УДК 665.52:581.135.51:543.544:582.475

S. A. Lamotkin, K. P. Kalnahorau, D. S. Vladykina, Yu. V. Nikolaichik, P. V. Nozdrin
Belarusian State Technological University

EVALUATION OF QUALITATIVE CHARACTERISTICS OF ESSENTIAL OIL OF TREES OF THE GENUS ABIES AND OBTAINING ON THEIR BASIS OF PERFUMES

Detailed analysis of the resource base essential oils into the Republic of Belarus. It is shown that one of the sources of essential oils may be of wood greenery of coniferous breeds of trees. Essential oil from five kinds of the fir growing in identical climatic and soil environments is received by the method of hydrodistillation. Conditions of the chromatography analysis of essential oils providing an exit of all components with the contents over 0.01% are selected up. The qualitative and quantitative analysis of essential oils is carried out. In the structure of essential oils 55 components are identified. Based on the analysis of the quantitative content of components, recommendations on the use of essential oils of certain types of fir. The formulations of perfumes and samples of shampoo and hair balm based on essential oil-color fir (*A. concolor*) and Siberian (*A. sibirica*). Tested indicators of quality and safety of the obtained samples. By all indicators the prototypes conform to the requirements of the standards. The experimental results obtained can be used for mass production of shampoo and hair balm.

Key words: shampoo, balm, essential oil, fragrance, fir, testing, index.

Introduction. Today the problem of environmental pollution is one of the most topical problems of our time. The ecological situation in the Republic of Belarus, as well as throughout the world, is getting worse every year, largely due to human activity.

This situation has harmful effect on human health, in particular on condition of the hair. High dust content in the air of our cities leads to the fact that hair quickly becomes dirty and must be washed frequently with chlorinated, hard water. As a result, hair becomes brittle, dry and split at the ends. An effective solution to the problem is the use of shampoo together with hair balms.

New generation shampoo has excellent cleaning and conditioning properties. It contains a balanced composition of ingredients and useful additives, which take care of the hair, protect it from aggressive external influences and contribute to its reconstruction [1].

Hair Balm is a cosmetic product for hair care that changes its texture and appearance. Shampooing opens hair scales, and balm nutrients (essential oils, proteins, minerals) can easily penetrate deep into their structure. Balm "closes" keratin scales allowing hair to get shine [1]. Many useful properties of perfumes are due to the presence of extractive plant substances in their composition. Most significantly is that natural renewability makes woody plants inexhaustible source of raw materials for the production of biologically active substances (BAS) [2]. Essential oils, particularly those of coniferous trees are widely used as raw materials to obtain BAS and impart various properties and flavors to perfumes.

Total area of the forest fund of the Republic of Belarus is 9.4 million ha. Coniferous plantations (spruce, pine, juniper, fir, arborvitae), dominate in Belarusian forests, representing more than 60% of the forest fund [3].

In this regard, the study of softwood extractives of our republic, which are used in the perfume and cosmetic production, is urgent.

Therefore, fir trees (*Abies gen.*) as a source of essential oils with a wide spectrum of biological activity, are of great interest [4]. These plants are grown in arboretums (13 species) and grow in natural conditions [5].

The aim of this work was to study the composition of essential oils of a number of fir trees (*Abies gen.*). These oils are a source of raw materials for perfumery and cosmetic products as well as for obtaining perfumes test samples.

Main part. The objects of study were essential oils derived from wood greenery of 40–50-year's old fir trees (*Abies gen.*): (Silver fir (European pine) (*A. alba*) (1), Caucasian fir (*A. nordmanniana*) (II), White fir (*A. concolor*) (III), Siberian fir (*A. sibirica*) (IY), Balsam fir (*A. Balsamea*) (Y)) which grow in the arboretum of BSTU (settlement Negoreloye), as well as in forests of the Republic of Belarus. Three samples of fir needles (different fir trees) were taken in December 2015 in order to control sample uniformity in the autumn and winter months, when essential oil yield reaches its maximum, and its composition is stabilized [6].

The selected needles were separated from stalks and ground to 3–5 mm in size, and then essential oil was distilled from it by hydrodistillation. Oil quantitative yield was determined volumetrically.

Integral characteristics (refraction index at 20°C) were measured and analyzed for the extracted essential oils. Chromatographic methods in combination with the standard (typical) chromatograms and data on the chemical composition of typical industrial essential oils are traditionally

used for quality control and certification of essential oils [7]. Qualitative and quantitative analysis of the oil composition was performed by gas-liquid chromatography (GLC) using chromatograph "Kristall 5000.1" with 60 meter long quartz capillary column with applied phase – 100% dimethylsiloxane. Chromatographic conditions: isothermal regime at 70°C for 20 min followed by programmed rise in temperature up to 150°C at 2°C/min and heated at final temperature for 40 minutes. Evaporator temperature was 250°C.

Chromatography of essential oil in this mode allows providing the most complete separation and identifying all essential oil components with the content greater than 0.01%. It is quite enough for expert work. The relative error of the quantitative content of components did not exceed 10%. Identification of individual components was carried out using reference compounds and well-known literary retention index data [9]. 55 compounds have been identified. The quantitative content of the main components of oils are shown in Table 1.

Table 1

Composition of the essential oil tested samples of the fir trees genus (*Abies*)

Component name	Retention time, *T*, min	Content, wt %				
		Silver fir (European pine) (*A. alba)*	Caucasian fir (*A. nordmanniana*)	White fir (*A. concolor)*	Siberian fir (*A. sibirica)*	Balsam fir (*A. balsamea)*
Santen	25.39	2.7	1.0	0.1	2.5	5.0
Tricyclene	29.51	2.5	0.9	1.2	2.8	2.4
α-Pinene	30.64	15.5	14.7	7.3	11.9	20.2
α-Fenchene	31.84	0.02	0.03	0.01	0.01	0.02
Camphene	32.17	18.9	6.4	14.2	28.5	22.9
Sabinene	34.21	0.02	0.2	0.04	0.03	0.01
β -Pinene	34.85	24.8	15.1	27.8	1.6	2.4
Myrcene	35.68	0.6	1.5	1.1	0.6	0.7
2-Carene	37.35	0.01	0.01	0.06	–	–
α-Phellandrene	37.49	0.06	1.2	0.03	0.03	0.1
3-Carene	38.47	0.08	22.6	0.4	6.7	0.05
α-Terpinene	38.83	0.03	0.1	0.01	0.03	0.05
ρ-Cymene	39.10	0.03	0.1	0.04	0.01	0.02
Limonene	40.24	8.2	5.6	6.0	5.3	7.0
γ-Terpinene	43.17	0.05	0.2	0.03	0.08	0.1
Terpinolene	46.52	0.5	1.7	0.3	0.9	0.9
Linalool	46.83	0.1	0.03	0.2	0.05	0.1
Camphor	51.35	0.1	0.03	0.1	0.1	0.1
Citronellal	52.62	0.05	0.02	0.4	0.01	0.05
Borneol	54.43	2.4	0.1	1.9	6.4	3.4
Terpinene-4-ol	55.60	0.03	0.1	0.07	0.03	0.03
α –Terpineol	56.67	0.4	0.1	0.6	0.03	0.07
γ-Terpineol	57.64	0.02	0.01	0.05	0.02	0.03
Verbenone	58.44	0.05	0.03	0.02	0.01	0.06
Borneolacetate	67.03	6.9	0.4	25.3	26.1	21.0
α –Longipinene	75.69	0.9	1.4	0.8	0.2	0.08
Geranyl acetate	78.50	0.2	0.2	0.4	0.01	0.06
Isolongifolene	79.31	0.2	0.01	0.05	0.3	0.04
β-Elemene	79.80	0.05	0.04	0.1	0.01	0.05
β-Longipinene	80.54	0.02	0.04	–	0.01	0.01
Longifolene	82.79	0.6	1.1	–	0.08	0.07
β-Caryophyllene	84.25	2.7	7.6	0.6	2.3	5.4
α-Humulen	88.98	1.1	2.9	0.1	1.1	2.6
γ-Muurolen	92.84	0.3	0.4	0.1	0.01	0.06
γ-Humulene	93.38	0.7	0.9	0.03	0.06	0.1
β-Selinene	94.14	1.5	2.5	0.5	0.03	0.3
α-Selinene	94.82	0.05	0.02	0.6	0.02	0.05
α-Muurolene	95.47	0.4	0.1	0.4	0.1	0.4
β-Bisabolene	96.78	0.6	0.8	0.03	0.3	0.3
γ-Cadinene	98.18	0.4	0.07	0.9	0.1	0.1
δ-Cadinene	99.57	0.8	0.08	1.3	0.1	0.4
Not identified		5.4	8.8	6.3	1.1	2.9

Besides oil components in Table 1, the following components with the content not higher than 1% were also identified: α- and β-thujene, 1.4-cineole, *trans*- *cis*-ocimene, α- and β-fenchol, terpinene-1-ol, isoborneol, ρ-cymene-8-ol, methylthymol, geraniol , α-terpineol acetate and longicyclen.

Essential oils derived from wood greenery of a fir, were almost colorless, with a characteristic balsam smell of needles.

Refraction coefficient of the test samples at 20°C varied in the range 1.4681–1.4728. The obtained similar values of the characteristics do not allow to use it as a standard for the identification of fir essential oils.

As it has been shown previously [10] and as it follows from the data in Table 1, the essential oils obtained from wood greenery of various fir species growing in Belarus in identical soil and climatic conditions, can serve as sources of organic compounds, which can be prepared in a pure form and used in the manufacture of various products.

Thus, essential oil derived from *A. alba*, may serve as a source for β-humulene and santen; essential oil obtained from *A. nordmanniana* is a source for camphene and limonene; essential oil obtained from *A. balsamea* is a source for β-pinene and limonene; essential oil derived from *A. concolor* is a source for β- pinene and borneolacetate; essential oil obtained from *A. sibirica* is a source for camphene and borniacetate.

Essential oils of Siberian fir (*A. sibirica*) and White fir (*A. concolor*) are of the greatest interest in production of perfumes and cosmetics, as these are the most common in the territory of the Republic of Belarus [11, 12]. Individual composition of terpenes and their oxygenated derivatives in essential oils of fir offered little variety, and remained stable. The number of identified compounds in the analyzed samples of essential oil accounted for 55 components, the overall amount being about 92–96 wt %. As can be seen from Table 1, the basic components of the essential oil of Siberian fir (*A. sibirica*) are α-pinene, camphene, 3-carene, limonene, borneol, borneolacetate. The main components of the essential oil of White fir (*A. concolor*) are α, β-pinenes, camphene, limonene, borneol, borneolacetate, geranyl acetate. Furthermore, a significant difference should be noted in the content of sesquiterpenes in all oils tested. This difference in the compositions is reflected on the specific use of these oils in perfumery products.

Shampoo and hair balm samples were produced in an accredited testing laboratory of LLC "Eksklyuzivkosmetik". During the experiment, formulations for two shampoo and balm samples with the addition of essential oil of Siberian fir and White fir were developed. Previously [13] perfume composition with the addition of essential oil of Siberian fir (*A. sibirica*) was formulated. Its quantitative composition was also optimized. Shampoo and balm bases were prepared according to the recipe [13]: cetyltrimethylammonium chloride, higher fatty alcohols (C_{16}–C_{18}), silicone DS 350 (dimethicone), glycerene emulsifier T 9, water, citric acid. 100 g batches of these bases were added with preservation agents and aroma compounds based on essential oils of Siberian fir (*A. sibirica*) and White fir (*A. concolor*) in the amount of 0.4% of the total.

The following parameters were determined for shampoo samples: appearance, colour and odour; mass fraction of chlorides, pH value; foam stability.

Test results of the experimental shampoo samples are shown in Table 2.

Based on the results obtained, we can conclude that all physical and chemical parameters of the tested samples meet the requirements of technological regulations [14].

The following parameters were determined for hair balm samples: appearance, colour and odour; mass fraction of volatile substances; pH value; colloidal stability; heat stability.

Test results of the experimental hair balm samples are shown in Table 3.

Table 2

Test results of shampoo samples

Parameter	Technological regulations	Shampoo with essential oil of Siberian fir (*A. sibirica*)	Shampoo with essential oil of White fir (*A. concolor)*
Appearance	Homogeneous thick liquid without impurities	Corresponds to technological regulations	Corresponds to technological regulations
Colour	Typical for the colour of this product	White	White
Odour	Typical for the odour of this product	Pine scent	Pine scent
pH value	5.0–8.5	5.3	5.5
Mass fraction of chlorides, %, not above	6.0	2.1	2.2
Foam stability, not less than, mm	0.8	9.5	9.7

Table 3

Test results of hair balm samples

Parameter	Technological regulations	Balm with essential oil of Siberian fir (*A. sibirica*)	Balm with essential oil of White fir (*A. concolor*)
Appearance	Homogeneous creamy mass without impurities	Corresponds to technological regulations	Corresponds to technological regulations
Odour	Typical for the odour of this product	Pine scent	Pine scent
Colour	Typical for the colour of this product	White	White
pH value	5.0–9.0	6.0	5.9
Mass fraction of water and volatile substances, %	5.0–98.0	92.3	91.8
Colloidal stability	Stable	Stable	Stable
Thermal stability	Stable	Stable	Stable

According to the results obtained, we can conclude that all physical and chemical parameters of the tested samples meet the requirements of technological regulations [15].

Test results of pilot samples of perfume and cosmetics confirmed the possibility of their practical application.

Conclusion. An essential oil of five species of fir growing in natural environment has been obtained. Qualitative and quantitative composition of essential oils obtained has been investigated.

Essential oil output of these types of fir is sufficiently high for conifers. This makes it possible to recommend further research of these samples as a promising source of raw materials for obtaining essential oil.

The high content of valuable biologically active substances in samples of the essential oil of Siberian fir (*A. sibirica*) and White fir (*A.* concolor) and the prevalence of these types of fir in Belarus allow to recommend these types as a raw material for the perfume and cosmetic products. The resulting samples of shampoo and hair balm with essential oil of Siberian fir and White fir fully meet the quality requirements and can be recommended for serial production.

References

1. Paronyan V. Kh., Krivov A. Yu. *Tekhnologiya proizvodstva parfyumerno-kosmeticheskikh produktov* [Technology of perfumery and cosmetic products]. Moscow, DELI Print Publ., 2009. 294 p.

2. Siksna S., Olfna J. Coniferous greenery – valuable natural raw material of biologically active substances. *Medicines teorija ir praktika* [Medical teory and praktice], 2012, vol. 18, no. 2, pp. 146–148.

3. The Ministry of forestry of the Republic of Belarus [Electronic resource]. Available at: http://mlh.by (accessed 08.12.2015).

4. Parshikova V. N., Stepen' R. A., Miroshnichenko V. V., Osmolovskaya N. A. *Sposob polucheniya biologicheski aktivnogo preparata iz drevesnoy zeleni pikhty sibirskoy* [Method obtaining a biologically active drug from wood greens of Siberian]. Patent RF, no. 2370272, 2009.

5. Shutova A. G., Spiridovich E. V., Garanovich I. M., Senkevich, G. G., Kurchenko V. P. Component composition of essential oils of species of the genus Abies (Pinaceae) under conditions of introduction in Belarus. *Rastitel'nye resursy* [Plant resources], 2009, vol. 4, pp. 60–67 (In Russian).

6. Stepen' R. A. Environmental and resource significance of volatile terpenes of pine forests of middle Siberia. *Khimiya rastitel'nogo syr'ya* [Chemistry of vegetable raw materials], 1999, no. 2, pp. 125–129 (In Russian).

7. Kuzmenko A. N. The use of gas-liquid chromatography for standardization of medicinal plant materials and dosage forms based on it. *Rossiyskiy khimicheskiy zhurnal* [Russian chemical magazine], 2010, vol. 54, no. 6, pp. 114–119 (In Russian).

8. Salanță L. C., Olonva G. Determination of the Volatile Compounds from Hop and Hop Products using ITEX GC-MS Technique. *Journal of Agroalimentary Processes and Technologies*, 2012, vol. 18, no. 2, pp. 110–115.

9. Tkachev A. V. *Issledovanie letuchikh veschestv rasteniy* [Study of volatile substances of plants]. Novosibirsk, Offset Publ., 2008. 969 p.

10. Lamotkin S. A., Klimchik, Y. G., Malakhovsky V. G., Popina O. A. Comparative analysis of the compositions of essential oils of some introduced species of trees of the genus Abies. *Trudy BGTU*

[Proceedings of BSTU], no. 4, Chemistry, Technology of Organic Substances and Biotechnology, 2013, pp. 150–153 (In Russian).

11. Yeroshkina I. F. Peculiarities of formation of forest fund in the Republic of Belarus in the postwar period. *Aktual'nye problemy lesnogo kompleksa* [Actual problems of forest complex], 2012, no. 33, pp. 32–35 (In Russian).

12. Baginskiy V. F. Forest resources in the Republic of Belarus and its use taking into account ecological imperative. *Ekopotentsial* [Equipotential], 2014, no. 2, pp. 99–99 (In Russian).

13. Nozdrin P. V., Lamotkin S. A. Development of a new type of shampoo with the addition of essential oil of fir. *Trudy BGTU* [Proceedings of BSTU], no. 4, Chemistry, Technology of Organic Substances and Biotechnology, 2015, pp. 246–250 (In Russian).

14. STB 1675-2006. Cosmetic products hygienic cleaning. General specifications. Minsk, State Committee for Standardization of the Republic of Belarus, 2011. 12 p. (In Russian).

15. STB 1673-2006. Cosmetic creams. General specifications. Minsk, State Committee for Standardization of the Republic of Belarus, 2011. 12 p. (In Russian).

Information about the authors

Lamotkin Siarhei Alexandrovich – PhD (Chemistry), Assistant Professor, Assistant Professor, the Department of Physical-Chemical Methods of Products Certification. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: jossby@rambler.ru

Kalnahorau Kiryl Petrovich – PhD (Engineering), Senior Lecturer, the Department of Physical-Chemical Methods of Products Certification. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: kolnogorov@belstu.by

Vladykina Darya Sergeevna – Master of Biology, assistant lecturer, the Department of Physical-Chemical Methods of Products Certification. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus). E-mail: VladykinaD@belstu.by

Nikolaichik Yulia Vladimirovna – student. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus).

Nozdrin Pavel Vladimirovich – Master's degree student. Belarusian State Technological University (13a, Sverdlova str., 220006, Minsk, Republic of Belarus).

Received 27.02.2016