ХИМИЯ РАСТИТЕЛЬНОГО СЫРЬЯ. 2026. №3. С. 308–314.
KHIMIYA RASTITEL'NOGO SYR'YA, 2026, no. 3, pp. 308–314.
DOI: 10.14258/jcprm.20260316678

UDC 581.19

THE FIRST DETECTION OF CANNABINOIDS IN SMOKE FROM THE INCENSE OF *RHODODENDRON TOMENTOSUM* (*LEDUM PALUSTRE L.*), USED IN THE FOLK SHAMANIC PRACTICE OF THE UDEGE PEOPLE BY HPLC-ESI-MS/MS SPECTROMETRY*

© ***V.I. Dunkay[1], M.P. Razgonova[2,3], A.M. Zakharenko[1,3,4], A.V. Razgonov[2], A.M. Panichev[4], K.S. Golokhvast[1,3,4]*****

[1] Siberian Federal Scientific Centre of Agrobiotechnology RAS, st. Centralnaya, Presidium, Krasnoobsk, 633501, Russia, droopy@mail.ru
[2] N.I. Vavilov All-Russian Institute of Plant Genetic Resources, st. B. Morskaya, 42-44, Saint-Petersburg, 190000, Russia
[3] Far Eastern Federal University, 10 Ayax Bay settlement, Russkiy Island, Vladivostok, 690950, Russia
[4] National Research Tomsk State University, ave. Lenina, 36, Tomsk, 634050, Russia
[5] Pacific Institute of Geography of the Far Eastern Branch of the Russian Academy of Sciences, st. Radio, 7, Vladivostok, 690041, Russia

Ledum palustre L. has been actively used in ethnomedicine in Mongolia, China and Russian Far East (indigenous peoples: Udege and Evenki) for centuries, as an antioxidant, immunomodulating, anti-inflammatory, vitality-restoring agent. *L. palustre* contain various phenolic compounds and fatty acids with valuable biological activity. This plant is especially actively used in shamanic and healing practices among the Udege people living in the Primorsky and Khabarovsk Territories, Russia. We used the method of extracting biological substances by incense from the *L. palustre* using the methods of shamanic practices thanks to the direct participation of the shaman of the Udege people Vasily I. Dunkay. Tandem mass-spectrometry was applied to detect target analytes. 113 different biologically active components have been identified in the *L. palustre* extracts. For the first time, compounds from the group of cannabinoids were identified in this plant. Also, 74 compounds from other chemical groups were identified for the first time.

Keywords: Ledum palustre, *Rhododendron tomentosum*, cannabinoids, tandem mass spectrometry, phenolic compounds.

For citing: Dunkay V.I., Razgonova M.P., Zakharenko A.M., Razgonov A.V., Panichev A.M., Golokhvast K.S. *Khimiya Rastitel'nogo Syr'ya*, 2026, no. 3, pp. 308–314. (in Russ.). https://doi.org/10.14258/jcprm.20260316678.

Introduction

Nineteen species of rhododendrons are growing at the territory of Russia, the main part of which (13 species) is found only in the flora of the Russian Far East and Eastern Siberia [1]. Russian researchers classify the genus *Rhododendron* somewhat differently than foreign ones [2–5]. At present, there is no unified classification scheme for a taxon, since the genus is very large – more than 800 species, as well as the presence of a large number of convergent characters among its representatives, complicating the construction of a natural classification.

A detailed study of plant metabolites is an extremely important research, as it makes it possible to identify chemical substances (or complexes of substances) that determine certain beneficial properties of plants [6]. At the same time, from a chemical point of view, many of these plants have been studied only superficially, although it is

* This article has electronic supplementary material (appendix), which is available to readers on the journal's website. https://doi.org/10.14258/jcprm.20260316678s.
** Corresponding author.

obvious that it is necessary to obtain comprehensive information about the composition of secondary metabolites, and in particular, this applies to those plants that have long been used in folk medicine [7, 8].

The widespread use of essential oils of rhododendrons in medicine is due to the presence of biologically active components in them, which have antimicrobial, antifungal, hypotensive, cytotoxic and anti-inflammatory, growth-regulating, insecticidal and other important properties. *L. palustre* also has very great potential for use in medicine. It contains a whole range of biologically active compounds: tannins, coumarins, flavonoids, phenols, phenolic acids, condensed tannins, anthocyanins, ascorbic acid, triterpenoids and phytosterols [9]. The greatest interest, however, is the study of the biological activity of the essential oil of *L. palustre*. First of all, attention should be paid to the excitation of the central nervous and cardiovascular systems and antiparasitic properties [10].

Ledum palustre L. (*Rhododendron tomentosum*) is most widely distributed in Siberia and the Far East. In official medicine, this plant is used as an expectorant. Traditional medicine uses *L. palustre* to treat a number of diseases of the respiratory system, gastrointestinal tract, chronic skin diseases, hypertension, rheumatism, helminthiasis, etc. [11]. The stupefying smell formed when the leaves are burned and caused by the sharp evaporation of volatile terpenes has long been used by small peoples of Siberia and the Far East as a psychoactive, analgesic and narcotic drug.

In particular, *L. palustre* is actively used in healing and shamanic practices by the Udege people living in the Primorsky and Khabarovsk Territories, regions in Russia (Fig. 1). Udege people is the native population of this region. They live along the tributaries of the Ussuri, Amur, Kungari, and Anyuy Rivers. Their religious beliefs include animism, animal worship, and shamanism [12].

At the same time, from a chemical point of view, *L. palustre* has been studied only superficially, although it is obvious that it is necessary to obtain comprehensive information about the composition of secondary metabolites, and in particular, this applies to those plants that have long been used in folk medicine.

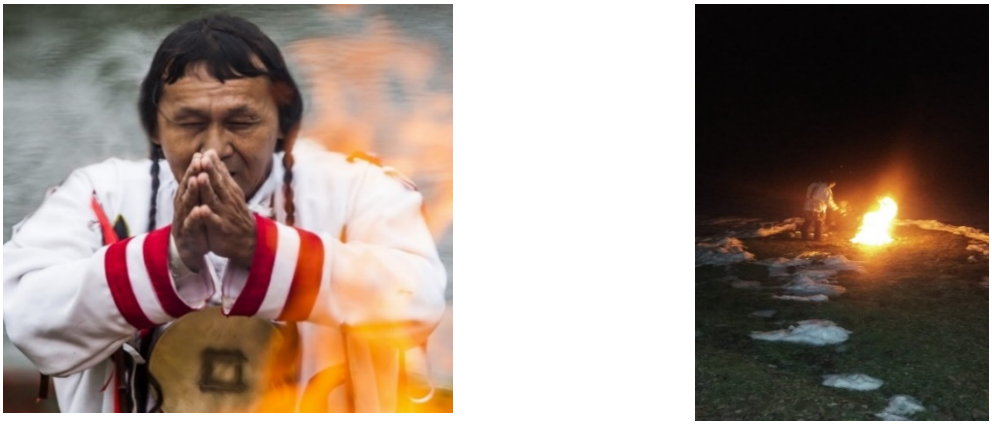
In this work, we used a tandem mass spectrometry to carry out a phytochemical study involving a detailed metabolomic and comparative analysis of *L. palustre*. Aboveground, phytomass of *L. palustre* was collected during expedition work near the Village Krasny Yar, Primorsky Territory (N 46°32’31’’ E 135°21’37’), during the period from 15 to 25 July 2020.

We also used the method of extracting biological substances using incense from the *L. palustre* using the methods of shamanic practices thanks to the direct participation of the shaman of the Udege people Vasily I. Dunkay.

Materials and methods

Materials. Phytomass soft part of a branch of *L. palustre* was collected during expedition work near the Village Krasny Yar, Primorsky Territory (N 46°32'31" E 135°21'37"), during the period from 15 to 25 July 2020. All samples were morphologically authenticated according to the current standard of Russian Pharmacopeia [13].

Chemicals and Reagents. HPLC-grade acetonitrile was purchased from Fisher Scientific (Southborough, UK), MS-grade formic acid was from Sigma-Aldrich (Steinheim, Germany). Ultra-pure water was prepared from a SIEMENS ULTRA clear (SIEMENS water technologies, Germany), and all other chemicals were analytical grade.



A *B*

Fig. 1. *A* – Shaman Vasily I. Dunkay in the national costume of the Udege people. *B* – Shamanistic ritual at the campfire with *Ledum palustre* L.

Extraction. The incense of the plant was carried out according to ancient ritual rules. A bundle of dried leaves (50–100 g) was set on fire and the room was incinerated with this smoke. The smoke was sampled through a sampler (a type of "wet trap") filled with hydrophobic media with methanol (polychrome I). The gas was pumped through the trap and all hydrophobic and alcohol-soluble components were retained in this way. Then after saturation, the trap was washed with an additional two volumes of methanol, the collected eluate was evaporated on a rotary evaporator, then the residue was redissolved in a 50% aqueous methanol solution and analyzed by tandem HPLC mass spectrometry.

Liquid chromatography. HPLC was performed using Shimadzu LC-20 Prominence HPLC (Shimadzu, Japan) was used, equipped with an UV-sensor and a Shodex ODP-40 4E reverse phase column to perform the separation of multicomponent mixtures. The water acetonitrile gradient elution program was as follows: 0.01–4 min, 100% A; 4–60 min, 100–25% A; 60–75 min, 25–0% A; control washing 75–120 min 0% A. Between analyses, an additional 15 minutes were waited for the column to equilibrate. The entire HPLC analysis was performed using a UV-VIS detector SPD-20A (Shimadzu, Japan) at wavelengths of 230 and 330 nm and mass detector ion trap amaZon SL (BRUKER DALTONIKS, Germany), at 17 °C provided with column oven CTO-20A (Shimadzu, Japan) with an injection volume of 20 μL.

Mass spectrometry. MS analysis was performed on an ion trap amaZon SL (BRUKER DALTONIKS, Germany) equipped with an ESI source in negative ion mode. The optimized parameters were obtained as follows: ionization source temperature: 70 °C, gas flow: 4 L / min, nebulizer gas (atomizer): 7.3 psi, capillary voltage: 4500 V, end plate bend voltage: 1500V, fragmentary: 280 V, collision energy: 60 eV. An ion trap was used in the scan range m/z 100 –1.700 for MS and MS/MS. The capture rate was one spectrum/s for MS and two spectrum/s for MS/MS. Data collection was controlled by Windows software for BRUKER DALTONIKS. All experiments were repeated three times. A four-stage ion separation mode (MS/MS mode) was implemented.

Results and discussion

Extracts of *L. palustre* were analyzed by an HPLC-MS/MS ion trap to better interpret the diversity of available phytochemicals. All of them have a rich bioactive composition. The structural identification of each compound was carried out on the basis of their accurate mass and MS/MS fragmentation by HPLC-ESI-ion trap-MS/MS. A total of 113 compounds were successfully characterized in extracts of *L. palustre* based on their accurate MS and fragment ions by searching online databases and the reported literature.

All the identified compounds along with molecular formulas, and MS/MS data for *L. palustre* are summarized in Table A1 (Appendix A). For the first time, compounds from the group of cannabinoids were identified in this plant. There are compounds: Cannabigerovarin (CBGV), Cannabigerol (CBG), Δ9-Tetrahydrocannabinol (Δ9-THC), 11-nor-9-carboxy-THC, 11-Hydroxy-Δ9-Tetrahydrocannabinol; Cannabidiolic acid. Also, 74 compounds from other chemical groups were identified for the first time. For example, there are compounds: Dihydrokaempferol, Herbacetin, Rhamnetin II, Syringetin, Quercetin 3-O-arabinoside, Isorhamnetin-3-O-glucoside,Isorhamnetin-O-dihexoside; flavones: Acacetin, Genkwanin, 4'-Methoxytectochrysin, Diosmetin, Chrysoeriol, Cirsimaritin, Salvigenin, Tricin, Gardenin B, Thymonin, Nevadensin; flavan-3-ol (epi)Afzelechin; anthocyanins Delphinidin 3-O-glucoside, Petunidin 3-O-glucoside; condensed tannins% Procyanidin A-type dimer, Proanthocyanidin B3, lignans: Secoisolariciresinol, Medioresinol, etc.

Figures 2–7 shows examples of the decoding spectra (collision-induced dissociation (CID) spectrum) of the ion chromatogram obtained using tandem mass spectrometry. The CID spectrum in positive ion modes of 11-nor-9-carboxy-THC (tetrahydrocannabinol) from *L. palustre* is shown in Figure 2.

$[M+H]^+$ ion produced one fragment ion with *m/z* 345.17 (Fig. 2). The fragment ion with *m/z* 345.17 produced three characteristic daughter ions with *m/z* 327.13, *m/z* 284.25 and *m/z* 183.83. The fragment ion with *m/z* 327.13 formed three daughter ions with *m/z* 257.20, *m/z* 300.99 and *m/z* 185.87. It was identified in the bibliography in extract from *Cannabis sativa* [14, 15]. The CID spectrum in positive ion modes of Δ9-Tetrahydrocannabinol (Δ9-THC) from *L. palustre* is shown in Figure 3.

$[M+H]^+$ ion produced one fragment ion with *m/z* 315.02 (Fig. 3). The fragment ion with *m/z* 315.02 produced one characteristic daughter ion with *m/z* 299.97. The fragment ion with *m/z* 299.97 formed one daughter ion with *m/z* 271.99. The fragment ion with *m/z* 271.99 formed four daughter ions with *m/z* 256.97, *m/z* 242.99, *m/z* 200.99 and *m/z* 166.99. It was identified in the bibliography in extracts from *Cannabis sativa* [14–16]. The CID spectrum in positive ion modes of 11-Hydroxy-Δ9-Tetrahydrocannabinol (11-OH-THC) from *L. palustre* is shown in Figure 4.

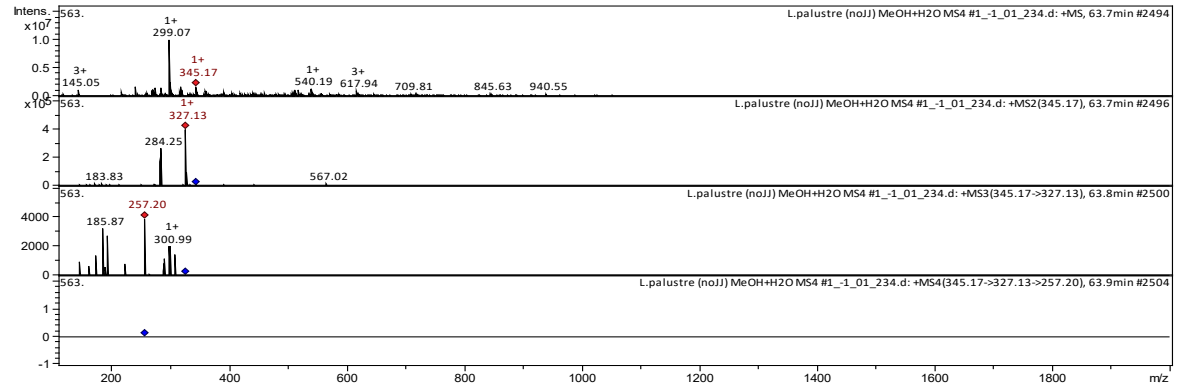


Fig. 2. CID spectrum of 11-nor-9-carboxy-THC from *L. palustre*, m/z 345.17

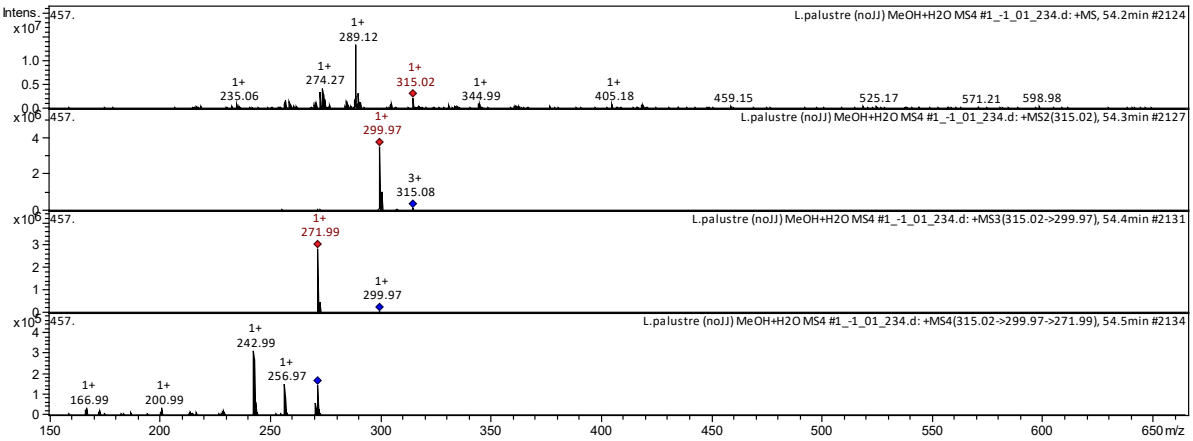


Fig. 3. CID spectrum of Δ9-Tetrahydrocannabinol from *L. palustre*, m/z 315.02

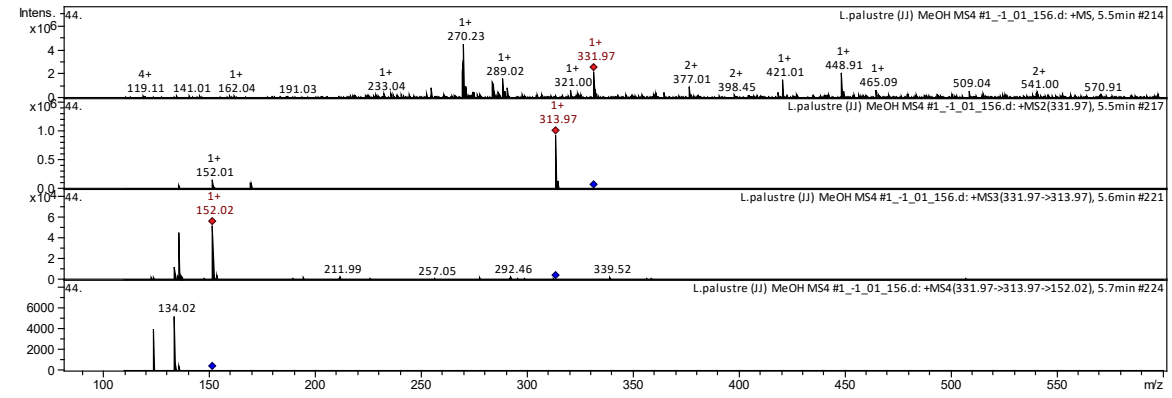


Fig. 4. CID spectrum of 11-Hydroxy-Δ9-Tetrahydrocannabinol (11-OH-THC) from *L. palustre*, m/z 331.97

$[M+H]^+$ ion produced one fragment ion with *m/z* 331.97 (Fig. 4). The fragment ion with *m/z* 331.97 produced two characteristic daughter ions with *m/z* 313.97 and *m/z* 152.01. The fragment ion with */z* 313.97 formed one daughter ion with *m/z* 152.02. The fragment ion with *m/z* 152.02 formed one daughter ion with *m/z* 134.02. It was identified in the bibliography in extracts from *Cannabis sativa* [14, 15]. The CID spectrum in positive ion modes of Cannabidiolic acid from *L. palustre* is shown in Figure 5.

$[M+H]^+$ ion produced four fragment ions with *m/z* 341.03, *m/z* 289.89, *m/z* 239.02, and *m/z* 196.99, (Fig. 5). It was identified in the bibliography in extract from *Cannabis sativa* [14, 17]. The CID spectrum in positive ion modes of Hyperoside from *L. palustre* is shown in Figure 6.

$[M+H]^+$ ion produced one fragment ion with *m/z* 464.99 (Fig. 6). The fragment ion with *m/z* 464.99 produced one characteristic daughter ion with *m/z* 302.97. The fragment ion with *m/z* 302.97 formed two daughter ions with *m/z* 256.97 and *m/z* 164.96. The fragment ion with *m/z* 256.97 produced one characteristic daughter ion with *m/z* 228.99. It was identified in the bibliography in extracts from *Malus toringoides* [18]; *Impatients glandulifera* Royle [19]; *Vaccinium macrocarpon* [20, 21]; *Lonicera japonicum* [22]; Cranberry [23]; *Vaccinium myrtillus* [24]; Andean blueberry [25]; *Camelia kucha* [26]; *Rosa rugosa* [27]. The CID spectrum in negative ion modes of Quercitrin from *L. palustre* is shown in Figure 7.

$[M-H]^-$ ion produced one fragment ion with *m/z* 447.13 (Fig. 7). The fragment ion with *m/z* 447.13 produced two characteristic daughter ions with *m/z* 300.97 and *m/z* 178.98. The fragment ion with *m/z* 300.97 formed two daughter ions with *m/z* 151.02 and *m/z* 270.99. The fragment ion with *m/z* 151.02 formed one daughter ion with *m/z* 168.90. It was identified in the bibliography in extracts from *Vaccinium macrocarpon* [20, 21], *Rhus coriaria* [28], *Camellia kucha* [26], *Embelia*, *Euphorbia hirta* [29], *Propolis* [30].

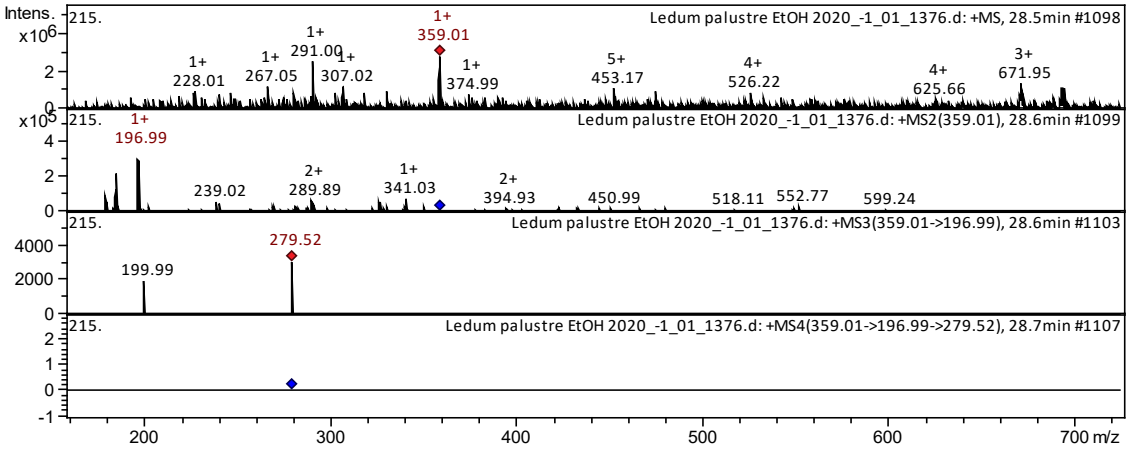


Fig. 5. CID spectrum of Cannabidiolic acid from *L. palustre*, m/z 359.01

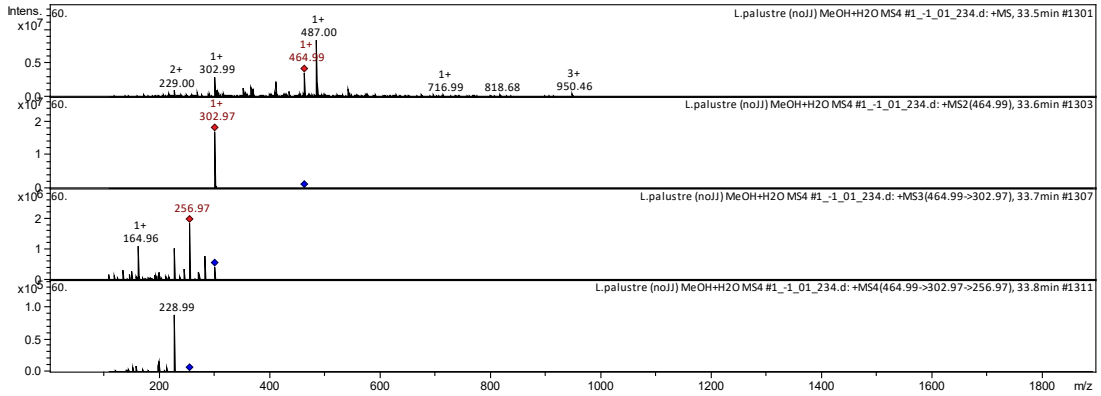


Fig. 6. CID spectrum of Hyperoside from *L. palustre*, m/z 464.99

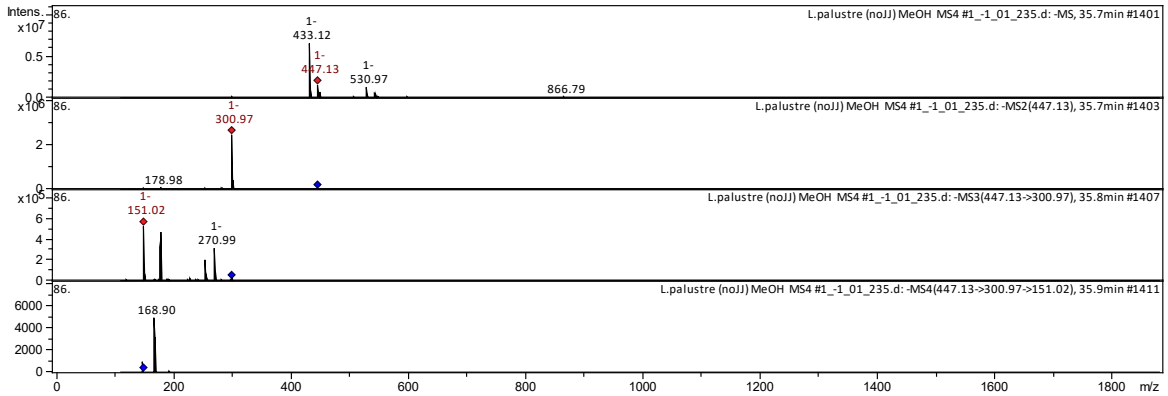


Fig. 7. CID spectrum of Quercitrin from *L. palustre*, m/z 447.13

Thus, it can be stated that as a result of the most detailed study by tandem mass spectrometry, new data on the content of biologically active substances in *L. palustre* have been obtained. Some of the presented compounds belong to the class of psychoactive compounds, and this to some extent explains the use of *L. palustre* in shamanic practices. At the same time, a wide range of other classes of biologically active substances are presented in *L. palustre* (for example: polyphenols, amino acids, Omega-3 fatty acids, Omega-5 fatty acids; sesquiterpenes, oxylipins, cannabinoids, sterols, triterpenoids, etc.), which undoubtedly classifies this plant as a widely used medicinal resource.

Conclusions

High-accuracy mass spectrometric data were recorded on an ion trap amaZon SL BRUKER DALTONIKS equipped with an ESI source in the mode of negative and positive ions. The four-stage ion separation mode was implemented. Under these conditions a total of 800 peaks were detected in the ion chromatogram. An optimized extraction process provided the samples for an accurate analytical study by HPLC-MS/MS technique. 113 different biologically active components have been identified in *L. palustre* extracts. 74 compounds have been identified for the first time in *L. palustre* extracts.

These data could support future research for the production of a variety of pharmaceutical products containing ultra-pure extracts of *L. palustre*. The richness of various biologically active compounds, including polyphenols, amino acids, Omega-3 fatty acids, Omega-5 fatty acids; sesquiterpenes, oxylipins, cannabinoids, sterols, triterpenoids, etc., provides great opportunities for the design of new drugs based on extracts from this genus *Rhododendron*.

Supplementary Information
The electronic supplement to the article (DOI: http://www.doi.org/10.14258/jcprm.20260316678s) provides additionalexperimental material that reveals the main points set out in the article.

Funding
This work was supported funding Siberian Federal Scientific Centre of Agrobiotechnology, N.I. Vavilov All-Russian Institute of Plant Genetic Resources, National Research Tomsk State University, Pacific Institute of Geography and Far Eastern Federal University. No additional grants to carry out or direct this particular research were obtained.

Conflict of Interest
The authors of this work declare that they have no conflicts of interest.

Open Access
This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (https://creativecommons.org/licenses/by/4.0/), which permits unrestricted use, distribution, and distribution in any medium provided you give appropriate credit to the original author(s) and the source and link to the Creative Commons license, and indicate if they were modified.

References

1. Pojarkova A.I. *Flora SSSR*. [Flora of the USSR]. Moscow, 1952, vol. 18, pp. 26–93. (in Russ.).
2. Aleksandrova M.S. *Rododendrony prirodnoy flory SSSR* [Rhododendrons of the natural flora of the USSR]. Moscow, 1975, 112 p. (in Russ.).
3. Zaytseva G.Y., Ambros E.V., Karakulov A.V., Novikova T.I. B*otanica Pacifica: A Journal of Plant Science and Conservation*, 2018, vol. 7(1), pp. 97–100. https://doi.org/10.17581/bp.2018.07110.
4. Belousova N.I., Khan V.A., Tkachev A.V. *Khimiya Rastitel'nogo Syr'iya*, 1999, no. 3, pp. 5–38. (in Russ.).
5. Belousov M.V., Komissarenko N.F., Berezovskaya T.P., Tochkova T.V. *Rastitel'nyye resursy*, 1994, no. 4, pp. 44–47. (in Russ.).
6. Okhlopkova Z.M., Chirikova N.K. *Fundamental Research*, 2012, vol. 11, pp. 1334–1336.
7. Bukreyeva T.V., Shavarda A.L., Matusevich O.V., Morozov M.A. *Rastitel'nyye resursy*, 2013, vol. 49(3), pp. 395–403. (in Russ.).
8. Butkiene R., Sakociute V., Latvenaite D., Mockute D. *Chemija,* 2008, vol. 19(2), pp. 19–24.
9. Razgonova M.P., Zakharenko A.M., Golokhvast K.S. *Khimiya rastitel'nogo syr'ya*, 2022, no. 1, pp. 179–191. https://doi.org/10.14258/jcprm.2022019506. (in Russ.).
10. Plyashechnik M.A. *Khimiya Rastitel'nogo Syr'iya*, 2012, no. 2, pp. 139–144. (in Russ.).
11. Ganina M.M., Popova O.I. *Khimiko-Farmatsevticheskiy Zhurnal*, 2015, vol. 49(7), pp. 33–35. https://doi.org/10.1007/s11094-015-1306-9. (in Russ.).
12. Arsenyev V.K. *Across the Ussuri Kray: travels in the Sikhote-Alin mountains.* Indiana University Press, 2016, 454 p. https://doi.org/10.2979/11625.0.
13. *Pharmacopoeia of the Eurasian Economic Union, Approved by Decision of the Board of Eurasian Economic Commission No. 100 Dated August 11, 2020*.

14. Roslawski M.J., Remmel R.P., Karanam A., Leppik I.E., Marino S.E., Birnbaum A.K. *Therapeutic Drug Monitoring*, 2019, vol. 41(3), pp. 357–370. https://doi.org/10.1097/FTD.0000000000000583.
15. Jamwal R., Topletz A.R., Ramratnam B., Akhlaghi F. *J. of Chromatogr. B*, 2017, vol. 1048, pp. 10–18. https://doi.org/10.1016/j.jchromb.2017.02.007
16. De A. Leite J., de Oliveira M.V.L., Conti R. et al. *Science & Justice*, 2018, vol. 58(5), pp. 355–365. https://doi.org/10.1016/j.scijus.2018.06.005.
17. Brighenti V., Pellati F., Steinbach M., Maran D., Benvenuti S. *J. of Pharm and Biomed Analys*, 2017, vol. 143, pp. 228–236.
18. Fan Z., Wang Y., Yang M., Cao J., Khan A., Cheng G. *Food Chem*., 2020, vol. 318, 126512. https://doi.org/10.1016/j.foodchem.2020.126512.
19. Viera M.N., Winterhalter P., Jerz G. *Phytochem. Anal*., 2016, vol. 27, pp. 116–125. https://doi.org/10.1002/pca.2606.
20. Rafsanjany N., Senker J., Brandt S., Dobrindt U., Hensel A. *J. Agric. Food Chem*., 2015, vol. 63, pp. 8804–8818.
21. Abeywickrama G., Debnath S.C., Ambigaipalan P., Shahidi F. *J. Agric. Food Chem*., 2016, vol. 64(49), pp. 9342–9351. https://doi.org/10.1021/acs.jafc.6b04291.
22. Cai Z., Wang C., Zou L., Liu X., Chen J., Tan M., Mei Y., Wei L. *Molecules,* 2019, vol. 24, 1936. https://doi.org/10.3390/molecules24101936.
23. Wang Z., Zhu W., Liu H., Wu G., Song M., Yang B., Yang D., Wang Q., Kuang H. *Molecules,* 2018, vol. 23(9), 2285. https://doi.org/10.3390/molecules23092285.
24. Liu S., Marsol-Vall A., Laaksonen O., Kortesniemi M., Yang B. *J. Agric. Food Chem*., 2020, vol. 68, pp. 7734–7744. https://doi.org/10.1021/acs.jafc.0c02842.
25. Aita S.E., Capriotti A.L., Cavaliere C., Cerrato A., Giannelli Moneta B., Montone C.M., Piovesana S., Lagana A. *Separations,* 2021, vol. 8, 58. https://doi.org/10.3390/separations8050058.
26. Qin D., Wang Q., Li H., Jiang X., Fang K., Wang Q., Li B., Pan C., Wu H. *Food Res. Int*., 2020, vol. 138 (B), 109789. https://doi.org/10.1016/j.foodres.2020.109789.
27. Nowak R., Olech M., Pecio L., Oleszek W., Los R., Malm A., Rzymowska J. *J. Sci. Food Agric*., 2014, vol. 94, pp. 560–567.
28. Abu-Reidah I.M., Ali-Shtayeh M.S., Jamous R.M., Arraes-Roman D., Segura-Carretero A. *Food Chem*., 2015, vol. 166, pp. 179–191. https://doi.org/10.1016/j.foodchem.2014.06.011.
29. Mekam P.N., Martini S., Nguefack J., Tagliazucchi D., Stefani E. *South African J. of Botany*, 2019, vol. 127, pp. 319–332. https://doi.org/10.1016/j.sajb.2019.11.001.
30. Belmehdi O., Bouyahya A., Jeko J., Cziaky Z., Zengin G. et al. *Int. J. Second Metab*., 2021, vol. 8(3), pp. 195–213. https://doi.org/10.21448/ijsm.947033.

Received 25 December 2024

Revised 30 June 2026

Accepted 30 June 2026

Information about authors

Dunkay Vasily Ivanovich – Researcher, rarf@yandex.ru

Razgonova Mayya Petrovna – Chief Researcher, Candidate of Biological Sciences, m.razgonova@vir.nw.ru

Zakharenko Alexander Mikhailovich – Leading Researcher, Candidate of Chemical Sciences, zakharenko@sfsca.ru

Razgonov Alexey Vladimirovich – Researcher, razgonov@dvfu.ru

Panichev Alexander Mikhailovich – Chief Researcher, Doctor of Biological Sciences, Professor, m.razgonova@vir.nw.ru

Golokhvast Kirill Sergeyevich – Director, Doctor of Biological Sciences, Professor of the Russian Academy of Sciences, droopy@mail.ru, golokhvast@sfsca.ru