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ECHINACEA AND VALERIANA EXTRACTION IN DIFFERENT SOLUTIONS BY ACOUSTIC INFLUENCE

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The article presents the results of studying the influence of a weak vibration effect on the extraction of plant raw materials, obtained as a continuation of the previous study [1].The article describes the option of intensification extraction process from the *Echinacea purpurea* L. and *Valeriana officinalis* L. The influence of acoustic action (tensile-pulse modulation) on an increase in the yield of extractive substances when using water, 40% and 70% ethanol is discussed. The influence of the frequency and amplitude of the action during the generation of a signal in the form of a meander has been studied. Solvents are selected taking into account the use in existing pharmaceutical factories. The extraction results were evaluated by the solid residue, the optical density of the solution after extraction of *Echinacea* and by GLC and GLC-MS after extraction of *Valeriana*. The greatest effect is achieved when using water. The explanation of the results is based on the effect of vibration on the rotation of solvent clusters. Cluster sizes decrease from water to 70% ethanol.

Keywords: Echinacea purpurea, Valeriana officinalis extraction, 70% ethanol, water, acoustic effect.

Introduction

Echinacea purpurea (L.) Moench is one of the most common and well-known medicinal plants. The popularity of the flower is associated with the high content of biologically active substances and the wide range of drugs from the plant [2]. Extracts from this plant species have traditionally been used to treat toothache, intestinal pain, cramps, skin diseases, chronic arthritis and infectious diseases of the upper and lower respiratory tract [3]. Drugs based on *E. purpurea* (EP) (infusions, tinctures and capsules) are generally used to improve immunity [4]. It is assumed that the immunostimulating properties of *E. purpurea* drugs are associated with the presence of alkamides, derivatives of caffeic acid and polysaccharides [5, 6].

It is known that different technologies for preparing tinctures and extracts change the content and ratio of substances and compounds extracted from plant raw materials, as well as their pharmacological activity [7].

Valeriana officinalis (*Valeriana officinalis* L. s.l.) is one of the most popular herbal remedies [8, 9].

The entire root system is used for medicinal purposes [10]. The activity of valerian extracts may be the result of an interaction between several components, not just one compound or class of compounds [11].

Rhizomes with roots are rich in essential oils, flavonoids, alkaloids, amino acids and lignanoids, which have a characteristic aroma. Valerian has a sedative, hypnotic and choleretic effect, improves coronary circulation, exhibits a pressor hypotensive effect, and prevents aging of the body. The most common preparations from valerian raw materials include valerian alcohol tincture [11–14]. The quantitative content of volatile oils, including valeric acids, is used to standardize valerian extracts. According to the pharmacopoeia, the minimum essential oil content should be 4 ml kg^{-1}, and valerenic acid – 0.17% (w/w) [15, 16].

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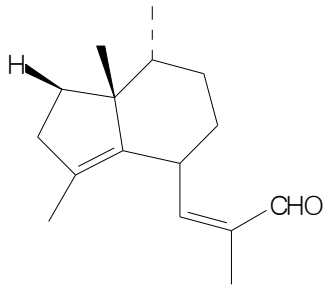
In addition to monoterpenoids about 30 sesquiterpenes are also found in the essential oils of *V.officinalis*. These have been classified to be of the guaiane type and valerian type. Valerian sesquiterpenoids include valerenal (1), valerenic acid (2) [17]. These substances are the main components of essential oils.



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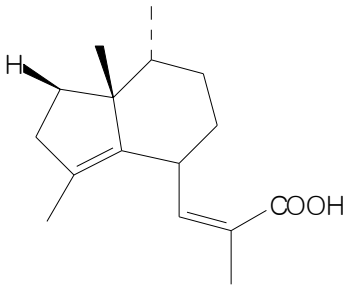

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In addition to essential oils, *V.officinalis* contains iridoids, alkaloids, flavonoids [18], γ-aminobutyric acid, tyrosine, glutamine, caffeic acid, chlorogenic acid, tannins and sitosterol.

Most methods of obtaining valerian tincture use 70% ethanol [19, 20]. There is even a method using ultrasonic treatment [21].

The tenso-pulse modulation method uses the conversion of a pulsed electrical signal into an antenna deformation. Acoustic impact, vibration transmitted by deformation of the antenna when creating a short circuit as a result of applying a pulsed signal, can increase heat transfer and mass transfer [22]. The tensile-pulse modulation is a change in the parameters of impulse signals in time or in space. Usually this process is a kind of modulated oscillations, where a sequence of pulses is used as a "bearer" of information [23, 24]. Application of low-energy tensile-pulse (acoustic) influence can be used for maximum extraction of extractive substances (ES) from plant raw materials.

We showed that acoustic exposure leads to an increase in the yield of phenol carboxylic acids when infused in 40% alcohol at room temperature [1]. Some industries use other solvents. In the Aleksandro-Svirsky Monastery (Leningrad Region) 70% ethanol is used, and in OOO «Kharms» they use hot water. Therefore, in this work, the conditions of acoustic exposure were determined, allowing to increase the yield of extractives during extraction in *E. purpurea* in these solvents. The results obtained allowed us to make assumptions about the mechanism of what is happening. Certain frequencies of optimal effects in the extraction of *E. purpurea* have been tested on the extraction of *V.officinalis*.

Experimental

Materials. A description of as *E. purpurea* a raw material has been described earlier [25].

V.officinalis. Dry rhizomes and roots were harvested in September 2020 in Adygea, Russia. Raw materials were cleaned from fines and dust. The size of the raw material is 0.315–2.0mm. The moisture content of plant materials is 12%.

Extraction conditions for E. purpurea . 1. Raw materials weighing about 10 g were placed in a 100 ml conical flask (1), filled in 65 ml of 70% of ethyl alcohol. The liquid level was at the top of the material. A foam stand of 1 cm height was installed between the flask and the table to avoid external vibration. Extraction within 5 hours.

2. Raw materials weighing about 10 g were placed in a 100 ml conical flask, filled in 65 ml of distilled water. Extraction with hot water was carried out in a boiling water bath using a reflux condenser and an electromagnetic generator connected to the flask through an antenna in the form of a steel clamp worn around the flask neck. The water bath was heated using an electric stove. Extraction was carried out for 2 hours. The resulting extract was cooled, filtered

Extraction conditions for V.officinalis. A sample of valerian rhizomes with a medicinal mass of 20 g was placed in a 200 ml flask, 130 ml of 40% ethyl alcohol was poured. The ratio of raw materials and solvent is 1 : 6. The flask was attached to a reflux condenser and heated in a water bath to an extraction temperature of 60 °C. The generator was connected to the neck of the flask through an antenna clamp. The extraction was carried out for 4 hours. The resulting extract was cooled, filtered.

The electromagnetic generator was short-circuited to a steel clamp – an antenna, mounted on a socket of the flask to perform vibration using electromagnetic-acoustic conversion. For the experiment, a UTG9002C signal generator was used with the following characteristics: wave shapes: meander, sinus, triangle; Frequency 0.2 Hz – 2

MHz. Accuracy ±1%. Resolution is 1 uHz. Amplitude range: from 1 mV to 20 V post. Accuracy ±5%. Resolution is 0.1 mV. The output power is less than 2 mW. Impedance – 50 Ω. A meander signal was used to determine optimal exposure conditions, frequencies ranging from 1 to 450 kHz and amplitudes ranging from 2.4 to 3.2 V.

Analysis of E. purpurea extraction results. The extract was filtered through a pleated paper filter, grade 3 in the end of the process. Solids were determined in the filtrate. To this end, 10 ml of the extract was transferred to a dried weighing bottle and dried to a constant weight. Extractive yield (ES) was estimated based on aliquot size as the ratio of filtrate solids to absolutely dry material. The standard deviation in the determination was 1.5%.

The content of phenolic compounds was determined by optical density. The resulting extract was diluted 500 times and the optical density of the solution was determined at 322 nm on a SF-26 spectrophotometer. Optical density was measured at 322 nm. Determination of the yield of hydroxycinnamic acids by optical density was described earlier [25].

Analysis of V.officinalis extraction results

V.officinalis extract (20 ml) and tert-butyl methyl ether (20 ml) of were mixed in a separatory funnel. The upper ether layer was used to determine valerenic acid in the extract using using gas-liquid chromatography

Qualitative analysis compounds of extract were carried out by GC-MS. The device is Agilent G2629A 6850 GC/MSD System (Agilent Technologies, Inc.) with A 5973N Series Mass Selective Detector. The ionizing energy was 70 eV. The temperatures of a separator and an ion source were 280 and 230 °C, respectively. To fractionate samples, Rxi®-5 Sil MS column (30000 × 0.18 mm ID) with a 0.10 μm (low polarity crossbond® silarylene phase; similar to 5% phenyl/95% dimethyl polysiloxane) was used. The thermostat temperature was programmed to increase from 100 to 280 °C at a rate of 5 °C per min. Subsequent exposure at the temperature of 280 °C was 30 minutes. The evaporator temperature was 290 °C. Inlet temperature was 290 °C. The flow rate of the carrier gas (helium) was 1 cm^3 per min. Dosed volume was 0.1 μL. Low molecular weight compounds were identified by comparison with the NIST 05 database.

Quantitative analysis compounds of extract were carried out by GLC.

A Shimadzu GC 2014 device was used. Quartz column SH-Rxi-5SilMS 30000×0.25 mm with a stationary phase (5% phenyl 95% dimethylsiloxane) 0.25 μm thick. Column temperature: programming temperature from 100 to 270 °C at a rate of 5 °C for a minute and 30 min isotherm at 270 °C. Evaporator temperature 270 °C. Detector temperature 290 °C – Carrier gas (nitrogen) velocity 1 cm^3/min. Dosed volume 0.1 μL. The standard deviation in the determination was 3%.

Results and discussion

1. Influence of frequency and amplitude on the *E. purpurea* extraction with 70% alcohol.

Change in the yield of extractives and the yield of chicoric acid and a pronounced maximum at a frequency of 350 kHz were observed in the range of the investigated frequencies (300–600 kHz) upon extraction with 70% alcohol (Table 1). The standard deviation in the results of the analysis after the experiment without vibration and the experience with the best results was 3%.

The mass of ES after extractions increased by 10%.

The ES yield depended on the signal amplitude set on the generator (Table 2). The standard deviation in the results of the analysis after the experiment without vibration and the experience with the best results was 5%.

The dry matter output increased by 17% compared to the experiment without vibration using a frequency of 475 kHz and an amplitude of 3.0 V.

2. Influence of frequency and amplitude on the *E. purpurea* extraction with hot water.

A change in the yield of extractives and chicoric acid was observed during the extraction of *E. purpurea* with hot distilled water at pH=7.5 in the frequency range 50–350 kHz (Table 3).

At a frequency of 228 kHz, the greatest effect from the tenso-pulse effect is noted. The dry matter yield increased by 27%.

The yield of solids during extraction with 70% ethyl alcohol increased by 17% with a frequency of 475 kHz and an amplitude of 3.0 V, by 10% with extraction with 40% ethyl alcohol at a frequency of 350 kHz and an amplitude of 2.8–3 V [1], by 35% when extracting with hot water at a frequency of 228 kHz and an amplitude of 3.2 V when using a tenso-pulse effect.

Table 1. The ES and CA yields at change of processing frequency, time 5 hours, amplitude 2.8 V, t=21 °C

Frequency, kHz	–	300	325	350	375	400	450	475	500	550	600
The ES yield, % to a.d.m.	10.9	10.2	10.1	11.1	10.4	10.8	9.7	12.1	10.8	10.3	9.9
The CA yield, % to a.d.m.	1.59	1.44	1.44	1.59	1.44	1.44	1.51	1.74	1.59	1.44	1.36

Table 2. Influence of signal amplitude on infusion, time – 5 h, frequency – 475 kHz

Amplitude, V	2.6	2.7	2.8	2.9	3.0	3.1	3.2
The ES yield, % to a.d.m.	10.9	12.5	12.1	12.1	**12.8**	12.3	12.1
The CA yield, % to a.d.m.	1.66	1.89	1.74	1.89	**2.04**	1.90	1.89

3. Influence of frequency and amplitude on the *V.officinalis* extraction with 40% alcohol.

An increase in the yield of valerenic acid (VA) at a frequency of 350 kHz was observed when extracting valerian rhizomes in 40% ethyl alcohol for 4 hours in the range of the investigated frequencies (200–400 kHz) (Table 5). The standard deviation in the results of the analysis after the experiment without vibration and the experience with the best results was 5%.

The peak area of VA has increased by 35% at 350 kHz.

It turned out that the optimal frequency is the same as for the *E. purpurea* extraction with 40% alcohol. It is possible that the optimal vibration frequency is weakly dependent on the raw material and its size. The dependence of the VA yield on the signal amplitude has a complex character, but there is an optimal amplitude, which differs from the most influencing *E. purpurea* extraction (Table 6). At a frequency of 350 kHz and an amplitude of 2.5 V, the greatest increase in the VA yield from *V.officinalis* was observed. The effect of amplitude on the extraction of bornyl acetate and valeranal differs from the effect on the extraction of VA.

Thus, during the *E. purpurea* extraction with 40% alcohol, the optimal frequency and amplitude: 350 kHz and 3.0V, allows to increase the yield of extractive substances by 13% [1], with the extraction of 70% alcohol, the frequency and amplitude – 475 kHz and 3.0V allowed to increase yield by 17%, during extraction with hot water – 228 kHz and 3.2V increased the yield by 35%. In water, the greatest effect from the use of tenso-impulse action.

For the *V.officinalis* extraction with 40% ethanol, the optimal frequency of exposure turned out to be similar to the one that showed the best results for the *E. purpurea* extraction with 40% alcohol – 350 kHz, the amplitude slightly differed – 2.5 V, instead of 3.0 V. Apparently, the determining factor influencing the optimal frequency is the composition of the solvent.

Table 3. The ES and CA yields at change of processing frequency, time 2 hours, amplitude 2.8 V, t=90 °C

Frequency, kHz	–	50	100	150	175	200	225	**228**	250	275	300	350
The ES yield, % to a.d.m.	25.8	29.7	19.1	21.5	23.8	30.4	31.5	**32.9**	29.8	29.6	30.7	30.8
The CA yield, % to a.d.m.	1.98	2.19	1.74	1.89	1.98	2.42	2.57	2.73	2.42	2.42	2.42	2.49

Table 4. Influence of signal amplitude on infusion, time – 2 h, frequency – 228 kHz, t= 90 °C

Amplitude, V	2.4	2.5	2.6	2.7	2.8	2.9	3.0	3.1	3.2	3.3
The ES yield, % to a.d.m	29.1	33.2	33.9	27.8	32.9	30.8	33.3	30.9	**34.9**	33.4
The CA yield, % to a.d.m.	2.42	2.65	2.65	2.19	2.72	2.49	2.57	2.49	**2.80**	2.57

Table 5. The VA, bornyl acetate, valerenal yields at change of processing frequency, time 4 hours, amplitude 2.8 V, t= 60 °C

Frequency, kHz	–	200	250	300	349	350	351	375	400
VA peak area	2020	1110	1480	1660	2560	**2860**	2630	2460	2230
Bornyl acetate peak area	1290	1020	980	1060	1240	**1430**	1160	1070	980
Valerenal peak area	1320	1090	1100	1170	1110	**1520**	1330	1270	1260

Table 6. Influence of signal amplitude on extraction, time – 4 h, frequency – 350 kHz, t=90 °C

Amplitude, V	2.4	**2.5**	2.6	2.7	2.8	2.9	3.0	3.1
VA peak area	1850	**3000**	2800	2850	2860	2500	1810	2730
Bornyl acetate peak area	1000	**1640**	1320	1210	1430	1510	1630	1530
Valerenal peak area	1150	**1570**	1510	1170	1520	1430	1680	1320

4. Explanation of the results obtained.

It is known that vibrations improve the movement of fluid through pipes, reducing the degree of turbulence, which slows down the movement [25]. It is possible that the impact of vibration (vibration is formed due to the electromagnetic conversion of current in a short-circuited conductor) causes the clots of liquid to vibrate and rotate inside the vessels of plants.

The optimal frequency required for cluster rotation depends on the mass and radius of the particles [26]. The size of wate clusters is larger [27] and a lower frequency is required to make them rotate [26] than the rotation of clusters in mixtures of water and ethanol. Probably, an increase in the frequency above the optimal one and a change in the vibration amplitude leads to a mismatch of the system and the regime of fluid movement inside the vessels becomes chaotic.

Conclusions

The conditions of low-energy strain-pulse action were selected, increasing the yield of extractive substances from the echinacea herb when extracted with water and 70% ethanol, when extracting valerian root with 40% ethanol. The greatest effect is observed when the echinacea herb is extracted with water. The yield of extractive substances at a frequency of 228 kHz and an amplitude of 3.2 V increased by 35%. It is shown that the optimal frequency of exposure depends on the composition of the solvent. An explanation of the obtained results is offered the conditions of strain-pulse action are selected.

References

1. Ipanova E.M., Zarembo D.V., Vedernikov D.N. *Khimiya Rastitel'nogo Syr'ya*, 2021. no. 2. pp. 327–331. DOI: 10.14258/jcprm.2021028249. (in Russ.).
2. Simonovich E.I., Goncharova L.Yu., Shimanskaia E.I. *Fundamentalnye issledovaniia*, 2012. no 9. pp. 69–72. (in Russ.).
3. Patel T., Crouch A., Dowless K., Freier D. *Brain Behav. Immun*., 2008, pp. 22–39. DOI: 10.1016/j.bbi.2008.04.124.
4. Barnes J., Anderson L.A., Gibbons S., Phillipson J.D. *J. Pharm Pharmacol*., 2005. pp. 929–954. DOI: 10.1211/0022357056127.
5. Bauer R., Wagner H., Farnswort N.R. *Econ. and med. plants res*., London, Acad, 1991. pp. 253–321.
6. Mamchur F.I., Vasilishin A.A. *Khimicheskii sostav i farmakologicheskie osobennosti rastenii roda Echinacea (Asteraceae)*. [Chemical composition and pharmacological features of plants of the genus Echinacea (Asteraseae)]. Rostov-on-Don, 2006, 413 p. (in Russ.).
7. Muravev I. A. *Tekhnologiia lekarstv* [Drug technology]. Moscow, 1980, vol. 1-2, 395 p. (in Russ.).
8. Chen H.-W., Wei J., He X.-H., Liu Y., Wang J. *Evidence-based Complementary and Alternative Medicine*, 2015, no. 3, pp. 1–12. DOI: 10.1155/2015/947619.
9. Penzkofer M., Baron A., Naumann A., Krähmer A., Schulz H., Heuberger H. *Plant Methods*, 2018, pp. 14–41. DOI: 10.1186/s13007-018-0309-4.
10. *Gosudarstvennaya farmakopeya Rossiyskoy Federatsii, XIV izd.* [State Pharmacopoeia of the Russian Federation, XIV ed.]. 2018, vol. 4, pp. 5951–5960. (in Russ.).
11. Blumenthal M., Goldberg A., Brinckmann J. *Herbal Medicine: Expanded Commission E Monographs*. Newton, MA: Integrative Medicine Communications, 2000, pp. 394–400.
12. Hendriks H., Geertsma H.-J., Malingre T.-M. *Pharmaceutisch Weekblad Scientific Edition*, 1981, vol. 116, pp. 1316–1320.
13. Sakamoto T., Mitani Y., Nakajima K. *Chemical and Pharmaceutical Bulletin*, 1992, vol. 40(3), pp. 758–761.
14. Muller D., Pfeil T., von den Driesch V. *Alternative Medicine Review*, 2004, vol. 9(4), pp. 438–441.
15. Thies P.-W. *Tetrahedron Letters*, 1966, vol. 7(11), pp. 1163–1170.
16. Reichling J., Horz K.H., Bodesheim U.B. *Hagers Handbuch der Pharmazeutischen Praxis*, Berlin: Springer, 1994, pp. 1067–1095.
17. Houghton P. *Valerian – the genus valeriana*. Amsterdam: Harwood Academic Publisher, 1997, pp. 21–54.
18. Shi J.-L., Xiao P.-G. *World Phytomedicines*, 2003, vol. 18(6), pp. 231–239.
19. Chueshov V.I. *Tekhnologiya promyshlennykh preparatov. V 2 tomakh* [Industrial drug technology. In 2 volumes]. Kharkiv, 2002, 716 p. (in Russ.).
20. Patent 2372935 (RU). 2009. (in Russ.).
21. Patent 2098115 (RU). 1997. (in Russ.).
22. Zarembo V.I., Kolesnikov A.A. *Theoretical Foundations of Chemical Engineering*, 2006, vol. 40(5), pp. 483–495. DOI: 10.1134/s0040579506050058.
23. Kolesnikov A.A., Zarembo V.I., Demin V.A., Zarembo D.V. *Alternativnaya energetika i ekologia*, 2011, no. 6, pp. 90–98. (in Russ.).

24. Bobkova E.O., Kostyukevich N.G., Vedernikov D.N., Bobkova E.O. *Khimiya Rastitel'nogo Syr'ya*, 2019, no. 3, pp. 285–290. DOI: 10.14258/jcprm2019034391.
25. Watson E.J. *J. Fluid Mech*., 1983, vol. 133, pp. 233–244.
26. Podgorskaya E.S. *Kristallizatsiya tsinka i splavov na osnove nikelya i kobal'ta v slabykh elektromagnitnykh polyakh radiochastotnogo diapazona: diss. ... kandidat khimicheskikh nauk*. [Crystallization of zinc and alloys based on nickel and cobalt in weak radio frequency electromagnetic fields: diss. … Candidate of Chemical Sciences]. St. Petersburg, 2002, 114 p. (in Russ.).
27. Zubova K.V., Zubov A.V., Zubov V.A. *Journal of Applied Spectroscopy*, 2005, vol. 72(3), pp. 305–312.

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