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ANALYSIS OF THE ESSENTIAL OILS IN LEAVES AND RHIZOMES WITH ROOTS OF ANGELICA ARCHANGELICA GROWING IN UKRAINE

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Essential oils, comprised of volatile compounds, have a wide range of biological effects, making them valuable in medicine, industry, and agriculture. They exhibit properties such as antimicrobial, anti-inflammatory, antiviral, antioxidant, anti-obesity, antidiabetic, and smooth muscle relaxation. In this aspect, plants belonging to the genus Angelica show promise. One of these essential oil plants is Angelica archangelica. There is insufficient information in the literature on the essential oils of the leaves and rhizomes with roots of Angelica archangelica.

The aim. *The aim of our study was to identify and determine the quantitative content of essential oils by GC/MS method in Angelica archangelica leaves and rhizomes with roots grown in Ukraine.*

Materials and methods. *The determination of the essential oils composition of Angelica archangelica was conducted using Agilent Technologies 6890 chromatograph with mass spectrometric detector 5973 (Agilent Technologies, USA).*

Results. *The leaves of Angelica archangelica were found to contain twenty-three components in their essential oil, while the rhizomes and roots of this plant contained fifteen components. Eleven components were common to both parts of the plant, namely cis-Pinane, α-Farnesene, α-Curcumene, α-Caryophyllene, Copaen, β-Bisabolene, δ-Amorphene, α-Muurolene, trans-Chrysanthemal, β-Guaiene, α-Elemene. Twelve components such as α-Pinene, β-Myrcene, 3-p-Menthene, Isoborneol, Anisole, Bornyl acetate, (Z)-β-Elemene, Caryophyllene, (-)-Spathulenol, α-Bergamotene, γ-Muurolene, α-Bisabolol were present only in leaves, and four components namely p-Isopropenylacetophenone, β-Cubebene, α-Zingiberene, Hexahydrofarnesyl acetone were present only in rhizomes with roots.*

Conclusions. *The component composition of the essential oil in the leaves and the rhizomes with roots of Angelica archangelica growing in Ukraine was investigated using the GS/MC method. We have defined for the first time the chemical composition of the essential oils of the leaves of Angelica archangelica, 23 components of essential oil were identified. In the rhizomes with roots, 15 components of essential oils were identified. The following pharmacologically important components, cis-Pinane and α-Farnesene, were found in both samples of the essential oil of Angelica archangelica in significant quantities. These results have been cross-analyzed and are particularly important for planning and defining the process of cultivation and use of this species plant in traditional and official medicine*

Keywords: *Angelica archangelica, leaves, rhizomes with roots, essential oils, GC/MS*

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1. Introduction

Essential oils have been of supreme importance for pharmacology applications and cosmetic and aroma preparations for a long time because of their pleasant, intense, sweet and floral, as well as their fixative properties [1–3]. Essential oils are derived from plants as secondary metabolites perfused with non-polar liquids that contain volatile ingredients. Generally, they are made up of terpenes and phenylpropanes [4]. Their therapeutic activities were widely reported, and they ranged from antifungal, antibacterial, antioxidant, anti-obesity, antidiabetic, anti-lipid peroxidation, etc. [5–8]. The remedial possibility of essential oils, like other plant-derived remedies, has yet to be fully realized.

Plant secondary products typically found in *Apiaceae* are essential oils, including terpenoids and phenylpropanoids, coumarins and furanocoumarins, sesquiterpenelactones, and polyacetylene [9]. Plants of the genus *Angelica* are promising in this regard. Angelica is among the largest genus of the Apiaceae family. It has approximately 110 species of biennial and perennial herbs [10].

Angelica archangelica (*A. archangelica*) is a perennial herb in the genus of *Angelica* with green-

ish-white flowers and large compound pinnately compound leaves [11]. A member of the umbelliferous family *Apiaceae*, *A archangelica* commonly is found in northern temperate regions of the world, including Finland, Norway, Sweden, Denmark, and Greenland. It requires moist shady areas for proper growth and often is found near riverbanks and ponds [12].

A. archangelica has been widely used in folk medicine and is one of the most respected medicinal herbs in northern countries, where it was cultivated during the Middle Ages [13]. This plant has the presence of essential oil, coumarins, acids, and flavonoids [14]. *A. archangelica* has been shown to stimulate gastric and pancreatic secretions. The rhizome with roots of this plant has been used internally for digestive problems, including gastric ulcers [15–18]. Research on coumarins has shown promising activities like anti-tumour, neurotoxic, antifungal, anticonvulsant, antiulcerogenic, and hepatoprotective [19–21].

The most characteristic secondary metabolites of *A. archangelica* are essential oils and furanocoumarins, both of which are more abundant in the roots and seeds than in the leaves. The whole plant has been used as a vegetable. In folk medicine *A. archangelica* has been used for respiratory catarrh, flatulent dyspepsia, asthma, anorexia nervosa, rheumatic diseases, and peripheral vascular diseases [22].

A. archangelica is a plant that is part of the European Pharmacopoeia, the Ukrainian Pharmacopoeia, the British Herbal Pharmacopoeia, the Complete German Commission E, the British Pharmacopoeia, and many other pharmacopeias [23].

Essential oil composition varies depending on many factors, including origin and variety. Researched that the essential oil of the roots of *Angelica archangelica* from France contained α-pinene (32.2 %) and δ-3-carene (16.2 %) as the main compounds, whereas in Italy, they were α-pinene (21.3 %) and δ-3-carene (16.5 %), followed by limonene (16.4 %) and α -phellandrene (8.7 %) [18]. Therefore, to make full use of the *Angelica archangelica* resource, it is important to determine the concentration and composition of the essential oils extracted from leaves and rhizomes with roots of the plant growing in Ukraine. To the best of our knowledge, this study represents the first report on the content of the essential oils in the leaves of *Angelica archangelica*. The aim of our investigation was to determine the chemical composition of the leaves and rhizome with roots of essential oil of a population of *Angelica archangelica* from Ukraine.

2. Planning (methodology) of research

In Fig. 1, a representation of the design of the experiment planning process is shown.

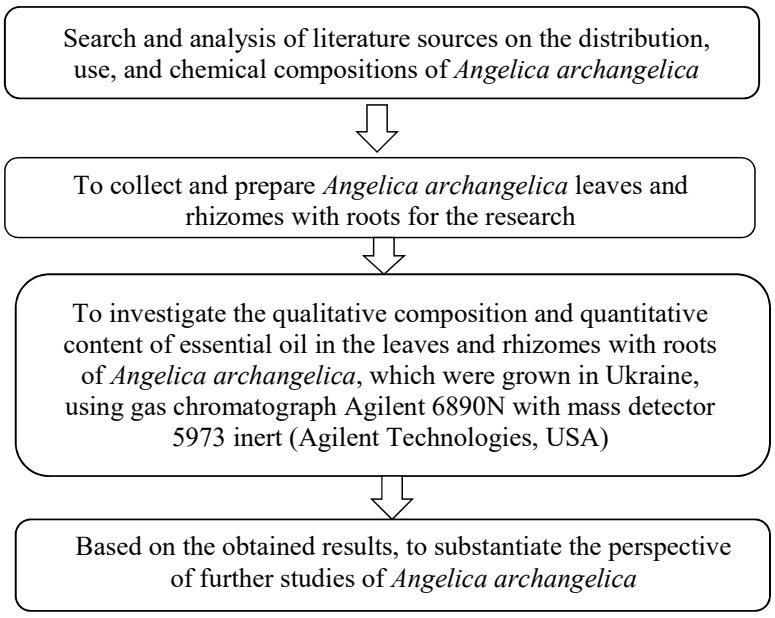

Fig. 1. Design of the experiment

3. Material and method

3. 1. Plant materials

Angelica archangelica leaves and rhizomes with roots were collected in the Ternopil region (Ukraine) in 2022. The identity of the plant was verified by Prof. Svitlana Marchyshyn, Department of Pharmacognosy and Medical Botany (TNMU, Ternopil, Ukraine) [24, 25]. The voucher specimens (No. 467) of herbal raw materials have been deposited in the departmental herbarium for future records [26, 27].

3. 2. Essential oil extraction

About 500 g of the fresh leaves and rhizomes with roots of each specimen were chopped and immersed in 2 L of distilled water contained in a flask. The essential oil was extracted for 3 h using a Clevenger apparatus. The temperature of water inside the condensers was maintained constant at 10 °C. The essential oils obtained were stored in amber glass vials in a refrigerator at 4 °C. The yield of essential oils in the leaves and rhizomes with roots was 0.11 % and 0.13 %, respectively.

3. 3. GC/MS determination of essential oil components

The qualitative composition and content of essential oil components were performed using a gas chromatograph Agilent 6890N with 5973inert mass detector (Agilent Technologies, USA) and a capillary column HP-5MS (30 m×0.25 mm×0.25 μm) [28, 29].

Apparatus and operating conditions. Agilent Technologies 6890 chromatograph with mass spectrometric detector 5973; capillary chromatographic column HP-5ms (ext. diam. 0.25 mm and 30 m long); carrier gas velocity (helium) 1.0 ml/min; the temperature of the sample heater – 250 degrees; the temperature of the thermostat is programmed from 50 to 320 degrees with a speed of 4 degrees/min. MS conditions: source temperature, 230 °C;

quadrupole temperature, 150 °C; energy, 70 eV; mass scan range, 50–300 amu. The components were identified based on the retention index and retention times and compared with reference spectra (NIST 08 and WILEY 2007) [28, 30, 31].

4. Results

The results obtained in the qualitative and quantitative analysis of the investigated essential oils compounds in the leaves and rhizomes with roots of *A. archangelica* are given in Fig. 2, 3.

In this research extracted the essential oils of *A. archangelica* in the leaves and the rhizomes with roots using the GC/MS technique and identified their constituents. Results of the compounds of *A. archangelica* are considered in Table 1, the most constituents of the compounds are terpene, terpenoids, and acyclic alkanes. We compared the volatile components among the leaves and the rhizomes with roots of *A. archangelica* growing in Ukraine. Some major components differed among the plant parts, and some components were present only in one part.

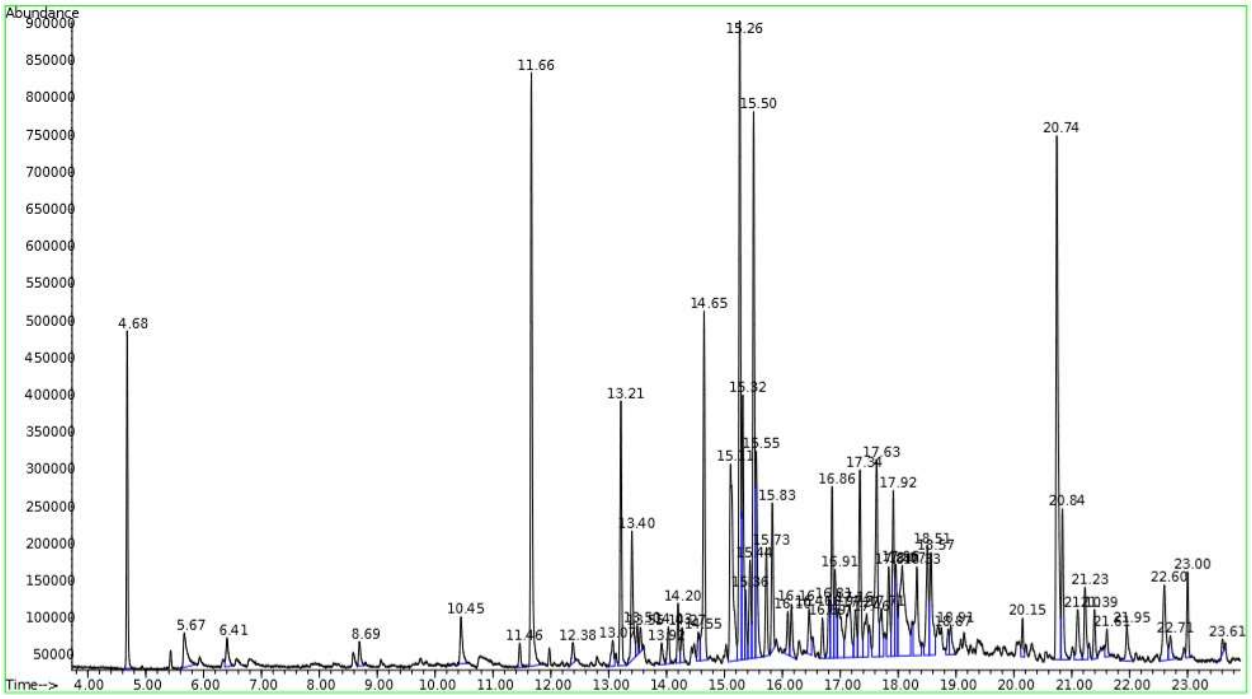

Fig. 2. GC/MS chromatogram of the components of the essential oil of *Angelica archangelica* L. leaves

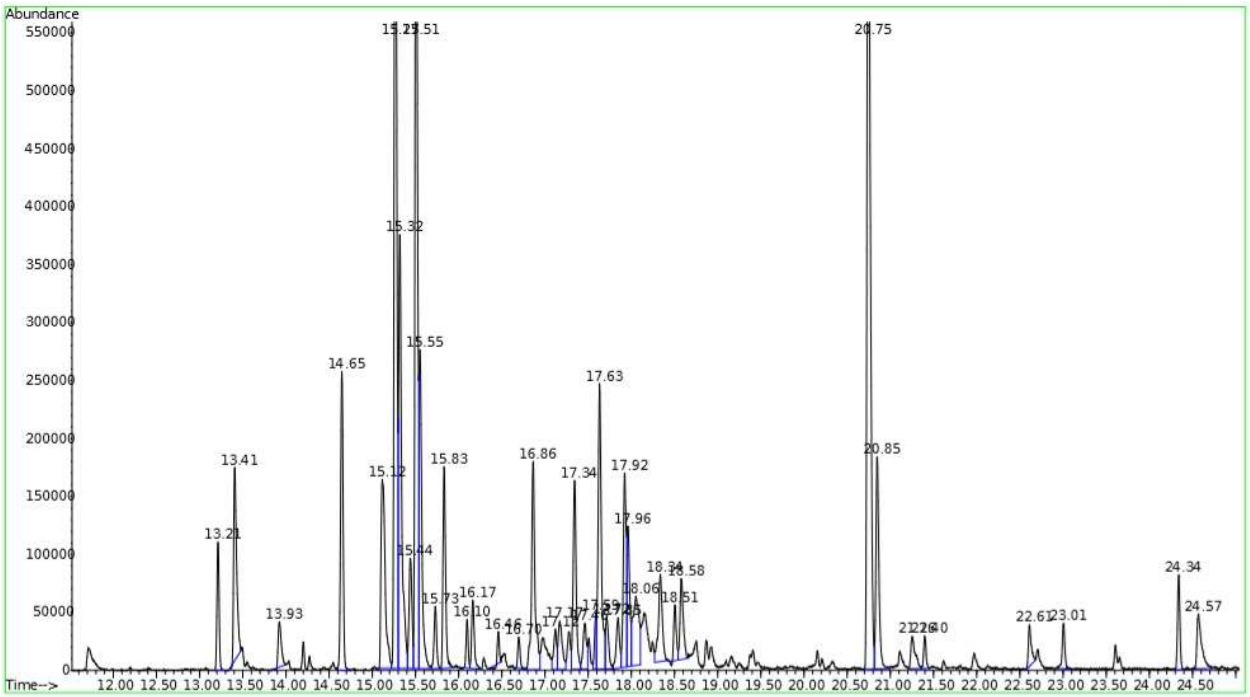

Fig. 3. GC/MS chromatogram of the components of the essential oil of *Angelica archangelica* L. rhizomes with roots

Table 1

The results of the determination of essential oil compositions (%) of *Angelica archangelica* L. growing in Ukraine

Component	RT, Min	RI (retention index)	Quantity, %	
			Leaves	Rhizomes with roots
α-Pinene	4.68	985	4.64	n/d
β-Myrcene	5.67	1005	1.05	n/d
3-*p*-Menthene	6.41	1086	1.62	n/d
Isoborneol	8.69	1125	2.43	n/d
Anisole	10.45	1196	2.92	n/d
Bornyl acetate	11.46	1211	1.39	n/d
Copaen	13.21	1235	4.64	2.41
p-Isopropenylacetophenone	13.41	1256	n/d	4.73
(Z)-β-Elemene	13.5	1278	1.41	n/d
Caryophyllene	14.03	1296	2.61	n/d
β-Cubebene	14.2	1301	n/d	0.77
(-)-Spathulenol	14.55	1314	2.51	n/d
α-Caryophyllene	14.65	1321	6.25	6.25
α-Curcumene	15.11	1334	6.42	6.91
α-Bergamotene	15.26	1347	16.41	n/d
α-Zingiberene	15.32	1354	n/d	10.64
γ-Muurolene	15.36	1359	0.91	n/d
α-Muurolene	15.44	1367	1.66	2.42
α-Farnesene	15.5	1379	9.76	17.85
β-Bisabolene	15.55	1384	4.24	5.88
δ-Amorphene	15.84	1396	2.10	3.48
β-Guaiene	16.1	1409	0.67	0.92
α-Elemene	16.7	1416	0.63	0.87
trans-Chrysanthemal	17.6	1487	4.07	5.53
α-Bisabolol	18.51	1502	2.18	n/d
cis-Pinane	20.75	1578	12.42	25.91
Hexahydrofarnesyl acetone	20.85	1583	n/d	4.26
Total	–	–	92.94	98.83

Note: n/d – not detected

The identity obtained from mass spectral analysis and the calculated RI of essential oil constituent for leaves and rhizomes with roots of *A. archangelica* are summarized in Table 1, and the components are reported according to the chromatography elution order in HP-5 ms column. The GC/MS preliminary analysis of the essential oil provided the identification of 27 compounds using their RI, and their mass spectra.

From the data shown in Table 1, we concluded that out of a total of 27 components detected in essential oils from leaves and rhizomes with roots of the plant, 11 components were common in both investigated parts of *A. archangelica*, 12 were present only in leaves, and 4 were present only in rhizomes with roots..

5. Discussion

Considering the bulk of published information on the content of essential oil compounds detected from this plant, it is interesting to note that there is limited information on the characteristics of essential oil in the leaves of *A. archangelica*. We have defined for the first time the chemical composition of the essential oils of the leaves of *A. archangelica* and determined 23 compounds, representing 92.94 % of the leaves essential oils were identified. The majority of them include α-Bergamotene (16.41 %), *cis*-Pinane (12.42 %), and α-Farnesene (9.76 %) (Table 1, Fig. 2). Biomass-derived compounds, such as pinanes, hold great potential for the pharmaceutical, bioenergy, fine chemistry, and flavour industries. The low abundance of the natural *cis*- and *trans*-pinane isomers in essential oils oblige the industry to use synthetic products. Pinane is an alkane that has the potential for an excellent added value as it can be synthesized from very abundant natural products such as pinenes. In addition to being very useful in cosmetology, pinane is an attractive building block for the preparation of various molecules used by the pharmaceutical industry, such as β-carotene and *p*-cresol [32–34]. α-Bergamotene is the predominant bergamotene found in many essential oils. It has a sweet and citrusy aroma, putting it in competition with popular spices such as black pepper and onions [35–37]. In particular, it is used in perfumery, food, and skin care products [38]. In plants, they mediate plant-plant interactions and attract pollinators [39]. Furthermore, some bergamotenes and their related structures have displayed a broad spectrum of biological activities, including antimicrobial and anti-inflammatory properties [40, 41].

Characterization of individual components of essential oils for leaves and rhizomes with roots of *A. archangelica* was performed using a commercial mass spectrometry library, and 15 components, representing 98.83 % of the rhizomes with roots of essential oil were identified. This analysis showed the presence of the majority of volatile components, including *cis*-Pinane (25.91 %), α-Farnesene (17.85 %), and α-Zingiberene (10.64 %) as the main compounds (Table 1, Fig. 3). Farnesene is a simple acyclic sesquiterpene of the terpenoids family, and it is an important component of plant essential oils in nature [42]. At present, farnesene plays an important role in industry, agriculture, and daily life. In industrial production, farnesene is used in lubricants, surfactants, and cosmetics due to its superior properties [43]. Farnesene also can be used as a precursor of vitamin E, which promotes the industrial synthesis of vitamin E [44]. α-Farnesene has uses as a food additive, fragrance, pest control, biofuel, antimicrobial, antiviral, and a constituent of essential oils that can reduce the symptoms of Covid-19 [45]. Zingiberene, one of the five major sesquiterpene hydrocarbons that are rich in ginger essential oil, is a natural antioxidant and serves as an antiviral and antifertility agent [46]. α-Zingiberene is known for its pungent and aromatic properties. In *Lipomyces starkeyi*, a yeast, transgenic strains expressing α-zingiberenesynthase genes can produce α-zingiberene, which can be further enhanced by overexpression of selected genes from the mevalonate pathway. The cytotoxic activity of α-zingiberene has also been studied, showing activity against tumour cell lines. Overall, α-zingiberene plays a role in the chemical composition, aroma, and potential medicinal properties of plants [47].

According to research carried out by scientists on the essential oil of *A. archangelica* root of European origin, it has shown diversity in its composition depending on the area of occurrence and the variety. The biggest differences concerned β-phellandrene level. Several types of oil can be distinguished according to the main ingredient, in which β-phellandrene, α-pinene, sabinene, and myrcene are the dominating ones, which are growing in northern Europe (Finland, Norway), Central and Eastern Europe. In most materials from Central, Southern, and Eastern Europe, the main compound of the oil in angelica root was α-pinene [48]. However, α-pinene was not determined in our research in the rhizomes with roots of *A. archangelica* growing in Ukraine, which is very interesting. This is supported by the distribution area, morphological traits, and differentiated chemotypes that resulted from the analysis of the volatiles of the essential oils.

Therefore, when developing new drugs based on essential oils from *A. archangelica*, growing in Ukraine, researchers should use not only the rhizomes with roots but also the leaves of the plant. In future research, it will be important to study the pharmacological effects of the components of essential oils, and of the essential oil mixtures from the leaves of *A. archangelica*.

Practical relevance. The established of essential oils content of *A. archangelica* growing in Ukraine, make it possible to more accurately morphological traits, and differentiated chemotypes that resulted from the analysis of the volatiles of the essential oils.

Study limitations. Through the study of the essential oils by GC/MS, several compounds were not identified due to the absence of their characteristics in NIST 08 mass spectra libraries, as well as in AMDIS and NIST programs.

Prospects for further research. The obtained results might be used in the standardization and quality assurance of new remedies containing *A. archangelica* leaves and rhizomes with roots.

6. Conclusion

The component composition of the essential oil in the leaves and the rhizomes with roots of *A. archangelica* growing in Ukraine was investigated using the GS/MC method. For the first time, we defined the chemical composition of the essential oils of the leaves of *A. archangelica*, and 23 components of essential oil were identified. The majority of them include α-Bergamotene 16.41 %, *cis*-Pinane 12.42 %, and α-Farnesene 9.76 %. In the rhizomes with roots, 15 components of essential oils were identified, including *cis*-Pinane (25.91 %), α-Far-nesene (17.85 %), and α-Zingiberene (10.64 %) as the main compounds. This study could give an explanation of the chemical diversity of the essential oils in the leaves and rhizomes with roots of *A. archangelica*, which indicates the prospects for further technological and pharmacological studies of the raw materials.

Conflict of interests

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this article.

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Data availability

The manuscript has no associated data.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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