Chromato-mass spectroscopy of tinctures from the underground part of Valerian plants growing in Zaporizhzhia region

V. M. Odyntsova *E,F, Yu. I. Korniievskyi A,D, D. Yu. Skoryna B,C, V. H. Korniievska B,D

Zaporizhzhia State Medical University, Ukraine

A – research concept and design; B – collection and/or assembly of data; C – data analysis and interpretation; D – writing the article; E – critical revision of the article; F – final approval of the article

Modern sedatives used in medical practice can be of both synthetic and natural origin. It is known that the best phytosedative is valerian. In the 18th century, valerian was included in all European pharmacopeias. High efficiency, good tolerability, and virtually no side effects ensure the widespread use of valerian and its phytopreparations in medical practice, especially for the treatment of geriatric patients. Despite this, valerian remains understudied due to its extreme polymorphism.

The aim of the work is to determine the component composition of valerian tinctures made from rhizomes with valerian roots of different species growing in the Zaporizhzhia region by gas chromatography and to carry out their comparative analysis.

Materials and methods. Samples of rhizomes with valerian roots made from medicinal plant raw materials of valerian according to the traditional production recipe (Tinctura Rhizomata cum radicibus Valerianae (1:5)) from different species of valerian growing in the Zaporizhzhia region were selected for experimental studies: *Valerian stolonifera* Czern. – Kantserivska Balka, Zaporizhzhia district, Zaporizhzhia region; *V. exaltata* Mikan. – Shyroke village, Vasylivskyi district, Zaporizhzhia region; *V. tuberosa* L. – Khortytsia Island, Zaporizhzhia; *V. collina* Wallr. – right bank of the Dnieper River, Zaporizhzhia. The component composition of valerian tinctures was studied using an Agilent 7890B gas chromatograph with a mass spectrometric detector 5977B.

Results. The component composition of tinctures from the underground part of valerian plants growing in the Zaporizhzhia region was identified and analyzed with chromato-mass spectrometry.

Conclusions. 55 components in valerian tincture from underground raw materials of *Valeriana stolonifera* Czern. were identified with gas chromatography: *V. exaltata* Mikan. – 48, *V. tuberosa* L. – 54, *V. collina* Wallr. – 51. Analyzing the obtained data, we can conclude that valerian tinctures differ in both quantitative and qualitative composition. Only compounds 7 and 9 coincide in tinctures from underground parts of all four types of valerian. Since the tinctures were made following the standard technology, the content of components in medicinal plant raw materials depends on the type, place of growth, environmental conditions, time of collection, drying of raw materials. The results of the study confirm the prospects of using the underground part of the studied plants of the genus Valerian to create new drugs and phytopreparations on their basis. However, given the extreme polymorphism of valerian for the introduction into the culture of promising species that grow in Ukraine, it is necessary to conduct more in-depth pharmacognostic and pharmacological studies of plants of this genus.

Key words: valerian tincture, gas chromatography, chromato-mass spectroscopy, component composition, quantitative content.

Current issues in pharmacy and medicine: science and practice 2022; 15 (3), 250–258

Хромато-мас-спектроскопія настойок із підземної частини рослин роду валеріана, що зростають у Запорізькому краї

В. М. Одинцова, Ю. І. Корнієвський, Д. Ю. Скорина, В. Г. Корнієвська

З-поміж сучасних седативних засобів, що використовують у медичній практиці, розрізняють препарати синтетичного та природного походження. Відомо, що кращим рослинним фітотранквілізатором є валеріана. У XVIII столітті валеріана була включена в усі європейські фармакопеї. Висока ефективність, хороша переносність і майже повна відсутність побічних ефектів забезпечують широке використання валеріани та її фітопрепаратів у медичній практиці, особливо для лікування геріатричних хворих. Незважаючи на це, валеріана лікарська залишається недостатньо вивченою через її надзвичайну поліморфність.

Мета роботи – методом газової хроматографії визначити компонентний склад настойок валеріани, виготовлених із кореневищ з коренями валеріани різних видів, які зростають у Запорізькому краї, та здійснити їх порівняльний аналіз.

Матеріали та методи. Для експериментальних досліджень обрали зразки настойок кореневищ із коренями валеріани, виготовлені з лікарської рослинної сировини валеріани за традиційною виробничою рецептурою (Tinctura Rhizomata cum radicibus Valerianae (1:5)) із різних видів валеріани, що зростають у Запорізькому краї: *Valeriana stolonifera* Czern. – Канцерівська балка, Запорізький район Запорізької області; *V. exaltata* Mikan. – с. Широке, Василівського району Запорізької обл.; *V. tuberosa* L. – о. Хортиця,

ARTICLE INFO

http://pharmed.zsmu.edu.ua/article/view/261819

UDC 615.451.1:615.322:582.971.3].074:543.51
DOI: 10.14739/2409-2932.2022.3.261819

Current issues in pharmacy and medicine: science and practice 2022; 15 (3), 250–258

Key words: valerian tincture, gas chromatography, chromato-mass spectroscopy, component composition, quantitative content.

***E-mail:** odyntsova1505@gmail.com

Received: 20.06.2022 // Revised: 05.07.2022 // Accepted: 20.07.2022

м. Запоріжжя; *V. collina* Wallr. – правий берег р. Дніпро, м. Запоріжжя. Компонентний склад настойок валеріани досліджували за допомогою газового хроматографа Agilent 7890B з мас-спектрометричним детектором 5977B.

Результати. За допомогою хромато-мас-спектрометрії ідентифікували та проаналізували компонентний склад настойок із підземної частини рослин роду валеріана, що зростають у Запорізькому краї.

Висновки. Методом газової хроматографії у настойці валеріани з підземної сировини *Valeriana stolonifera* Czern. Ідентифікували 55 компонентів, з *V. exaltata* Mikan. – 48, з *V. tuberosa* L. – 54, з *V. collina* Wallr. – 51. Проаналізувавши одержані дані, зробили висновок, що настойки валеріани відрізняються і за кількісним, і за якісним складом. У настойках з підземних органів усіх чотирьох видів валеріани збігаються лише сполуки 7 і 9. Оскільки настойки виготовлені за стандартною технологією, вміст компонентів у лікарській рослинній сировині залежить від виду, місця зростання, екологічних умов, часу збирання, сушіння сировини. Результати дослідження підтверджують перспективність використання підземної частини досліджених рослин роду валеріана для створення на їхній основі нових лікарських засобів і фітопрепаратів. Враховуючи надзвичайну поліморфність валеріани, для введення в культуру перспективних видів, які зростають на території України, необхідно здійснювати глибші фармакогностичні та фармакологічні дослідження рослин цього роду.

Ключові слова: настойка валеріани, газова хроматографія, хромато-мас-спектроскопія, компонентний склад, кількісний вміст.

Актуальні питання фармацевтичної і медичної науки та практики. 2022. Т. 15, № 3(40). С. 250–258

Valerian has long been used in scientific and traditional medicine both independently (in the form of tinctures, decoctions and alcohol tinctures of fresh phytomass or air-dried raw materials, thick extract, fresh juice, powder of underground organs) and as part of various multicomponent phytocompositions, which allows varying their composition and, thus, intensively affect various parts of pathological disorders in the body [2].

Valerian grows all over the globe and has more than 250 species. In Ukraine, 13 species belong to the collective species cycle *Valeriana officinalis* L. s. l. of these, the most important are: *Valeriana grossheimii* Worosch., *V. sambucifolia* Mikan, *V. collina* Wallr., *V. simplicifolia* Kabath., *V. tripteris* L., *V. transsylvanica* Schur, *V. exaltata* Mikan, *V. rossica* P. Smirn., *V. tanaitica* Worosch., *V. nitida* Kr., *V. stolonifera* Czern. The next plants grow in the Zaporizhzhia region: *V. stolonifera* Czern., *V. exaltata* Mikan, *V. collina* Wallr., *V. tuberosa* L. [1,3,4,6–12].

Aim

The aim of the work is to determine the component composition of valerian tinctures made from rhizomes with valerian roots of different species growing in the Zaporizhzhia region by gas chromatography and to carry out their comparative analysis.

Materials and methods

Samples of rhizomes with valerian roots made from medicinal plant raw materials of valerian according to the traditional production recipe (Tinctura Rhizomata cum radicibus Valerianae (1:5)) from different species of valerian growing in the Zaporizhzhia region were selected for experimental studies:

– *Valerian stolonifera* Czern. – Kantserivska Balka, Zaporizhzhia district, Zaporizhzhia region;

– *V. exaltata* Mikan. – Shyroke village, Vasylivskyi district, Zaporizhzhia region;

– *V. tuberosa* L. – Khortytsia Island, Zaporizhzhia;

– *V. collina* Wallr. – right bank of the Dnieper River, Zaporizhzhia.

The component composition of valerian tinctures was studied using an Agilent 7890B gas chromatograph with a mass spectrometric detector 5977B. Chromatography conditions: DB-5ms column 30 m long, with an inner diameter of 250 μm and a phase thickness of 0.25 μm. The speed of the carrier gas (helium) – 1.3 ml/min. The injection volume is 0.5 μl. The division of the flow is 1:5. The temperature of the sample injection unit – 265 °C. Thermostat temperature: programmable – 70 °C (exposure 1 min), up to 150 °C at a speed of 20 °/min (exposure 1 min), up to 270 °C at a speed of 20 °/min (exposure 4 min). The NIST 14 mass spectrum library was used to identify the components.

Results

The component composition of tinctures from the underground part of Valerian plants growing in the Zaporizhzhia region was identified and analyzed with chromato-mass spectrometry. 153 components were identified in the analysis of chromatograms (*Fig. 1–4*, *Table 1*) of the valerian tinctures (*Table 1*) belonging to different classes of biologically active compounds.

In the tincture of valerian from *Valeriana stolonifera* Czern. (Kantserivska Balka) 55 compounds were identified, of which 9 components are quantitatively distinguished in terms of peak areas and retention time: 13.814 RT (*E*)-3-((4*S*,7*R*,7*aR*)-3,7-Dimethyl-2,4,5,6,7,7*a*-hexahydro-1*H*-inden-4-yl)-2-methylacrylaldehyde – 18.21 %; 3.825 RT 7,7-Dimethyl-2-methylidenebicyclo[2.2.1]heptane – 7.25 %; 8.424 RT [(1*S*,2*R*,4*S*)-1,7,7-Trimethyl-2-bicyclo[2.2.1]heptanyl] acetate – 5.26 %; 18.155 RT Ethyl linoleate – 3.35 %; 7.214 RT (6,6-Dimethyl-2-bicyclo[3.1.1]hept-2-enyl)methanol – 3.29 %; 15.365 RT [(1*S*,2*R*,5*R*,6*R*,8*S*,12*S*)-1,5,9,9-Tetramethyl-10-oxatricyclo[6.2.2.0^{2,6}]dodecan-12-yl] acetate – 2.75 %; 11.943 RT Myrtenyl isovalerate – 2.04%; 20.671 RT 6-Isopropenyl-4,8*a*-dimethyl-1,2,3,5,6,7,8,8*a*-octahydronaphthalene-2,3-diol – 0.93 %; 4.826 RT *D*-Limonene – 0.37 %.

In the tincture of *V. exaltata* Mikan. (Shyroke village, Vasylivskyi district, Zaporizhzhia region) 48 components were identified, of which 8 components are quantitatively distinguished in terms of peak areas and retention time: 8.426 RT [(1*S*,2*R*,4*S*)-1,7,7-Trimethyl-2-bicyclo[2.2.1]heptanyl] acetate – 9.33 %; 13.80 RT (*E*)-3-((4*S*,7*R*,7*aR*)-3,7-Dimethyl-2,4,5,6,7,7*a*-hexahydro-1*H*-inden-4-yl)-2-methylacrylaldehyde – 7.72 %; 17.822 RT 11,14-Dihydroxy-2-methyltricyclo[8.4.0.0^{2,7}]tetradec-6-en-5-one – 5.44 %; 15.363 RT [(1*S*,2*R*,5*R*,6*R*,8*S*,12*S*)-1,5,9,9-Tetramethyl-10-oxatricyclo[6.2.2.0^{2,6}]dodecan-12-yl] acetate

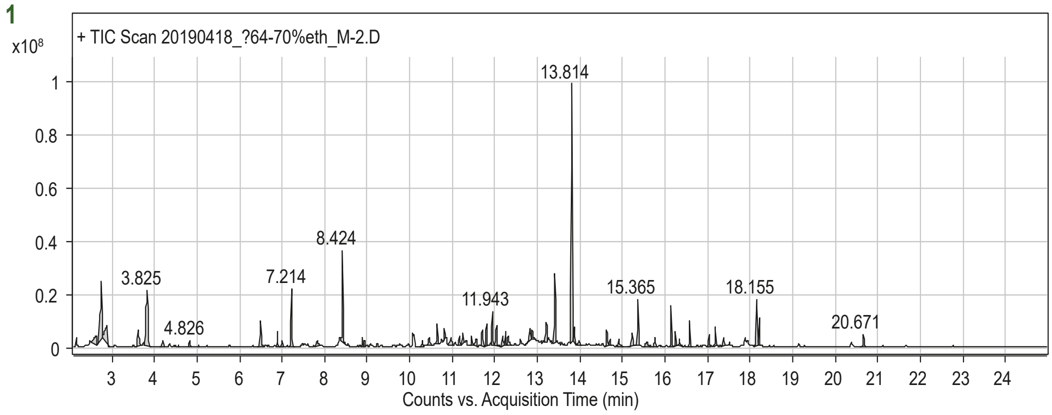

Fig. 1. Chromatogram of valerian tincture of *V. stolonifera* Czern.

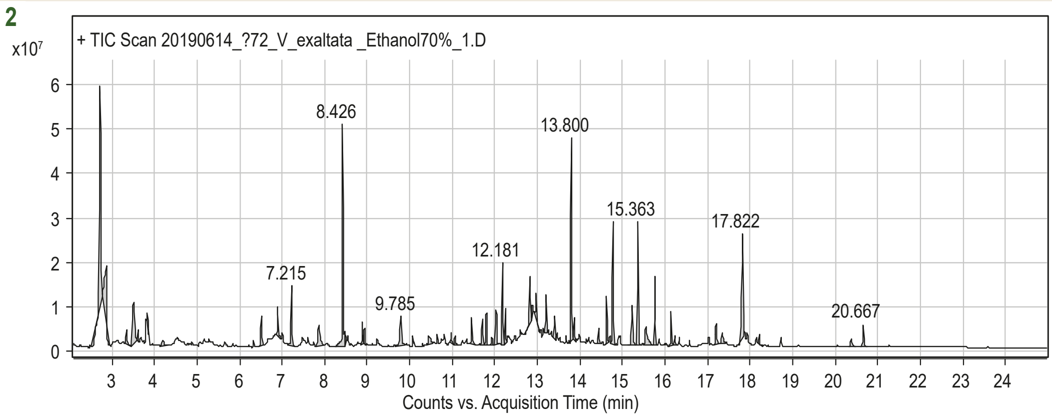

Fig. 2. Chromatogram of valerian tincture of *V. exaltata* Mikan.

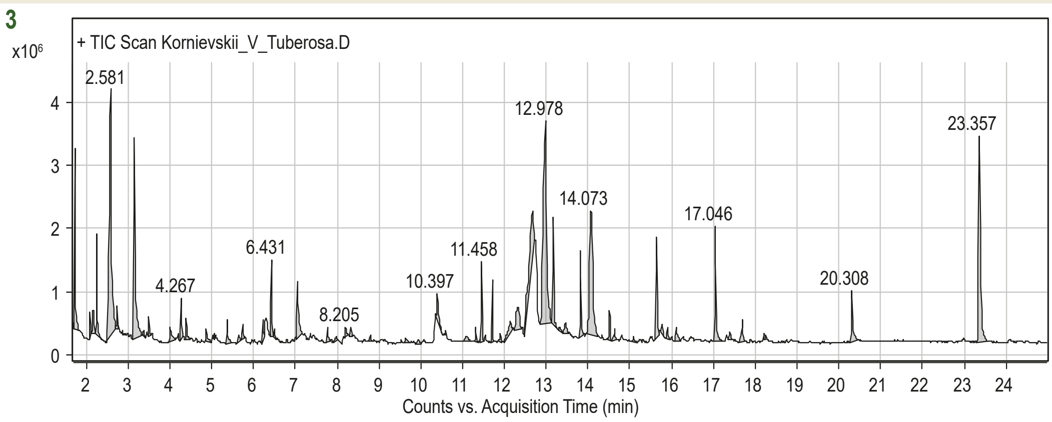

Fig. 3. Chromatogram of valerian tincture of *V. tuberosa* L.

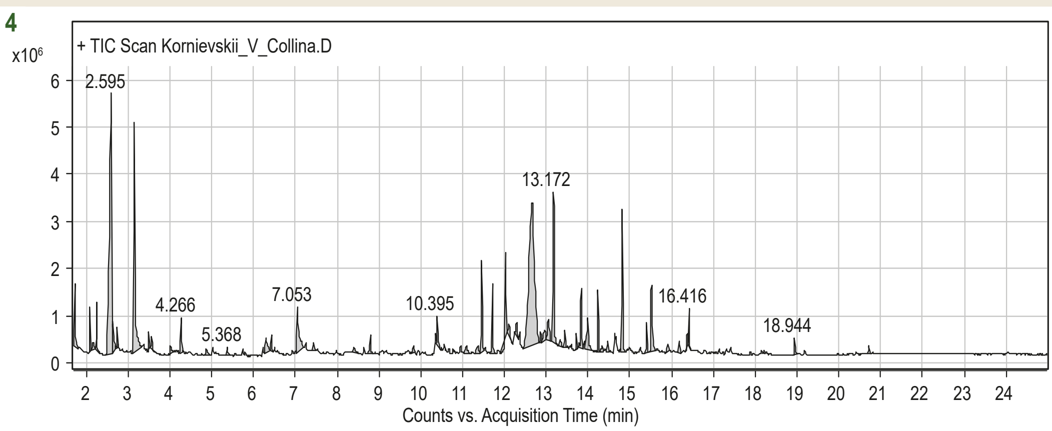

Fig. 4. Chromatogram of valerian tincture of *V. collina* Wallr.

Table 1. Comparative characteristics of mass spectroscopy of tinctures from the underground part of Valerian plants growing in the Zaporizhzhia region

Sl. No.	Chemical name of the component	Molecular formula	*V. stolonifera*		*V. exaltata*		*V. tuberosa*		*V. collina*	
			Rt	Content, %	Rt	Content, %	Rt	Content, %	Rt	Content, %
1	1-Hydroxypropan-2-one	$C_3H_6O_2$					1.732	2.70	1.731	1.50
2	2,2'-Bioxirane	$C_4H_6O_2$							2.086	0.74
3	1,2,3,4-Diepoxybutane	$C_4H_6O_2$					2.088	0.42		
4	Acetoxyacetic acid	$C_4H_6O_4$							2.164	0.30
5	Methyl acetate	$C_3H_6O_2$					2.166	0.84		
6	Methyl 2-oxopropanoate	$C_4H_6O_3$			3.338	0.53	2.247	1.77	2.246	1.01
7	3-Methylbutanoic acid	$C_5H_{10}O_2$	2.625 2.877	1.53 2.39	2.862	4.12	2.581	13.37	2.595	17.64
8	2-Methylbutanoic acid	$C_5H_{10}O_2$							2.627	1.10
9	Ethyl 3-methylbutanoate	$C_7H_{14}O_2$	2.75	7.05	2.72	14.71	2.733	0.30	2.734	0.36
10	Dihydroxyacetone	$C_3H_6O_3$			3.504	4.09	3.144	7.09	3.145	8.66
11	3-Carene	$C_{10}H_{16}$			3.607	0.39				
12	1,3,3-Trimethyltricyclo[2.2.1.0^{2,6}]heptane	$C_{10}H_{16}$	3.609	1.97						
13	2-[(Tetrahydro-2*H*-pyran-2-yl)oxy]propanoic acid	$C_8H_{14}O_4$					3.375	0.20		
14	1,2-Cyclopentanedione	$C_5H_6O_2$					3.5	0.42	3.497	0.53
15	3-Methylpentanoic acid	$C_6H_{12}O_2$							3.56	0.37
16	7,7-Dimethyl-2-methylidenebicyclo[2.2.1]heptane	$C_{10}H_{16}$	3.825	7.25						
17	(1*S*)-2,2-Dimethyl-3-methylenebicyclo[2.2.1] heptane	$C_{10}H_{16}$			3.826	0.44				
18	Glycerin	$C_3H_8O_3$					4.006	0.64	4.018	0.36
19	*β*-Phellandrene	$C_{10}H_{16}$			4.184	0.41				
20	6,6-Dimethyl-2-methylidenebicyclo[3.1.1]heptane	$C_{10}H_{16}$	4.189	0.47						
21	2-Hydroxy-*γ*-butyrolactone	$C_4H_6O_3$					4.267	0.82	4.266	0.90
22	Aminopyrazole	$C_3H_5N_3$					4.387	0.57		
23	*D*-Limonene	$C_{10}H_{16}$	4.826	0.37						
24	*N*-(2-Fluorophenyl)-3-morpholin-4-ylpropanamide	$C_{13}H_{17}FN_2O_2$					4.872	0.37	4.872	0.32
25	Clindamycin	$C_{18}H_{33}ClN_2O_5S$							5.368	0.33
26	Thymine	$C_5H_6N_2O_2$					5.371	0.65		
27	2-Methylhept-2-en-4-one	$C_8H_{14}O$					5.642	0.23		
28	2-Nonen-1-ol	$C_9H_{18}O$					5.739	0.32	-	-
29	*N*-Methoxycarbonyl-*L*-alanine nonyl ester	$C_{14}H_{27}NO_4$					6.228	0.29	-	-
30	*D,L*-Arabinose	$C_5H_{10}O_5$							6.296 6.431	1.10 0.42
31	3,5-Dihydroxy-6-methyl-2,3-dihydropyran-4-one	$C_6H_8O_4$	6.493	1.83	6.506	1.23	6.431	1.47		
32	(2*R*)-1,7,7-Trimethylbicyclo[2.2.1]heptan-2-ol	$C_{10}H_{18}O$	6.891	0.80						
33	*endo*-Borneol	$C_{10}H_{18}O$			6.895	1.30				
34	4-Hydroxyoxolan-2-one	$C_4H_6O_3$					6.496	0.23		
35	Terpinen-4-ol	$C_{10}H_{18}O$	6.993	0.37						
36	(6,6-Dimethyl-2-bicyclo[3.1.1]hept-2-enyl)methanol	$C_{10}H_{16}O$	7.214	3.29						
37	Catechol	$C_6H_6O_2$					7.053	1.92	7.053	2.47
38	(–)-Myrtenol	$C_{10}H_{16}O$			7.215	2.08				

Cont. of table 1.

Sl. No.	Chemical name of the component	Molecular formula	*V. stolonifera*		*V. exaltata*		*V. tuberosa*		*V. collina*	
			Rt	Content, %	Rt	Content, %	Rt	Content, %	Rt	Content, %
39	2,3-Dihydro-1-benzofuran	C_8H_8O							7.43	0.35
40	2,3-Dihydroxypropyl acetate	$C_5H_{10}O_4$	7.819	0.88	7.864	1.85				
41	Hexyl 3-oxobutanoate	$C_{10}H_{18}O_3$					7.764	0.43		
42	9-Oxabicyclo[3.3.1]nonan-2-yl acetate	$C_{10}H_{16}O_3$					7.979	0.17		
43	Methyl 6-oxoheptanoate	$C_8H_{14}O_3$					8.205	0.31		
44	Glucuronamide	$C_6H_{11}NO_6$					8.326	0.26		
45	[(1*S*,2*R*,4*S*)-1,7,7-Trimethyl-2-bicyclo[2.2.1] heptanyl] acetate	$C_{12}H_{20}O_2$	8.424	5.26	8.426	9.33				
46	1-(2-Hydroxy-5-methylphenyl)ethanone	$C_9H_{10}O_2$							8.791	0.71
47	(4-*tert*-Butylphenyl) 5-hydroxypentanoate	$C_{15}H_{22}O_3$								
48	2-(2-Butynyl)cyclohexanone	$C_{10}H_{14}O$					8.792	0.20		
49	1-(2,6,6-Trimethylcyclohexen-1-yl)ethanol	$C_{11}H_{20}O$	8.882	0.44						
50	2-(3-Oxobutyl)cyclohexan-1-one	$C_{10}H_{16}O_2$			8.882	0.74				
51	Myrtenyl acetate	$C_{12}H_{18}O_2$	8.932	0.39	8.933 11.935	0.64 0.45				
52	Phorone	$C_9H_{14}O$					9.65	0.17		
53	5-Butyloxolan-2-one	$C_8H_{14}O_2$			9.785	1.99				
54	Vanillin lactoside	$C_{20}H_{28}O_{13}$					9.931	0.18	9.821	0.24
55	Caryophyllene	$C_{15}H_{24}$	10.296	0.42						
56	1-Nitro-3-(propoxymethyl)benzene	$C_{10}H_{13}NO_3$							10.395	0.99
57	Inosine	$C_{10}H_{12}N_4O_5$					10.397	0,89%		
58	2,10,10-Trimethyltricyclo[7.1.1.0^{2,7}]undec-7-en-6-one	$C_{14}H_{20}O$	10.452	0.62						
59	(4*R*,4*aR*)-1,1,4,7-Tetramethyl-1*a*,2,3,4,4*a*,5,6,7*b*-octahydrocyclopropa[*e*]azulene	$C_{15}H_{24}$	10.648	1.39						
60	*β*-Panasinsene	$C_{15}H_{24}$	10.813	0.58						
61	(*E*)-4-(2,6,6-trimethylcyclohexen-1-yl)but-3-en-2-one	$C_{13}H_{20}O$	10.969	1.04						
62	*trans-β*-Ionone	$C_{13}H_{20}O$			10.972	0.40				
63	6-*epi*-Shyobunol	$C_{15}H_{26}O$			11.059	0.37				
64	*D*-Mannose	$C_6H_{12}O_6$					11.093	0.37	8.396	0.36
65	2-Methyl-5-(6-methylhept-5-en-2-yl)cyclo-hexa-1,3-diene	$C_{15}H_{24}$	11.163	0.58						
66	(1*S*,2*E*,6*E*,10*R*)-3,7,11,11-Tetramethylbicyc-lo[8.1.0]undeca-2,6-diene	$C_{15}H_{24}$	11.251	0.59						
67	Octahydro-1*H*-cyclopropa[*c*]inden-7-ol	$C_{10}H_{16}O$					11.314	0.34		
68	Ethyl (4*E*)-2-nitrodeca-4,9-dienoate	$C_{12}H_{19}NO_4$							11.365	0.44
69	Acetylvanillin	$C_{10}H_{10}O_4$							11.459	2.46
70	2-(Bromomethyl)adamantan-2-ol	$C_{11}H_{17}BrO$	11.455	0.82	11.457	1,27%	11.458	1.51%		
71	*α*-Panasinsen	$C_{15}H_{24}$	11.557	0.70						
72	Kessane	$C_{15}H_{26}O$	11.706	1.63						
73	Pulegone	$C_{10}H_{16}O$			11.709	1.48				

Cont. of table 1.

Sl. No.	Chemical name of the component	Molecular formula	*V. stolonifera*		*V. exaltata*		*V. tuberosa*		*V. collina*	
			Rt	Content, %	Rt	Content, %	Rt	Content, %	Rt	Content, %
74	3-Ethoxyphenylhydrazine	$C_8H_{12}N_2O$							11.712	2.22
75	(3-Ethoxyphenyl)hydrazide	$C_8H_{12}N_2O$					11.71	1.30		
76	Pacifigorgiol	$C_{15}H_{26}O$	11.795	1.44	11.791	1.43				
77	13-Oxadispiro[5.0.5.1]tridecane	$C_{12}H_{20}O$					11.9	0.18		
78	Myrtenyl acetate	$C_{12}H_{18}O_2$			11.935	0.45				
79	Myrtenyl isovalerate	$C_{15}H_{24}O_2$	11.943	2.04						
80	4-Hydroxy-2,6,6-trimethyl-3-oxocyclohexa-1,4-dienecarbaldehyde	$C_{10}H_{12}O_3$							12.025	3.02
81	(7*S*)-4,4,7,9*a*-Tetramethyl-1,2,3,6,8,9-hexahydrobenzo[7]annulen-7-ol	$C_{15}H_{26}O$	12.03	1.89	12.023	2.09				
82	Methyl *β-D*-glucopyranoside	$C_7H_{14}O_6$							12.108	0.57
83	*D*-Mannopyranoside	$C_6H_{12}O_6$					12.147	0.76		
84	(1*aR*,3*aS*,7*S*,7*aS*,7*bR*)-1,1,3*a*,7-Tetramethyl-decahydro-1*H*-cyclopropa[*a*]naphthalen-7-ol	$C_{15}H_{26}O$	12.184	0.62	12.181	2.78				
85	(7*S*)-1,1,7-Trimethyl-4-methylidene-1*a*,2,3,4*a*,5,6,7*a*,7*b*-octahydrocyclopropa[*h*]azulen-7-ol	$C_{15}H_{24}O$	12.251	0.95	12.245	1.48				
86	3,4-Dihydroxy-5-(1,2,3,4-tetrahydroxybutyl) oxolan-2-one	$C_8H_{14}O_8$							12.292	0.50
87	Spirojatamol	$C_{15}H_{26}O$	12.308 12.88	0.97 0.86						
88	3-Deoxy-*D*-mannoic lactone	$C_6H_{10}O_5$					12.322	1.68		
89	Ethyl-*α-D*-glucopyranoside	$C_8H_{16}O_6$							12.658	23.35
90	Ethyl hexopyranoside	$C_8H_{16}O_6$					12.668	5.54		
91	Isospathulenol	$C_{15}H_{24}O$	12.818	0.89	12.817	1.76				
92	(–)-Spathulenol	$C_{15}H_{24}O$							12.861	0.32
93	*γ*-Himachalene	$C_{15}H_{24}$			12.881	0.51				
94	*D,L*-3-Camphorcarboxylic acid	$C_{11}H_{16}O_3$			12.971	1.22				
95	[5,5-Dimethyl-6-(3-methyl-buta-1,3-dienyl)-7-oxa-bicyclo[4.1.0]hept-1-yl]-methanol	$C_{14}H_{22}O_2$							12.96	0.70
96	Undefined structure component	–					12.978	15.80		
97	Methyl (5*Z*,8*Z*,11*Z*,14*Z*)-icosa-5,8,11,14-tetraenoate	$C_{21}H_{34}O_2$							13.046	1.15
98	[Benzyl(dimethyl)silyl]furan-2-carboxylate	$C_{14}H_{16}O_3Si$	13.214	2.13			13.166	2.62		
99	*tert*-Butyl(dimethyl)silyl-2-furoate	$C_{11}H_{18}O_3Si$			13.21	1.82			13.172	5.95
100	*L*-Gala-l-ido-octonic lactone	$C_8H_{14}O_8$					13.318	0.20		
101	*N*-[4-(3-hydroxypyrrolidin-1-yl)but-2-ynyl]-*N*-methylacetamide	$C_{11}H_{18}N_2O_2$							13.332	0.35%
102	(4*aR*,7*S*,8*aS*)-4*a*,8*a*-dimethyl-7-propan-2-yl-3,4,5,6,7,8-hexahydro-2*H*-naphthalen-1-one	$C_{15}H_{26}O$	13.407	4.72	13.402	0.87				
103	Patchouli alcohol	$C_{15}H_{26}O$							13.447	0.51
104	Methyl octadeca-2,5-diynoate	$C_{19}H_{30}O_2$					13.457	0.41		
105	(*E*)-3-((4*S*,7*R*,7*aR*)-3,7-Dimethyl-2,4,5,6,7,7*a*-hexahydro-1*H*-inden-4-yl)-2-methylacrylaldehyde	$C_{15}H_{22}O$	13.814	18.21	13.80	7.72				
106	1-Hydroxy-3-(4-hydroxy-3-methoxyphenyl)propan-2-one	$C_{10}H_{12}O_4$					13.819	2.11		

Cont. of table 1.

Sl. No.	Chemical name of the component	Molecular formula	V. stolonifera		V. exaltata		V. tuberosa		V. collina	
			Rt	Content, %	Rt	Content, %	Rt	Content, %	Rt	Content, %
107	(*E*)-3-(3,7-dimethyl-2,4,5,6,7,7*a*-hexahydro-1*H*-inden-4-yl)-2-methylprop-2-enal	$C_{15}H_{22}O$							13.84	2.09
108	Valerenol	$C_{15}H_{24}O$	13.863	0.75	13.86	0.74				
109	(*E*)-4-(3-Hydroxyprop-1-en-1-yl)-2-methoxyphenol	$C_{10}H_{12}O_3$	13.978	0.42%					13.991	1.60
110	Bicyclopentyl-1'-en-1-ol	$C_{10}H_{16}O$					14.073	9.22		
111	Corymbolone	$C_{15}H_{24}O_2$							14.344	0.27
112	Isospathulenol	$C_{15}H_{24}O$			14.436	0.56				
113	Drim-7-en-11-ol	$C_{15}H_{26}O$					14.513	0.69		
114	12-Hydroxy-14-methyl-oxa-cyclotetradec-6-en-2one	$C_{14}H_{24}O_3$					14.639	0.35		
115	Khusimyl methyl ether	$C_{16}H_{26}O$	14.701	0.38						
116	*α*-Kessyl acetate	$C_{17}H_{28}O_3$			14.773	4.51			13.725 14.817 15.406	0.46 3.78 0.84
117	Isospathulenol	$C_{15}H_{24}O$							14.474	0.30
118	*trans*-Valerenyl acetate	$C_{17}H_{26}O_2$	14.909	0.46%						
119	2,5,5,8*a*-Tetramethyl-4-methylene-6,7,8,8*a*-tetrahydro-4*H*,5*H*-chromen-4*a*-yl-hydroperoxide	$C_{14}H_{22}O_3$					15.083	0.17		
120	Valerenic acid	$C_{15}H_{22}O_2$	15.23	1.13	15.23	2.01				
121	[(1*S*,2*R*,5*R*,6*R*,8*S*,12*S*)-1,5,9,9-Tetramethyl-10-oxatricyclo[6.2.2.0^{2,6}]dodecan-12-yl] acetate	$C_{17}H_{28}O_3$	15.365	2.75	15.363	4.38			14.244	1.69
122	Ethyl 14-oxotetradecanoate	$C_{16}H_{30}O_3$	15.581	0.59						
123	(*E*)-8-Methyl-9-tetradecen-1-ol acetate	$C_{17}H_{32}O_2$			15.555	1.64				
124	3,5-Dihydroxy-5',7-dimethyl-2'-propan-2-yl-spiro[8,10-dioxatricyclo[5.4.0.0^{2,6}]undecane-9,1'-cyclohexane]-11-one	$C_{19}H_{30}O_5$							15.519	2.92
125	[(2*E*)-Dodeca-2,11-dien-4-yl] acetate	$C_{14}H_{24}O_2$					15.64	2.56		
126	(8*S*,14)-Cedran-diol	$C_{15}H_{26}O_2$	14.633 15.763 17.028	1.22 0.70 0.72	14.629 15.762	1.75 2.48				
127	Methyl 11,13-dihydroxytetradec-5-ynoate	$C_{15}H_{26}O_4$					15.764	0.27		
128	12-Hydroxy-14-methyl-oxa-cyclotetradec-6-en-2-one	$C_{14}H_{24}O_3$					15.899	0.43		
129	Ethyl (2*E*)-3-(4-hydroxy-3-methoxyphenyl)-2-propenoate	$C_{12}H_{14}O_4$							15.904	0.45
130	2-Dodec-7-ynoxyoxane	$C_{17}H_{30}O_2$					16.107	0.71		
131	[4-Methoxy-2-(3-methyloxiran-2-yl)phenyl] 2-methylbutanoate	$C_{15}H_{20}O_4$	16.146	2.32	16.141	1.45				
132	3-Hydroxy-1*a*,3,6,6-tetramethylhexahydro-2-oxa-cyclopropa[*d*]naphthalen-5-one	$C_{14}H_{22}O_3$							16.177	0.39
133	Hexadecanoic acid	$C_{16}H_{32}O_2$	16.248	0.98	16.231	0.42				
134	(2*R*,3*R*,4*aR*,5*S*,8*aS*)-2-Hydroxy-4*a*,5-dimethyl-3-(prop-1-en-2-yl)octahydronaphthalen-1(2*H*)-one	$C_{15}H_{24}O_2$	16.338	0.51					16.375	0.29
135	4,8*a*-Dimethyl-6-prop-1-en-2-yl-2,3,4,4*a*,5,6,7,8-octahydronaphthalen-1-one	$C_{15}H_{24}O$							16.416	1.19
136	Ethyl hexadecanoate	$C_{18}H_{36}O_2$	16.579	1.93						
137	Undefined structure component	–					17.046	3.32		

Cont. of table 1.

Sl. No.	Chemical name of the component	Molecular formula	V. stolonifera		V. exaltata		V. tuberosa		V. collina	
			Rt	Content, %	Rt	Content, %	Rt	Content, %	Rt	Content, %
138	(*E*)-Valerenyl isovalerate	$C_{20}H_{32}O_2$	17.182	1.40						
139	5,8-Dihydroxy-4*a*-methyl-4,4*a*,4*b*,5,6,7,8,8*a*,9,10-decahydro-2(3*H*)-phenanthrenone	$C_{15}H_{22}O_3$			17.201	1.28				
140	6-(4-Hydroxy-2-methylbutan-2-yl)-2,3-dimethylphenol	$C_{13}H_{20}O_2$			17.342	0.70				
141	4,8*a*-Dimethyl-6-prop-1-en-2-yl-2,3,4,4*a*,5,6,7,8-octahydronaphthalen-1-one	$C_{15}H_{24}O$	17.371	0.59						
142	2,5,5,8*a*-Tetramethyl-6,7,8,8*a*-tetrahydro-5*H*-chromen-8-ol	$C_{13}H_{20}O_2$					17.396	0.23		
143	11,13-Dihydroxy-tetradec-5-ynoic acid	$C_{18}H_{36}O_2$					17.689	0.84		
144	11,14-Dihydroxy-2-methyltricyclo[8.4.0.0^{2,7}]tetradec-6-en-5-one	$C_{15}H_{22}O_3$			17.822	5.44				
145	Ethyl linoleate	$C_{20}H_{36}O_2$	18.155	3.35						
146	Ethyl (9*Z*,12*Z*,15*Z*)-octadeca-9,12,15-trienoate	$C_{20}H_{34}O_2$	18.21	1.55						
147	Desacetylanguidine	$C_{17}H_{24}O_6$			18.21	0.44				
148	[(*E*)-2-(2,2,6-Trimethyl-7-oxabicyclo[4.1.0]heptan-1-yl)prop-1-enyl] acetate	$C_{14}H_{22}O_3$							18.944	0.63
149	(5,9-Diacetyloxycyclododecyl) acetate	$C_{18}H_{30}O_6$					20.308	2.04		
150	(+)-Longicamphenylone	$C_{14}H_{22}O$			20.375	0.44				
151	6-Isopropenyl-4,8*a*-dimethyl-1,2,3,5,6,7,8,8*a*-octahydronaphthalene-2,3-diol	$C_{15}H_{24}O_2$	20.671	0.93	20.667	1.09				
152	3,5-*Bis*-(2,5-dimethylphenyl)-2,3-dihydro-1*H*-inden-1-one	$C_{25}H_{24}O$					23.357	9.09		
153	6-Isopropenyl-4,8*a*-dimethyl-1,2,3,5,6,7,8,8*a*-octahydronaphthalene-2,3-diol	$C_{15}H_{24}O_2$							20.714	0.32

– 4.38 %; 12.181 RT (1*aR*,3*aS*,7*S*,7*aS*,7*bR*)-1,1,3*a*,7-Tetramethyldecahydro-1*H*-cyclopropa[*a*]naphthalen-7-ol – 2.78 %; 7.215 RT (–)-Myrtenol – 2.08 %; 9.785 RT 5-Butyloxolan-2-one – 1.99 %; 20.667 RT 6-Isopropenyl-4,8*a*-dimethyl-1,2,3,5,6,7,8,8*a*-octahydronaphthalene-2,3-diol – 1.09 %.

In the comparative characterization of tinctures of *V. stolonifera* and *V. exaltata* it was found that 4 components coincide: 13.80–13.814 RT 7.72–18.21%; 3.825–8.426 RT 7.25–9.33 %; 15.363–15.365 RT 2.75–4.38 %; 20.667–20.671 RT 0.37–1.09 %.

Analyzing the retention time and peak areas (*Fig. 3*) of valerian tincture of *V. tuberosa* L. (Khortytsia Island) 54 components were identified, of which 11 components are quantitatively distinguished in terms of peak areas and retention time: 2.581 RT 3-Methylbutanoic acid – 13.37 %; 14.073 RT Bicyclopentyl-1'-en-1-ol – 9.22 %; 23.357 RT 3,5-*Bis*-(2,5-dimethylphenyl)-2,3-dihydro-1*H*-inden-1-one – 9.09 %; 20.308 RT (5,9-Diacetyloxycyclododecyl) acetate – 2.04 %; 11.458 RT 2-(Bromomethyl)adamantan-2-ol – 1.51 %; 6.431 RT 3,5-Dihydroxy-6-methyl-2,3-dihydropyran-4-one – 1.47 %; 10.397 RT Inosine – 0.89 %; 4.267 RT 2-Hydroxy-*γ*-butyrolactone – 0.82 %; 8.205 RT Methyl 6-oxoheptanoate – 0.31 %; two components of undefined structure (12.978 RT – 15.8 %; 17.046 RT – 3.32 %).

During the study of tincture of *V. collina* Wallr. (right bank of the Dnieper River, Zaporizhzhia) 51 components were identified, of which 8 components are quantitatively distinguished in terms of peak areas and retention time: 2.595 RT 3-Methylbutanoic acid – 17.64%; 13.172 RT *tert*-Butyl(dimethyl)silyl-2-furoate – 5.95 %; 7.053 RT Catechol – 2.47 %; 16.416 RT 4,8*a*-Dimethyl-6-prop-1-en-2-yl-2,3,4,4*a*,5,6,7,8-octahydronaphthalen-1-one – 1.19 %; 10.395 RT 1-Nitro-3-(propoxymethyl)benzene – 0.99 %; 4.266 RT 2-Hydroxy-*γ*-butyrolactone – 0.90 %; 18.944 RT [(*E*)-2-(2,2,6-Trimethyl-7-oxabicyclo[4.1.0]heptan-1-yl)prop-1-enyl] acetate – 0.63 %; 5.368 RT Clindamycin – 0.33 %.

Carrying out a comparative characterization of tincture of *V. tuberosa* and *V. collina*, we can determine that only one component is the same – 2.581–2.595 RT 13.37–17.64 %.

Discussion

Using chromato-mass spectrometry in tinctures from the underground part of Valerian plants growing in the Zaporizhzhia region, the component composition was identified and its quantitative assessment was carried out. In the tincture of *Valeriana stolonifera* Czern. (Kantserivska Balka) 55 compounds were identified, of which 9 components are quantitatively distinguished in terms of peak areas and retention time. In the tincture of *V. exaltata* Mikan. (Shyroke village, Vasylivskyi district, Zaporizhzhia region) 48 components were identified, of which 8 components are quantitatively distinguished in terms of peak areas and retention time. In the tincture of *V. tuberosa* L. (Khortytsia Island) 54 components were identified, of which 11 components are quantitatively distinguished in terms of peak areas and retention time. In the tincture of *V. collina* Wallr. (right bank of the Dnieper River, Zaporizhzhia) 51 components were identified, of which 8 components are quantitatively distinguished in terms of peak areas and retention time.

Note that during the analysis of 153 identified components of valerian tinctures from raw materials of different growth sites (*Table 1*), in all tinctures more than 50 compounds are present in the amount of more than 1 % (1, 6, 7, 9, 10, 12, 16, 31, 36, 37, 38, 40, 45, 53, 59, 61, 69, 70, 72, 73, 74, 75, 76, 79, 80, 84, 88, 89, 90, 91, 94, 97, 98, 99, 102, 105, 106, 107 , 109,110, 116, 120, 121, 123, 124, 125, 126, 131, 135, 136, 138, 139, 144, 145, 146, 149, 151, 152).

Conclusions

1. 55 components were identified in valerian tincture from underground raw materials *Valeriana stolonifera* Czern. by gas chromatography; *V. exaltata* Mikan. – 48, *V. tuberosa* L. – 54, *V. collina* Wallr. – 51.

2. Analyzing the obtained data, we can conclude that valerian tinctures differ in both quantitative and qualitative composition. Only compounds 7 and 9 coincide in tinctures from underground parts of all four types of valerian.

3. Since the tinctures were made following the standard technology, the content of components in medicinal plant raw materials depends on the type, place of growth, environmental conditions, time of collection, drying of raw materials.

4. The results of the study confirm the prospects of using the underground part of the studied plants of the genus Valerian to create new drugs and phytopreparations on their basis.

5. Given the extreme polymorphism of valerian for the introduction into the culture of promising species that grow in Ukraine, it is necessary to conduct more in-depth pharmacognostic and pharmacological studies of plants of this genus.

Prospects for future studies. The underground part of valerian can be used as an affordable and valuable medicinal plant raw material due to the content of numerous biologically active substances. It can be introduced into various phytotherapeutic prescriptions for the treatment of many diseases and the correction of pathological conditions. The results are the basis for the creation of new drugs and phytopreparations.

Conflicts of interest: authors have no conflict of interest.
Конфлікт інтересів: відсутній.

Information about authors:
Odyntsova V. M., PhD, DSc, Professor of the Department of Pharmacognosy, Pharmacology and Botany, Zaporizhzhia State Medical University, Ukraine.
ORCID ID: 0000-0002-7883-8917
Korniievskyi Yu. I., PhD, Associate Professor of the Department of Pharmacognosy, Pharmacology and Botany, Zaporizhzhia State Medical University, Ukraine.
ORCID ID: 0000-0001-7863-6736
Skoryna D. Yu., PhD, Senior Lecturer of the Department of Pharmaceutical Chemistry, Zaporizhzhia State Medical University, Ukraine.
ORCID ID: 0000-0002-8851-8757
Korniievska V. H., PhD, Associate Professor of the Department of Pharmacognosy, Pharmacology and Botany, Zaporizhzhia State Medical University, Ukraine.
ORCID ID: 0000-0001-8307-1282

Відомості про авторів:
Одинцова В. М., д-р фарм. наук, професор каф. фармакогнозії, фармакології та ботаніки, Запорізький державний медичний університет, Україна.
Корнієвський Ю. І., канд. фарм. наук, доцент каф. фармакогнозії, фармакології та ботаніки, Запорізький державний медичний університет, Україна.
Скорина Д. Ю., канд. фарм. наук, старший викладач каф. фармацевтичної хімії, Запорізький державний медичний університет, Україна.
Корнієвська В. Г., канд. фарм. наук, доцент каф. фармакогнозії, фармакології та ботаніки, Запорізький державний медичний університет, Україна.

References
[1] State Enterprise Ukrainian Scientific Pharmacopoeial Center of Medicines Quality. (2014). *Derzhavna Farmakopeia Ukrainy* [The State Pharmacopoeia of Ukraine] (2nd ed.). Kharkiv: State Enterprise Ukrainian Scientific Pharmacopoeial Center of Medicines Quality. [in Ukrainian].
[2] Korniievskyi, Yu. I., Korniievska, V. H., Panchenko, S. V., & Bohuslavska, N. Yu. (2014). *Valeriana likarska.* [Valerian Medicines]. Zaporizhzhia : ZSMU. [in Ukrainian].
[3] Korniievskyi, Yu. I. Odyntsova, V. M. Korniievska, V. H. Kandybei, N. V. & Bohuslavska, N. Yu. (2019). Tekhnolohiia vyrobnytstva ta khromato-mas-spektroskopiia nastoiok valeriany likarskoi [Production technology and chromato-mass spectroscopy of the valeriana officinalis tinctures]. *Current issues in pharmacy and medicine: science and practice, 12*(2), 172-180. [in Ukrainian]. https://doi.org/10.14739/2409-2932.2019.2.171002
[4] Ministry of Health of Ukraine. (2017). *Tekhnolohichnyi rehlament TP 64-01973472-069-17 na vyrobnytstvo likarskoho zasobu “Valeriany nastoika, nastoika po 25 ml u flakonakh v pachtsi abo bez pachky”* [Valerian tincture, tincture of 25 ml in vials in a pack or without a pack]. Zaporizhzhia: Viola. [in Ukrainian].
[5] Kryvenko, V. I., Korniievskyi, Yu. I., Kolesnyk, M. Yu., Korniievska, V. H., & Demchenko, A. V. (2018). *Fitoterapiia insomnia* [Phytotherapy of insomnia]. Zaporizhzhia: ZSMU. [in Ukrainian].
[6] Upton, R., & Petrone, C. (Eds.). (1999). *Valerian Root*. American Herbal Pharmacopoeia and Therapeutic Compendium. Santa Cruz.
[7] Bos, R., Hendriks, H., Pras, N., St.Stojanova, A., & Georgiev, E. V. (2000). Essential oil composition of valeriana officinalis ssp. Collina cultivated in Bulgaria. *Journal of Essential Oil Research*, *12*(3), 313-316. https://doi.org/10.1080/10412905.2000.9699524
[8] ESCOP. (2003). *Monographs* (pp. 539-546). Thieme.
[9] Council of Europe. (2005). *European Pharmacopoeia* (Vol. 2, 5th ed.), (pp. 2667-2668). Strasbourg.
[10] Pavlovic, M., Kovacevic, N., Tzakou, O., & Couladis, M. (2004). The essential oil of valeriana officinalis l. s.l. growing wild in western serbia. *Journal of Essential Oil Research*, *16*(5), 397-399. https://doi.org/10.1080/10412905.2004.9698753
[11] Raal, A., Orav, A., Arak, E., Kailas, T., & Müürisepp, M. (2007). Variation in the composition of the essential oil of Valeriana officinalis L. roots from Estonia. *Proceedings of the Estonian Academy of Sciences: Chemistry*, *56*(2), 67-74.
[12] World Health Organization. (1999). *Monographs on Selected Medicinal Plants* (Vol. 1, pp. 267-276). WHO.