
6	Furfural	16.584	1442	3.3	–
7	*α*-Cubebene	17.465	1472	0.7	0.8
8	Pentadecane	17.637	1500	–	1.4
9	Camphor	18.158	1516	–	1.7
10	Benzaldehyde	18.301	1520	1.8	1.1
11	Linalool	19.142	1549	1.1	11.1
12	1-Octanol	19.491	1560	1.9	1.5
13	(*E*)-*β*-Caryophyllene	20.475	1593	7.0	12.5
14	Acetophenone	21.923	1624	24.2	10.4
15	*α*-Caryophyllene	22.461	1644	1.1	1.7
16	*α*-Terpineol	23.319	1676	0.6	1.2
17	*γ*-Himachalene	23.886	1697	2.7	2.4
18	*δ*-Cadinene	24.841	1733	0.8	0.5
19	Grandlure II	27.290	1829	–	0.7
20	(*Z*)-Geranylacetone	27.387	1833	0.5	–
21	Benzyl alcohol	27.960	1856	2.1	1.3
22	2-Phenylethanol	28.835	1892	1.2	0.7
23	(*E*)-*β*-Ionone	29.476	1918	0.4	0.5

24	Caryophyllene oxide	30.546	1961	8.9	6.6
25	Alloaromadendrene oxide-(1)	30.866	1974	–	0.5
26	*o*-Cresol	31.038	1981	1.6	–
27	(*Z*)-Nerolidol	31.845	2015	0.6	–
28	4-Phenyl-3-buten-2-one	33.573	2092	0.4	–
29	Hexahydrofarnesyl acetone	33.882	2120	3.0	2.1
30	Eugenol	34.769	2145	12.3	1.3
31	*α*-Muurolol	35.101	2159	0.6	0.9
32	9*β*-Acetoxy-3,4,8-trimethyltricyclo[6.3.1.0(1,5)]dodec-3-ene	35.272	2167	–	0.8
33	*p*-Vinyl-guaiacol	35.393	2172	1.3	0.6
34	Caryophylla-4(12),8(13)-dien-5*α*-ol	37.647	2272	1.5	1.2
35	Dihydroactinidiolide	38.471	2309	1.3	1.8
36	8-Cedren-13-ol	39.335	2347	–	0.9
37	2,3-Dihydro-benzofuran	39.650	2361	2.1	–
38	Coumarin	40.863	2416	0.7	–
39	Pentacosane	42.528	2500	0.8	1.1
40	Phytol	45.601	2643	2.8	11.4
41	Acetovanillone	46.253	2675	0.8	–
42	Methoxyacetic acid 2-pentadecyl ester	47.260	2723	0.9	1.1
Oxygenated monoterpenes – 1, 9, 11, 16, 19, 35.				3.0	17.4
Sesquiterpene hydrocarbons – 7, 13, 15, 17, 18.				12.3	17.9
Oxygenated sesquiterpenes – 24, 25, 31, 32, 34, 36.				11.0	10.9
Aldehydes and ketones – 2, 6, 10, 14, 20, 23, 28, 29.				35.2	19.2
Alcohols – 3, 4, 5, 12, 21, 22, 27, 40.				12.4	26.1
Phenols – 26, 30, 33, 41.				16.0	1.9
Others – 8, 37, 38, 39, 42				4.5	3.6
Total				94.4	97.0
Identified compounds				33	33

*LRI– Linear retention indices on DB-Wax column;Conc., % calculated from FID data.

In the essential oil of *S. comosa* thirty five components, representing 97.0% of the total ones were characterized (Tab. 1). In the studied essential oil alcohols (26.1%) dominated. Aldehydes and ketones (19.2%), sesquiterpene hydrocarbons (17.9%), oxygenated monoterpenes (17.4%) and oxygenated sesquiterpenes (10.9%)were the remaining groups of components (Tab. 1).

β-Caryophyllene (12.5%), phytol (11.4%), linalool (11.1%), acetophenone (10.4%), caryophyllene oxide (6.6%), 1-hexanol (5.3%), and (*E*)-2-hexenal (5.1%) were found as the main constituents. Literature information indicated that *β*-caryophyllenewas the main component of the essential oils of *S. brevibracteata* [6], *S. sibthorpii* [7], *S. luteo-caerulea* [9], *S. albida*[12] and other species. Acetophenone was the main component of *S. schachristanica* and *S. immaculate* essential oil [10], while linalool was determined as a major component for *S. cypria* var. *elatior* [7]. In total, forty four volatile compounds were identified in two *Scutellaria* species from Uzbekistan. Aldehydes and ketones, alcohols, phenols and sesquiterpene hydrocarbons are the dominant components of the essential oil of the plant *S. adenostegia*. Sesquiterpene hydrocarbons and oxygenated monoterpenes were the major group of terpenes found in the essential oil of *S. comosa*. On the contrary, monoterpene hydrocarbons were not detected in both oil of *S. adenostegia*and *S. comosa*.

*Evaluation of antibacterial activity.*The literature contains data on the antimicrobial activity of essential oils of some plants of the *Scutellaria* genus [7, 11–14]. That is, we have studied the antibacterial properties of the isolated essential oils. The essential oils of *S. adenostegia* and *S. comosa* showed significant antimicrobial properties against *Bacillus subtilis* (318.0±8.62 and 401.1±14.49 μg/mL), moderate effect against *Salmonella enterica* (519.4±16.29 and 803.1±31.62 μg/mL) and *Escherichia coli* (528.3±14.63 and 802.4±32.57 μg/mL), and weak effect against *Staphylococcus aureus* (1297.6±34.78 and 1676.3±52.94 μg/mL) respectively (Table 2). We are inclined to believe that the antibacterial activity of essential oils is due to the presence of *β*-caryophyllene and eugenol in their composition [17, 18]. Pure *β*-caryophylleneshowed more pronounced antibacterial activity against Gram-positive bacteria than Gram-negative bacteria [17]. Overall, the antibacterial activity of the essential oils can be related to the content of many of the compounds identified in the oils, including eugenol and *β*-caryophyllene.

Table 2. Minimum inhibition concentration (MIC) of essential oils of *S. adenostegia and S. comosa* against four bacterial strains

Samples	MIC (μg/mL)[a]			
	E. coli	*S. aureus*	*B. substilis*	*S. enterica*
Streptomycin[b]	25.8±1.23	3.1±0.12	25.8±1.07	25.8±1.28
S. adenostegia.	528.3±14.63	1297.6±34.78	318.0±8.62	519.4±16.29
S.comosa.	802.4±32.57	1676.3±52.94	401.1±14.49	803.1±31.62

[a] All results are presented as mean±standard deviations for triplicate assays.
[b] Reference.

Conclusions

For the first time, the chemical composition of the essential oils grown in Uzbekistan of two *Scutellaria* species was studied. Acetophenone and *β*-caryophyllene are the dominant terpenes of the essential oils of *S. adenostegia* and *S. comosa*. On the other hand the high amount of eugenol and caryophyllene oxide in essential oil of *S. adenostegia* and linalool, phytol and caryophyllene oxide in essential oil of *S. comosa* were revealed. The essential oils of these plants showed significant antibacterial properties against *Bacillus subtilis*, moderate effect against *Salmonella enteric* and *Escherichia coli.*

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