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Ribes fragrans Pall.: Supercritical CO_2-extraction and complete plant metabolome

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ABSTRACT

Supercritical fluid technology was used to obtain bioactive substances from leaves of *Ribes fragrans* Pallas. Supercritical fluid technology showed the strongest extractive effect, which helped to extract the maximum amount of bioactive substances. Several experimental conditions were investigated in the pressure range 50–300 bar, with the used volume of co-solvent ethanol in the amount of 2.5 % in the liquid phase at a temperature in the range of 31–70°C. The most effective extraction conditions were: pressure 200 Bar and temperature 55°C. The CO_2-extract of leaves of *R. fragrans* contain various polyphenolic compounds and compounds of other chemical groups with valuable biological activity. For the first time, the metabolome of supercritical extracts of *R. fragrans* leaves was studied in this research. Using the method of supercritical extraction of plant matrices with the method of tandem mass spectrometry, it was possible to tentatively identify 79 bioactive compounds, of which 53 compounds are of polyphenol group. 20 chemical compounds from polyphenol group and 12 chemical compounds from other chemical groups were identified for the first time in genus *Ribes*.

Keywords: *Ribes fragrans*, supercritical fluid technology, tandem mass spectrometry, polyphenols, metabolome

РЕЗЮМЕ

Разгонова М.П., Сабитов А.С., Сенотрусова Т.А., Ли Н.Г., Витомскова Е.А., Голохваст К.С. *Ribes fragrans* Pall.: Сверхкритическая CO_2-экстракция и полный метаболом растения. Для получения биоактивных веществ из листьев *Ribes fragrans* Pall. использовали сверхкритическую флюидную технологию. Сверхкритическая флюидная технология показала самый сильный экстрактивный эффект, который позволил извлечь максимальное количество биоактивных веществ. Было исследовано несколько экспериментальных условий в диапазоне давлений 50–300 бар, с используемым объемом сорастворителя этанола в количестве 2,5 % в жидкой фазе при температуре в диапазоне 31–70°C. Наиболее эффективными условиями экстракции оказались: давление 200 бар и температура 55°C. CO_2-экстракт листьев *R. fragrans* содержит различные полифенольные соединения и соединения других химических групп, обладающие ценной биологической активностью. В данном исследовании впервые изучен метаболом сверхкритических экстрактов листьев *R. fragrans*. Используя метод сверхкритической экстракции растительных матриц с применением метода тандемной масс-спектрометрии, удалось предварительно идентифицировать 79 биологически активных соединений, из которых 53 соединения относятся к группе полифенолов. 20 химических соединений из группы полифенолов и 12 химических соединений из других химических групп были впервые идентифицированы в роде *Ribes*.

Ключевые слова: *Ribes fragrans*, технология сверхкритического флюида, тандемная масс-спектрометрия, полифенолы, метаболом

The research of the metabolomic composition of *Ribes fragrans* Pall. (Grossulariaceae) family from extracts obtained by supercritical fluid (SCF) technology was first undertaken in this study.

Species of the genus *Ribes* are grouped into eight subgenera according to Berger (1924), of which four have the greatest practical and breeding value: *Eucoreosma* Jancz. – black currants, *Ribesia* (Berl.) Jancz. – red currants, *Symphocalyx* Berl. – golden currants, *Calobotrya* Spach – ornamental currants. Subgenus *Eucoreosma* comprises 20 species including *R. fragrans*.

Ribes fragrans is widely distributed throughout the Far East in the alpine belt of the Sikhote-Alin Mt. range, the Zhdugdzhur Mt. range, in the Kolyma region, in the Amur Region, in Eastern Siberia and North-Eastern Mongolia (Fig. 1). It grows on rocky areas, usually inhabits the subalpine belt of mountainous regions, is found in pine and larch forests.

This type of currant grows in mountainous regions, mainly in the subalpine zone, and also grows well on stone placers. The plant lives up to its name: its leaves contain resins and essential oils, and therefore are much more fragrant than other blackcurrant leaves. Outwardly, they are smaller, rounded and with folded edges. The plants are not higher than 50–70 cm (Boczkarnikova 1973, Kharkevich 1988). This species is quite rare, despite the vast range, but it mainly occupies a narrow niche in the bald zone of the alpine belt. This species is considered an ancient species and is very poorly introduced into the culture (Malyshev 1994).

The leaves are similar in shape to a blackcurrant leaf, but more rounded and smaller with edges curled down. The

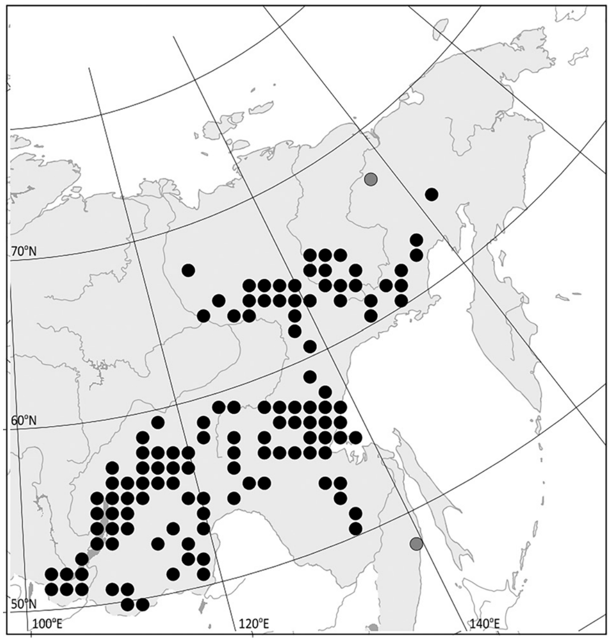

Figure 1 Geographical distribution area of *Ribes fragrance* Pall. in Russia (simplified from Dudov & Seregin 2024)

Figure 2 General habitus of *Ribes fragrance* Pall., in flowers (Voroshilova 2021)

high content of fragrant resins and essential oils in currant leaves makes them more fragrant, which influenced the choice of the name of this species (Fig. 2).

Plant metabolomics strategies are based on two analytical technologies; namely, MS and nuclear magnetic resonance (NMR). However, NMR based approaches are inferior to MS based approaches due to fewer compounds that can be separated given its relatively lower sensitivity. Despite continuous progress in MS technology, the study of the plant metabolome is a major challenge in plant metabolomics research. Currently, only a few thousand metabolites (>14,000) can be measured, while in the plant kingdom, 200,000 to one million metabolites are expected and its analysis is concentration dependent. However, it is difficult to predict the full extent of the complete plant metabolome because, unlike the transcriptome and proteome, it is genome-independent. In addition, due to the wide dynamic range of plant metabolite concentrations and high chemical diversity, no single analytical technology can cover the entire plant metabolome, so various extraction methods and a combination of additional analytical technologies are often used for analysis.

In this research, supercritical CO_2-extraction of the samples of *R. fragrans* was used to obtain an effective amount of biologically active substances. Traditionally used methods for obtaining biologically active substances from plants for further preparation of pharmaceutical substances, such as spray drying, solvent evaporation and jet milling, usually require the use of large amounts of solvent, and often require processing steps that require a lot of time / energy to remove residual solvent from product (Matos et al. 2019). Additional problems are the use of high temperatures and the difficult control of particle size and particle size distribution. SCF technology is a new and promising direction in pharmaceutical development and belongs to the near-critical region, i.e. relatively close to the critical point of the system, in which the fluids have liquid-like properties, such as high density, and gaseous properties, such as low viscosity and high diffusivity. These properties change quite dramatically with small changes in pressure and/or temperature, which helps to provide process flexibility and produce products with different characteristics. Supercritical carbon dioxide ($scCO_2$) is chosen in most applications due to its relatively low critical conditions (Tc = 31°C). It is also non-toxic, non-flammable and inexpensive. These properties make $scCO_2$ especially attractive in the pharmaceutical industry, since the processing of labile compounds can be carried out at low temperatures and in most cases without the help of organic solvents, which are easily removed from the composition if necessary. The applicability of SCF for the production of compositions based on lipids (Beh et al. 2012, Santo et al. 2013), polymer composites (Tandya et al. 2007), as well as for the sterilization of biomaterials (Foster et al. 2003, Karajanagi et al. 2011) has been considered in recent years.

We decided to use the SCF technology using various temperatures and pressures for the most efficient production of the entire complex of biologically active substances in this study. We suggested that the polar organic cosolvent ethanol can be used to better separate the biologically active substances of *R. fragrans*. As a rule, supercritical extraction is most successful when used together with the main solvent CO_2 co-solvent ethanol or methanol. We used tandem mass spectrometry to conduct a metabolomic study involving a detailed analysis of *R. fragrans* bioactives.

MATERIALS AND METHODS

Plant matrices of *R. fragrans* was collected during expedition work near Magadan region, Russia (59°33'49"N 150°48'10"E). All samples were morphologically authenticated according to the current standard of Russian Pharmacopeia (Pharmacopoeia... 2020).

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.

Experimental work on supercritical extraction was carried out using an SFE-500 system supercritical pressure extraction apparatus (Thar SCF Waters, Milford, USA). The device of the supercritical extraction system consists of: a co-solvent pump (Thar Waters P-50 High Pressure Pump), to introduce EtOH into the co-solvent extraction process to increase the polarity of the solvent. CO_2 flow meter (Siemens, Germany) to measure the flow of supercritical CO_2 supplied to the system, three extraction vessels, for extracting samples at different system pressures or different extraction times.

Flow rate was 10–25 mL/min for liquid CO_2 and 1.00 mL/min for EtOH. Extraction samples of 200 g of leave substance of *R. fragrans* were used. The extraction time was counted after reaching the working pressure and equilibrium flow, and it was 60 min for each sample.

Supercritical extracts filtered through a Millex HA 0.5 µm filter (Millipore Corp., MA, USA) and were analyzed on a Shimadzu LC-20 Prominence HPLC (Shimadzu, Kyoto, Japan) equipped with a UV sensor and an ion trap amaZon SL (BRUKER DALTONIKS, Germany) equipped with an ESI source in negative ion mode. The chemical compounds were separated on a C18 silica reverse phase column (4.6×150 mm, particle size: 2.7 µm) with mobile phases consisting of A, deionized water / formic acid (0.1 % v/v); B, acetonitrile, and the following gradient: 0–2 min, 0 % B; 2–50 min, 0–100 % B; control washing 50–60 min 100 % B. The injection volume was 10 µL. The solvent flow rate was 0.25 ml/min and the column temperature were 50°C. The HPLC eluate was introduced directly to the ESI interface and analyzed by ion trap (MS/MS).

The optimized parameters of ion trap amaZon SL (BRUKER DALTONIKS, Germany) in the experiments were the following values: ionization source temperature: 70°C, gas flow: 4 L/min, nebulizer gas (atomizer): 7.3 ψ, capillary voltage: 4500 V, end plate bend voltage: 1500 V, 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 chemical constituents were identified by comparing with a home-library database built by the Group of Biotechnology, Bioengineering and Food Systems at the Far-Eastern Federal University (Russia), based on data of nuclear magnetic resonance (NMR), ultraviolet spectroscopy, and MS, as well as data from the literature that is continually updated and revised. 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.

RESULT AND DISCUSSION

Several samples of the *R. fragrans* plant matrix were extracted by supercritical CO_2–extraction at various pressures and extraction temperatures. The supercritical pressure used in the experiments ranged from 50 to 300 bar and the extraction temperature varied from 31 to 70°C. The EtOH co-solvent, which affects the polarity and is necessary for successful extraction in the supercritical process, was used in an amount of 2.5 % of the total amount of the solvent. The three-dimensional graph (Fig. 3) shows a pronounced extremum, showing the highest yield of bioactive substances during supercritical extraction for a given plant matrix *R. fragrans*. The best conditions for the extraction of bioactive substances from the leaves of *R. fragrans* were obtained as follows: pressure 200 bar and temperature 55°C. The total yield of bioactive components under these extraction conditions was 3.9 mg per 100 mg of supercritical CO_2 extract of *R. fragrans*. Structural identification of each chemical constituents of *R. fragrans* was performed based on their exact mass and MS/MS fragmentation using HPLC-ESI-ion trap-MS/MS.

There were tentatively identified 79 compounds in CO_2-extracts from leaves of *R. fragrans* (53 compounds from polyphenol group and 26 compounds from other chemical groups). All the identified polyphenols and other compounds along with molecular formulas, and MS/MS data for *R. fragrans* are summarized in Table 1. Polyphenols are represented by the following chemical groups: flavones, flavonols, flavan-3-ols, flavanones, phenolic acids, anthocyanidins, lignans, coumarins. For the first time, twenty compounds from polyphenol group and twelve compounds from other chemical groups were identified in plant matrix of *R. fragrans*. There are flavones: Formononetin, Acacetin, Rhamnocitrin, 5,7-Dimethoxyluteolin, Eupatolitin-di-O-hexoside, flavonols: Herbacetin, Rhamnetin I, Isorhamnetin, Padmatin, Myricetin-3-O-glucuronide, Rhamnetin-di-O-hexoside, Myricetin-O-galloyl-hexoside; flavan-3-ols (epi)-galoocatechin-3-gallate, (epi)-afzelechin derivative; flavanone Hemiphloin, lignans: Secoisolariciresinol, Dimethyl-secoisolariciresinol, coumarin Fraxin, etc. Constituents from other chemical groups are benzofuran Loliolide; aminoalkylindole 5-Methoxydimethyltryptamine; sesquiterpenoid Caryophyllene oxide; aporphine alkaloid Anonaine.

Figure 4 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 p-Hydroxybenzoic acid hexoside from *R. fragrans* is shown in Fig. 4A.

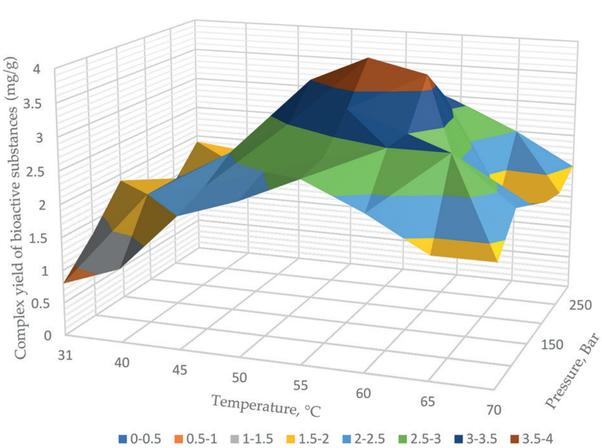

Figure 3 3D graph data of supercritical CO_2-extraction from leaves of *Ribes fragrans*

Table 1. Compounds identified from the CO_2-extracts of *Ribes fragrans* in positive and negative ionization modes by HPLC-ion trap-MS/MS.

No.	Class of compounds	Identified compounds	Formula	Mass	Molecular ion [M-H]⁻	Molecular ion [M+H]⁺	Fragmentation number MS/MS 2	3	4	References
POLYPHENOLS										
1	Flavone	**Formononetin** [Biochanin B; Formononetol]*****	$C_{16}H_{12}O_4$	268.2641		269	231; 199	171		Astragali Radix (Huang et al. 2009, Zhang et al. 2014, Wang et al. 2014); Isoflavones (Hanganu et al. 2010); Huolisu Oral Liquid (Yin et al. 2021); *Maackia amurensis* (Razgonova et al. 2023); *Dracocephalum jacutense* (Razgonova et al. 2022)
2	Flavone	**Apigenin** [5,7-Dixydroxy-2-(40Hydroxyphenyl)-4H-Chromen-4-One]	$C_{15}H_{10}O_5$	270.2369		271	253	224		*Lonicera henryi* (Jaiswal et al. 2014); *Ribes meyeri* (Zhao et al. 2021); *Lonicera japonica* (Cai et al. 2019); *Vaccinium floribundum* (Aita et al. 2021); Mexican lupine species (Wojakowska et al. 2023)
3	Flavone	**Trihydroxy(iso)flavone**	$C_{15}H_{10}O_5$	270.2369		271	215	173		Propolis (Belmehdi et al. 2021)
4	Flavone	**Luteolin**	$C_{15}H_{10}O_6$	286.2363		287	153; 171			*Lonicera henryi*; *Ribes meyeri*; *Lonicera japonica*; Propolis; *Chamaecrista nictitans* (Mateos-Martin et al. 2021); *Phyllostachys nigra* (Van Hoyweghen et al. 2014); *Jatropha* (Zengin et al. 2021)
5	Flavone	**Acacetin** [Linarigenin; Buddleoflavonol]*****	$C_{16}H_{12}O_5$	284.2635		285	239; 203; 149	183; 159	168	Mexican lupine species; Propolis; *Mentha* (Cirlini et al. 2016, Xu et al. 2017); *Dracocephalum moldavica* (Martinez-Vazquez et al. 2012); *Wissadula periplocifolia* (Teles et al. 2015)
6	Flavone	**Dihydroxy-methoxy(iso)flavone**	$C_{16}H_{12}O_5$	284.2635		285	267; 159	223	195	Propolis
7	Flavone	**2'-Hydroxygenistein***	$C_{15}H_{10}O_6$	286.2363		287	205	187	159	Mexican lupine species
8	Flavone	**Eriodictyol** [3',4',5,7-tetrahydroxy-flavanone]	$C_{15}H_{12}O_6$	288.2522		289	271; 163	201		*Vaccinium floribundum*; Propolis; *Jatropha*; *Artemisia absinthium* (Trifan et al. 2022); *Mentha* (Li & Tian 2018); *Embelia* (Vijayan & Raghu 2019); *Rosmarinus officinalis* (Mena et al. 2016)
9	Flavone	**Rhamnocitrin***	$C_{16}H_{12}O_6$	300.2629		301	167; 161	133		Astragali radix (Zhang et al. 2014); *Mentha* (Li & Tian 2018)
10	Flavone	**Diosmetin** [Luteolin 4'-Methyl Ether; Salinigricoflavonol]	$C_{16}H_{12}O_6$	300.2629		301	255	199	157	*Lonicera japonica*; *Vaccinium floribundum* ; *Mentha* (Xu et al. 2017); *Dracocephalum moldavica*; *Zostera marina* (Razgonova et al. 2022)
11	Flavone	**5,7-Dimethoxyluteolin***	$C_{17}H_{14}O_6$	314.2895		315	269	251	195	*Syzygium aromaticum* (Fanthoni et al. 2016); *Rosa rugosa* (Razgonova et al. 2022)
12	Flavone	**Diosmetin-6-C-hexoside**	$C_{22}H_{22}O_{11}$	462.4035	461		298	283	255	Lemon (Spinola et al. 2015)
13	Flavone	**Chrysoeriol C-hexoside-C-pentoside**	$C_{27}H_{30}O_{15}$	594.5181		595	577; 277	563; 199		*Triticum aestivum* L. (Cavaliere et al. 2005, Stallmann et al. 2020, Geng et al. 2016)
14	Flavone	**Diosmin** [Diosmetin-7-*O*-rutinoside; Barosmin; Diosimin]	$C_{28}H_{32}O_{15}$	608.5447		609	591; 531; 355	531	487	*Mentha* (Xu et al. 2017); Lemon; *Ferocactus glaucescens* (Hamed et al. 2021); Grataegi Fructus (Huang et al. 2018)
15	Flavone	**Eupatolitin-di-*O*-hexoside***	$C_{29}H_{34}O_{18}$	670.5695	669		347	303	233	*Artemisia absinthium*
16	Flavonol	**Kaempferol** [3,5,7-Trihydroxy-2-(4-hydro- xyphenyl)-4H-chromen-4-one]	$C_{15}H_{10}O_6$	286.2363		287	285; 161	270	242	*Ribes meyeri; Lonicera japonica*; *Vaccinium floribundum* ; *Polygala sibirica* (Song et al. 2013); *Rhus coriaria* (Abu-Reidah et al. 2015)
17	Flavonol	**Quercetin**	$C_{15}H_{10}O_7$	302.2357		303	285; 177	267; 185	197; 135	*Ribes meyeri*; Propolis; *Vaccinium macrocarpon* (Rafsanjany et al. 2015, Abeywickrama et al. 2016); *Capsicum annuum* (Pascale et al. 2020); *Bougainvillea* (El-Sayed et al. 2021)
18	Flavonol	**Herbacetin** [3,5,7,8-Tetrahydroxy-2-(4-hydro- xyphenyl)-4H-chromen-4-one]*	$C_{15}H_{10}O_7$	302.2357		303	203; 275	157		*Rhodiola rosea* (Zapesochnaya et al. 1985, Petsalo et al. 2006, Jeong et al. 2009)
19	Flavonol	**Dihydroquercetin** (Taxifolin; Taxifoliol)	$C_{15}H_{12}O_7$	304.2516		305	287; 163	269	241	*Vaccinium floribundum*; *Larix dahurica* (Voskoboinikova et al. 1993); *Camellia kucha* (Qin et al. 2020)

Table 1. Continued.

No.	Class of compounds	Identified compounds	Formula	Mass	Molecular ion [M-H]⁻	Molecular ion [M+H]⁺	Fragmentation number MS/MS 2	3	4	References
20	Flavonol	**Rhamnetin I** [beta-Rhamnocitrin; Quercetin 7-Methyl ether]*	$C_{16}H_{12}O_7$	316.2623		317	270; 177	163	145	*Polygala sibirica*; *Rhus coriaria* (Abu-Reidah et al. 2015); *Phlomis* (Aghakhani et al. 2019); *Mangifera indica* (Navarro et al. 2019)
21	Flavonol	**Isorhamnetin** [Isorhamnetol; Quercetin 3'-Methyl ether; 3-Methylquercetin]*	$C_{16}H_{12}O_7$	316.2623		317	271	253	197	Astragali Radix (Huang et al. 2009); Propolis; *Embelia*; *Rosmarinus officinalis*; *Syzygium aromaticum*; rapeseed petals (Yin et al. 2019)
22	Flavonol	**Quercetin 3-O-methyl ether**	$C_{16}H_{12}O_7$	316.2623		317	271; 299; 215; 177	253; 211; 197; 183; 159	211; 197; 183; 159	Propolis; *Jatropha*; Brazilian propolis (Xu et al. 2020)
23	Flavonol	**Myricetin**	$C_{15}H_{10}O_8$	318.2351		319	273	255	199	*Vaccinium floribundum*; *Vaccinium macrocarpon* (Rafsanjany et al. 2015); *Sanguisorba officinalis* (Kim et al. 2018); *Clidemia rubra* (Gordon et al. 2011); *Taraxacum officinale* (Aabideen et al. 2020)
24	Dihydroflavonol	**Padmatin** [7-Methoxy-3,3',4',5-tetrahydroxyflavanone]*	$C_{16}H_{14}O_7$	318.2782		319	273	255; 149	199; 159	Propolis
25	Flavonol	**Quercitrin** [Quercetin 3-L-rhamnoside; Quercetrin]	$C_{21}H_{20}O_{11}$	448.3769	447		301; 247; 145	283; 221	221	Propolis; *Embelia*; Grataegi Fructus; *Vaccinium macrocarpon* (Rafsanjany et al. 2015, Abeywickrama et al. 2016); *Rhus coriaria* (Abu-Reidah et al. 2015); *Camellia kucha*; *Euphorbia hirta* (Mekam et al. 2019)
26	Flavonol	**Kaempferol-3-O-glucuronide**	$C_{21}H_{18}O_{12}$	462.3604		463	287	213; 165	183	Strawberry (Spinola et al. 2015); *A. cordifolia* (Hamed et al. 2021); *Glottiphyllum linguiforme* (Hamed et al. 2021); *Rhus coriaria* (Abu-Reidah et al. 2015); *Euphorbia hirta*; *Rhus coriaria* (Taskin et al. 2021); *Rosa canina* (Ieri et al. 2015)
27	Flavonol	**Quercetin-3-O- glucoside**	$C_{21}H_{20}O_{12}$	464.3763		465	303	257; 165	229	*Lonicera henryi*; *Ribes meyeri*; *Lonicera japonica*; *Vaccinium floribundum*; cranberry (Wang et al. 2018); *Vaccinium myrtillus* (Liu et al. 2014)
28	Flavonol	**Quercetin-3-O-glucuronide** [Miquelianin]	$C_{21}H_{18}O_{13}$	478.3598		479	303	257; 165	229	*Bougainvillea*; *Euphorbia hirta*; *Rosa canina*; *Vaccinium myrtillus*
29	Flavonol	**Myricetin-3-O-glucuronide***	$C_{21}H_{18}O_{14}$	494.361		495	319	273; 165	245	*Rhus coriaria* (Abu-Reidah et al. 2015); *Parkinsonia aculeata* (Hassan et al. 2019)
30	Flavonol	**Rhamnetin-di-*O*-hexoside***	$C_{28}H_{32}O_{17}$	640.5435		641	303	285	197	*Artemisia absinthium*
3	Flavonol	**Myricetin-O-galloyl-hexoside***	$C_{28}H_{24}O_{17}$	632.4800	631		315	221		*Rhus coriaria* (Abu-Reidah et al. 2015); Myrtle (D'Urso et al. 2017); *Rhododendron* (Jaiswal et al. 2012)
32	Flavan-3-ol	**(epi)catechin**	$C_{15}H_{14}O_6$	290.2681		291	261; 157	173	191; 143	*Vaccinium floribundum*; *Vaccinium macrocarpon* (Abeywickrama et al. 2016); cranberry; *Vaccinium myrtillus*
33	Flavan-3-ol	**Epiafzelechin derivative***	$C_{18}H_{16}O_{10}$	392.3136		393	275	245; 175	157	*Zostera marina*
34	Flavan-3-ol	**Derivative of (epi)-Catechin**	$C_{22}H_{32}O_8$	424.4847		425	291	261; 173	173	Pubchem
35	Flavan-3-ol	**Epigallocatechin-3-gallate***	$C_{22}H_{18}O_{11}$	458.3717	457		411	305; 261	261	*Camellia kucha*; *Ferocactus glaucescens*; *Clidemia rubra* (Gordon et al. 2011); *Rhododendron*
36	Flavanone	**Butin [7,3',4'-Trihydroxyflavanone]**	$C_{15}H_{12}O_5$	272.0681		273	255	185; 199	143	*Ribes meyeri*
37	Flavanone	**Naringenin** [Naringetol; Naringenine]	$C_{15}H_{12}O_5$	272.5228		273	153; 255	171		*Vaccinium floribundum*; Mexican lupine species; *Syzygium aromaticum*; *Glottiphyllum linguiforme*; *Phlomis*
38	Flavanone	**Hesperitin** [Hesperetin]	$C_{16}H_{14}O_6$	302.2788		303	203	157		*Vaccinium floribundum*; *Rosmarinus officinalis*; *Rhinacanthus nasutus* (Songserm et al. 2022)
39	Flavanone	**Dihydrokaempferol** [Aromadendrin; Katuranin]	$C_{15}H_{12}O_6$	288.2522		289	271; 231; 177	215; 145		*Vaccinium floribundum*; *Ferocactus glaucescens*; *Camellia kucha*; *Phoenix dactylifera* (Said et al. 2017)

Table 1. Continued.

No.	Class of compounds	Identified compounds	Formula	Mass	Molecular ion [M-H]⁻	Molecular ion [M+H]⁺	Fragmentation number MS/MS 2	3	4	References
40	Flavanone	**Hemiphloin [Naringenin 6-*C*-glucoside]***	$C_{21}H_{22}O_{10}$	434.3934		435	399; 345; 271; 211	363; 271; 211; 137	331; 303; 173	*Jatropha*
41	Phenolic acid	**p-Hydroxybenzoic acid hexoside**	$C_{13}H_{16}O_8$	300.2613		301	255; 283; 199; 167	199; 145	157	*Ribes meyeri*; *Vaccinium floribundum*; *Embelia*; *Ribes* sp. (Maatta et al. 2003); *Punica granatum* (Mena et al. 2012)
42	Hydroxybenzoic acid	**Ellagic acid** [Benzoaric acid; Elagostasine; Lagistase; Eleagic acid]	$C_{14}H_6O_8$	302.1926		303	257; 203; 165	185		*Ribes meyeri*; strawberry (Seeram et al. 2006, Sun et al. 2014); *Rubus occidentalis* (Paudel et al. 2012)
43	Phenolic acid	**3-O-caffeoylshikimic acid** [3-CSA]	$C_{16}H_{16}O_8$	336.2934	335		317; 234	299; 234	253	*Ribes meyeri*; Grataegi Fructus; *Phoenix dactylifera*
44	Phenolic acid	**p-Coumaroylquinic acid**	$C_{16}H_{18}O_8$	338.3093		339	147	119		*Ribes meyeri*; *Vaccinium floribundum*; *Ribes nigrum* (Ieri et al. 2015); *Vaccinium myrtillus*; *Ribes magellanicum* (Burgos-Edwards et al. 2018)
45	Phenolic acid	**Chlorogenic acid** [3-O-Caffeoylquinic acid]	$C_{16}H_{18}O_9$	354.3087		355	273; 255; 235; 193; 149	255; 215; 161; 143	227; 199; 161; 143	*Lonicera henryi*; *Lonicera japonicum*; *Vaccinium floribundum*; *Vaccinium macrocarpon* (Rafsanjany et al. 2015, Abeywickrama et al. 2016); cranberry; *Vaccinium myrtillus*; *Ribes magellanicum*
46	Phenolic acid	**Cryptochlorogenic acid** [4-O-Caffeoylquinic acid; Quinic acid 4-O-Caffeate]	$C_{16}H_{18}O_9$	354.3087		355	163	145		*Lonicera japonica*; *Vaccinium myrtillus*; *Ribes magellanicum*; *Rubus ulmifolius* (da Silva et al. 2019)
47	Phenolic acid	**Caffeic acid derivative***	$C_{16}H_{18}O_9Na$	377.2985	377		341; 215	179	227; 199; 161; 143	*Bougainvillea*
48	Phenolic acid	**Ferulic acid derivative***	$C_{21}H_{20}O_{10}$	432.3775		433	386	340	284; 164	*Embelia*
49	Anthocyanidin	**Cyanidin-3-O-glucoside** [Cyanidin 3-O-beta-D-Glucoside; Kuromarin]	$C_{21}H_{21}O_{11}^+$	449.3848	447		285	255		*Vaccinium floribundum*; *Ribes magellanicu*m; *Rubus ulmifolius*; *Berberis ilicifolia; Berberis empetrifolia; Ribes maellanicum; Ribes cucullatum; Myrteola nummalaria; Gaultheria mucronata; Gaultheria antarctica; Rubus geoides*; *Fuchsia magellanic*a (Ruiz et al. 2013); *Berberis lycium* (Pradhan & Saha 2016)
50	Anthocyanidin	**Delphinidin 3-O-Beta-D-sambubioside**	$C_{26}H_{29}O_{16}$	597.4989		597	303	257; 165	229	*Berberis microphylla* (Ruiz et al. 2010); *Triticum aestivum* (Garg et al. 2016)
51	Coumarin	**Fraxin** (Fraxetin-8-O-glucoside)*	$C_{16}H_{18}O_{10}$	370.3081		371	208; 165	165; 191		*Actinidia deliciosa* (Razgonova et al. 2023); *Rosa rugosa*; *Actinidia* (Chen et al. 2021)
52	Lignan	**Secoisolariciresinol***	$C_{20}H_{26}O_6$	362.4168	361		329	285; 220	243	*Ferocactus pottsii* (Hamed et al. 2021); *Punica granatum* (Mena et al. 2012); *Triticum aestivum* L. (Dinelli et al. 2011); *Punica granatum* (Bonzanini et al. 2009), lignans (Eklund et al. 2008)
53	Lignan	**Dimethyl-secoisolariciresinol***	$C_{22}H_{30}O_6$	390.4700		391	372	305	287	lignans
		OTHERS								
54	Carboxylic acid	**Gluconic acid** [Dextronic acid; Maltonic acid; Glycogenic acid; Pentahydroxy hexanoic acid]	$C_6H_{12}O_7$	196.1553		197	179; 161	161		*Ribes meyeri* (Zhao et al. 2021); *Colchicum micranthum* 90. (Gulsoy-Tolpan et al. 2018);
55	Benzofuran	**Loliolide***	$C_{11}H_{16}O_3$	196.2429		197	179; 135	161	133	*Jatropha*
56	Amino acid	**L-Tryptophan** [Tryptophan; (S)-Tryptophan]	$C_{11}H_{12}N_2O_2$	204.2252		205	149	147		Huolisu Oral Liquid; *Camellia kucha*; Rapeseed petals; *Euphorbia hirta*; *Rosa acicularis* (Razgonova et al. 2022)
57	Amino-alkylindole	**5-Methoxydimethyltryptamine***	$C_{13}H_{18}N_2O$	218.2948		219	201	159		*Camellia kucha*
58	Sesquiterpenoid	**Caryophyllene oxide** [Caryophyllene-alpha-oxide]*	$C_{15}H_{24}O$	220.3505		221	201; 135	145		*Rosa davurica* (Razgonova et al. 2022); olive leaves (Suarez Montenegro et al. 2021); *Ledum palustr*e (Razgonova et al. 2022b)

Table 1. Continued.

No.	Class of compounds	Identified compounds	Formula	Mass	Molecular ion [M-H]⁻	Molecular ion [M+H]⁺	Fragmentation number MS/MS 2	3	4	References
59	Omega-5 fatty acid	**Myristoleic acid** [Cis-9-Tetradecanoic acid]*	$C_{14}H_{26}O_2$	226.3550		247	209	139; 127	122	*Maackia amurensis*; *Ferocactus glaucescens*
60	Aporphine alkaloid	**Anonaine***	$C_{17}H_{15}NO_2$	265.3065		266	248	230	182	*Rosa rugosa*; *Magnolia* (Guo et al. 2019)
61	Omega-3 fatty acid	**Stearidonic acid** [6,9,12,15-Octadecatetraenoic acid; Moroctic acid]*	$C_{18}H_{28}O_2$	276.4137		277	259; 195; 163; 149	121		*Jatropha*; *Glottiphyllum linguiforme*; *Rhus coriaria*; Salviae Miltiorrhizae (Yang et al. 2015)
62	Omega-3 fatty acid	**Linolenic acid** (Alpha-Linolenic acid; Linolenate)	$C_{18}H_{30}O_2$	278.4296		279	243; 195; 173; 137	131		*Maackia amurensis*; *Jatropha*; *Pinus sylvestris* (Ekeberg et al. 2006)
63	Long-chain fatty acid	**Dihydroxypalmitic acid***	$C_{16}H_{32}O_4$	288.4229		289	147; 121	121		*Rhus coriaria*
64		**1-(3,4-Dihydroxyphenyl)-3-(2,4,6-trihydroxyphenyl)-2-propanol**	$C_{15}H_{16}O_6$	292.2839		293	261; 243; 191	243	173	*Ribes magellanicum*
65	Omega-3 fatty acid	**Hydroxy linolenic acid**	$C_{18}H_{30}O_3$	294.4290		295	276; 179	179	161	*A. cordifolia*
66	Omega-3 fatty acid	**Hydroxy octadecatrienoic acid**	$C_{18}H_{30}O_3$	294.4290	293		275; 195	231		*Glottiphyllum linguiforme*; *Ferocactus glaucescens*; *Ferocactus pottsii*
67	Oxylipins	**9,10-Dihydroxy-8-oxooctadec-12-enoic acid** [oxo-DHODE; oxo-Dihydroxy-octadecenoic acid]	$C_{18}H_{32}O_5$	328.4437	327		229; 291; 171	211		*Dracocephalum jacutense*; *Taraxacum officinale*; *Rosa acicularis*; *Bituminaria* (Llorent-Martinez et al. 2015)
68	Diterpenoid	**Gibberellin A5**	$C_{19}H_{22}O_5$	330.3750		331	285	203; 157	157	(Urbanova et al. 2013)
69		**Cyclohexa-2,4-diene-1-carboxylic acid***	$C_{14}H_{20}O_{10}$	348.3026	347		303	233	233	*Actinidia*
70	Diterpenoid	**Gibberellin A29**	$C_{19}H_{24}O_6$	348.3903	347		303	299	257; 227	*Euphorbia hirta*
71	Unsaturated fatty acid	**Pentacosenoic acid**	$C_{25}H_{48}O_2$	380.6474	379		303	233	231	*Ferocactus glaucescens*
72	Cholestanoid	**Desmosterol** [24-Dehydrocholesterol; 3beta-Cholesa-5,24-Dien-3-Ol]	$C_{22}H_{24}O_6$	384.4224		385	367	349	331; 187	*A. cordifolia* (Hamed et al. 2021)
73		**Trehalose (+FA adduct) CH_2O_2**	$C_{13}H_{24}O_{13}$	388.3219	387		341	179		Pubchem
74	Sterol	**Beta-Sitostenone** [Stigmast-4-En-3-One; Sitostenone]*	$C_{29}H_{48}O$	412.6908		413	354; 191	298	255; 140	*Ferocactus herrerae* (Hamed et al. 2021); *Cryptomeria japonica bark* (Li et al. 2008); *Xanthium sibiricum* (Kan et al. 2009); *Terminalia laxiflora* (Salih et al. 2018)
75	Long-chain fatty acid	**Nonacosanoic acid**	$C_{29}H_{58}O_2$	438.7696		439	393	344		*C. edulis* [43]
76	Product of degradation of chlorophyll	**Pheophorbide a**	$C_{35}H_{36}N_4O_5$	592.6841		593	533	461	433	(van Breemen et al. 1991)
77	Saponin	**Sibiricasaponin B***	$C_{35}H_{55}O_{11}S$	683.8698		684	595; 429	341	324	*Polygala sibirica*]
78	Phenyl-propanoid	**Glomeratose D [3-O-[(E)-3,4,5-trimethoxycinnamoyl]-beta-D-fructofuranosyl(2-1)-[33-O-(E)-3,4,5-trimethoxycinnamoyl]-alpha-D-glucopyranoside***	$C_{36}H_{46}O_{19}$	782.7390		783	723; 599; 428; 301	598		*Polygala glomerata* (Zhang et al. 1998)
79	Steroidal alkaloid	**Alpha-chaconine***	$C_{45}H_{73}NO_{14}$	852.0594		852	706; 560; 398	560; 398	398	*Solanum tuberosum* (Shakya & Navarre 2008, Deuber et al. 2012, Hossain et al. 2016)

*Chemical constituents identified for the first time in *R. fragrans*.

[M+H]⁻ ion produced four fragment ions with m/z 255.3, m/z 283.22, m/z 199.29, and m/z 167.17 (Fig. 4A). The fragment ion with m/z 255.3 produced three characteristic daughter ions with m/z 227.26, m/z 199.17, and m/z 145.28. The fragment ion with m/z 199.17 produced one characteristic ion with m/z 157.24. It was identified in the references in extract from *Ribes meyeri* (Zhao et al. 2021), *Vaccinium floribundum* (Aita et al. 2021), *Embelia* (Vijayan & Raghu 2019), *Ribes* sp. (Maatta et al. 2003), *Punica granatum* (Mena et al. 2012). The CID spectrum in positive ion modes of dihydroquercetin (taxifolin) from *R. fragrans* is shown in Fig. 4B.

$[M+H]^+$ ion produced two fragment ions with m/z 287.28, and m/z 163.28 (Fig. 4B). The fragment ion with m/z 287.28 produced one characteristic daughter ion with m/z 269.28. The fragment ion with m/z 269.28 produced one characteristic daughter ion with m/z 241.27. It was identified in the bibliography in extracts from *Vaccinium floribundum* (Aita et al. 2021), *Larix dahurica* (Voskoboinikova et al. 1993), *Camellia kucha* (Qin et al. 2020). The CID spectrum in negative ion modes of Cyanidin-3-O-glucoside [Cyanidin 3-O-beta-D-Glucoside; Kuromarin] from *R. fragrans* is shown in Fig. 4C.

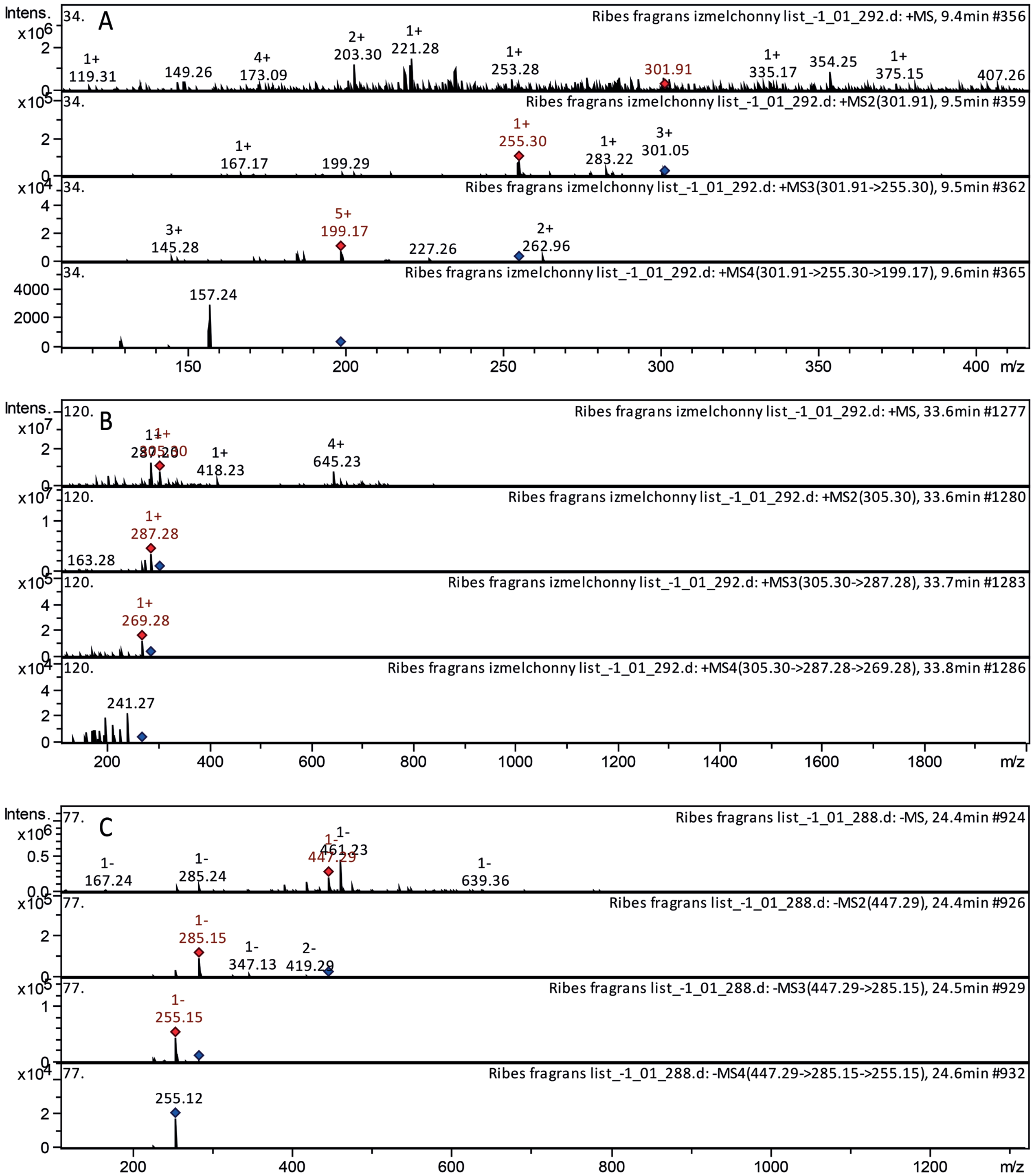

Figure 4 CID spectra of A – p-Hydroxybenzoic acid hexoside from R. fragrans, m/z 301.91; B – dihydroquercetin (taxifolin) from R. fragrans, m/z 305.3; C – Cyanidin-3-O-glucoside [Cyanidin 3-O-beta-D-Glucoside; Kuromarin] from R. fragrans, m/z 447.29

[M–H]⁻ ion produced three fragment ions with m/z 285.15, m/z 419.29, and m/z 347.13 (Fig. 4C). The fragment ion with m/z 285.15 produced one characteristic daughter ion with m/z 255.15. It was identified in the bibliography in extracts from *Disterigma* (Aita et al. 2021); *Ribes magellanicum* (Burgos-Edwards et al. 2018); *Rubus ulmifolius* (da Silva 2019); *Berberis ilicifolia, B. empetrifolia*; *Fuchsia magellanica*, *Gaultheria mucronata*, *G. antarctica*, *Myrteola nummalaria*, *Ribes maellanicum*; *R. cucullatum*, *Rubus geoides* (Ruiz et al. 2013), *Berberis lycium* (Pradhan & Saha 2016). Separately, it should be noted that a detailed analysis of the presence of polyphenols and biologically active substances from other chemical groups showed the highest number of flavonoids at supercritical CO_2-extraction at a pressure of 200 bar and extraction temperature 55°C – 53 compounds.

Thus, as a result of a detailed study of the metabolomic composition by supercritical extraction combined with tandem mass spectrometry, new data on the content of chemical constituents in *R. fragrans* were obtained, including a number of chemical components found for the first time in the plant matrix of *R. fragrans*.

CONCLUSION

Our scientific group was used supercritical fluid technology to obtain maximum compound of chemical constituents from leaves of *R. fragrans*. The supercritical extraction method proved to be the most effective type of extraction, giving the highest yield of bioactive substances. Several experimental conditions were investigated in the pressure range 10–300 bar, with the used volume of co-solvent ethanol in the amount of 2.5 % in the liquid phase at a temperature in the range of 31–70°C. The most effective extraction conditions are: pressure 200 Bar and temperature 55°C for leaves of *R. fragrans*. The leaves of *R. fragrans* contain various polyphenolic constituents and constituents of other chemical groups with valuable bioactivity. Tandem mass-spectrometry (HPLC-ESI – ion trap) was applied to detect target analytes. 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. 79 different bioactive components have been identified in *R. fragrans* extracts. 21 polyphenol were identified for the first time in genus *Ribes*.

These data could support future research for the production of a variety of pharmaceutical products containing ultra-pure extracts of *R. fragrans*. The richness of various biologically active compounds, including compounds of polyphenol group and compounds of other chemical groups (oxylipins, Omega-fatty acids, sterols, diterpenoids, etc.), provides great opportunities for the design of new nutritional and dietary supplements based on supercritical extracts from the leaves, stems and berries of *R. fragrans*.

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Author contribution

Conceptualization, K.G. and M.R.; methodology, T.S., N.L., M.R.; software, M.R.; validation, E.V., and K. G.; formal analysis, A.S., M.R.; investigation, K.G. and M.R.; resources, K.G. and M.R.; data curation, A.S.; writing—original draft preparation—M.R.; writing—review and editing E.V. and T.S.; visualization, M.R., N.L., E.V.; supervision, T.S.; project administration, K.G., M.R. All authors have read and agreed to the published version of the manuscript.

Conflicts of interest

The authors declare no conflict of interest.

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