A PROMISING TREND IN THE PROCESSING OF FENNEL (*FOENICULUM VULGARE MILL.*) WHOLE PLANTS

L. A. Timasheva* and E. V. Gorbunova

Crimean Agrotechnological University, South Branch,
National University of Life and Environmental Science of Ukraine,
Agrarnoe, Simferopol, Crimea, 95492 Ukraine,
*phone/fax: +3(0652)22-39-66, e-mail: admin@csau.crimea-ua.com

(Received January 22, 2014; Accepted in revised form March 4, 2014)

Abstract: Aromatic plants are a valuable source of biologically active substances. The use of aromatic plant processing products in the pharmaceutical, perfume and cosmetic, and food industries is of great interest. The search for new plant sources of biologically active substances and the study of their composition and properties are still topical. Fennel (*Foeniculum vulgare Mill.*) is a promising aromatic raw material containing a number of biologically active substances. Until now, essential oils were obtained only from fennel fruits and, less frequently, from whole plants. However, fennel raw materials contain microelements and macroelements, organic acids, proteins, carbohydrates, vitamins, tannins, polysaccharides, amino acids, coumarins, and flavonoids, which make the processing of whole plants reasonable. A rich spectrum of valuable fennel components requires the search for methods of their exhaustive recovery from plant raw materials, and this can be provided only with a complex processing technology. For this reason, the objective of our work was to develop a technology for the processing of fennel, a promising plant, on the basis of the steam distillation of raw materials and the aqueous alcoholic extraction of waste solid residues remaining after the recovery of essential oil with the purpose of obtaining aqueous alcoholic extracts, to study the other types of wastes formed in the course of processing, and to determine the field of their application. A promising trend in the processing of fennel was scientifically substantiated. Some regularities in the change of the yield of fennel essential oil components and their distribution between the plant organs depending on plant vegetation stages and weather in the submountain Crimea were established. The technical maturity of plants for industrial processing was defined. Waste residues after the extraction of essential oil were studied, and some new natural biologically active products were obtained.

Key words: fennel, raw materials, processing, essential oil, aqueous alcoholic extract of fennel waste residues

UDC 635.757:665.52
DOI 10.12737/4134

INTRODUCTION

At present, the demand for natural fragrances, food additives, and flavors considerably grows. Fennel (*Foeniculum vulgare Mill.*) is a raw material for the production of a number of fragrances forming the basis of contemporary perfumery and cosmetics and widely applied in medicine and food industry.

Fennel is a perennial (biennial, if cultivated) herbal plant of the Apiaceae family with a height of up to 2 m. Leaves are multi-pinnatisect. Flowers are small golden-yellow and form a complex double multiradiate umbrel. Fennel fruits are fragrant, greenish-brown or grey-green, naked, costate, large, elongated and represent nearly cylindrical cremocarps, which can easily split into two mericarps after maturation [1, 2].

Fennel fruits are used in industrial processing, but their uneven maturation and fall lead to considerable harvest losses, so some studies on the processing of whole plants were performed in 1970, although the essential oil from whole plants differed from the essential oil from mature fruits in quality: the content of anethol, a principal component, was less than 60% and did not satisfied the fennel essential oil quality standard [3].

It should be noted that all the technology for the processing of fennel in the form of whole plants basically have a character of research rather than recommendation, as indicated by the fact that the attention in each communication is paid only to the yield of essential oil. The proposed technology for the processing of whole fennel plants allows the more exhaustive utilization of initial raw materials and their diversification depending on the demand for the target product.

It is commonly known that the processing of plant raw materials for the production of products of different quality and destination is accompanied by the generation of bulky waste residues at each stage. In this connection, the problem of the complex processing of essential oil and medicinal plant raw materials with the use of resource-saving technologies is topical [4, 5].

Such an approach to the processing of plant raw materials necessitates the complex studies of initial essential oil raw materials and waste residues of their processing, and also the improvement of methods for the production of essential oil, extracts, and other biologically active components. Special attention is currently paid to the development of environmentally-safe and low-waste technologies for the complex processing of plant raw materials [6].

The lack of works on the complex utilization of fennel plants has necessitated the more detailed study of the biochemical composition of raw materials and the development of complex fennel processing technologies,

which must provide the most exhaustive extraction of biologically active substances with different spectra of activity.

Objective of our studies was to substantiate the possibility of the complex processing of fennel (*Foeniculum vulgare Mill.*) plants from theoretical and experimental viewpoints.

According to the stated objective, we solved the following *problems*:

(1) To study the dynamics of the accumulation and distribution of essential oil in fennel plants during the vegetation period in Southern Ukraine;

(2) To study the qualitative composition of raw materials at different vegetation stages of a plant and to determine the optimal time period for the harvesting of raw materials;

(3) To study the qualitative change of raw materials during the storage of fennel and to determine the period of its storage; and

(4) To study the qualitative composition of fennel waste residues after steam distillation and to propose efficient methods of their processing.

OBJECTS AND METHODS OF STUDY

The studies were performed for the period of 2011–2013 at the Department of Technology and Equipment of Fat and Essential Oil Production of the Crimean Agrotechnological University (South Branch, National University of Life and Environmental Science of Ukraine) in the Research Laboratory of Quality of Raw Materials and Processing Products of the Institute of Essential Oil and Medicinal Plants of the National Academy of Sciences of Ukraine (now, the Crimea Institute of Agricultural Industry).

The object of study was fennel (*Foeniculum vulgare Mill.*) whole plants, which were cut at a level of 50 cm from the ground surface and grown in Southern Ukraine, and also its distillate, essential oil, distillation water, aqueous and aqueous alcoholic extracts, and essential oil extraction waste residues.

The mass content of essential oil in raw materials was determined via steam distillation on a Clevenger apparatus [7]. Samples of fennel essential oil, distillation water, and obtained extracts were taken for analysis in compliance with GOST 30145-94. The qualitative composition of essential oil, distillation water, and aqueous alcoholic extracts and the quantitative content of components in them were established by gas-liquid chromatography on a Kristall 2000 M chromatograph with a PEG 20 M quartz capillary column. The identification of components was performed in the temperature-programmed regime. The yield of extracted substances in the extract of fennel waste residues was determined via exhaustive extraction, which consisted in their preliminary and complete evaporation on a water bath and subsequent holding in a thermocabinet and the terminal weighting of a residue. The result was calculated in percents with respect to the initial material mass [9].

The mass content of flavonoids in the extract of fennel waste residues on a rutin basis was determined by the adopted method for plant raw materials [1], the qualitative analysis of tannins was performed by means of qualitative reactions, their quantitative estimation was performed via redox titration [10], and ascorbic acid was determined titrimetrically. The products obtained from fennel—essential oil and aqueous and aqueous alcoholic extracts—were analyzed by the standard methods [10]. In addition to the quantitative estimation of yield and dynamics, the obtained products were analyzed by organoleptic, physicochemical, and biochemical methods. In the analysis of extracts and essential oils, the color, odor, density, refraction index, and component composition of target products were determined [1, 10].

RESULTS AND DISCUSSION

The performed studies were aimed at determining the technical maturity of fennel raw materials and studying the dynamics of the accumulation of essential oil and biologically active substances in the different organs of a plant at various vegetation stages.

The development stages of fennel plants and the content of essential oil and biologically active substances were determined beginning from the stage of shooting to the complete maturation of central umbrel fruits.

The vegetation stages of fennel plants are usually the following:

(1) Shooting (formation of stems);

(2) Budding (formation of flowers on umbrels);

(3) Early blossom of central umbrels (10% of plants have open flowers on their umbrels);

(4) Full blossom of central umbrels (75% of plants have open flowers on their umbrels);

(5) Milky maturity of fruits on the central umbrel (fruits begins to maturate on the umbrels of 10% of plants, and the crushing of their endosperm gives a dense milky-white liquid);

(6) Milky-wax maturity of fruits on the central umbrel (the fennel fruit maturation stage, at which endosperm is uncrushable, but easily cuttable for 10% of plants);

(7) Wax maturity of fruits on the central umbrel (the fennel fruit maturation stage, at which endosperm is uncrushable, but easily cuttable for 75% of plants); and

(8) Complete maturation of fruits on the central umbrel (the terminal maturation stage, at which fruits are colored as ripe).

It has been established that the amount of essential oil is minimal at the budding stage and maximal at the stage of the milky-wax maturity of fruits on the central umbrel (Fig. 1). Hence, the stage of the milky-wax maturity of fruits on the central umbrel is the stage of the technical maturity of fennel plants, i.e., the period of the maximum accumulation of essential oil. Relying on the obtained data incorporated into the project of the National Standard of Ukraine on industrial fennel raw materials, it is possible to recommend the epigeal fennel part cut at the stage of milky-wax maturity of fruits on the central umbrel for the industrial processing in the form of whole plants.

Essential oil from whole fennel plants represents a colorless or slightly yellow sweetish liquid with bitter taint and specific fennel odor. The relative density was from 0.950 to 0.963 g/cm^3, and the refractory index was 1.5300 to 1.5350 at a temperature of 20°C. A typical chromatographic pattern of fennel essential oil from whole plants at the milky-wax maturity stage is shown in Fig. 2.

As is shown by the performed studies, the component composition of essential oil also changes in different vegetation periods of plants [3, 11]. The amount of anethol,

a principal essential oil component, was observed to be minimal at the stages of the budding and early blossom of fennel plants and maximal at the stage of the milky-wax maturity of fruits on the central umbrel.

The results of studying the component composition of freshly cut fennel plants show that the mass content of essential oil in the different organs of plants is various and changes in the process of vegetation from 0.44 to 1.5% in stems, from 0.6 to 1.3% in leaves, and from 3.5 to 5.3% in umbrels with fruits on absolute dry matter basis (Fig. 3).

The complex technology of the processing of fennel raw materials is proposed to be implemented as follows (Fig. 4).

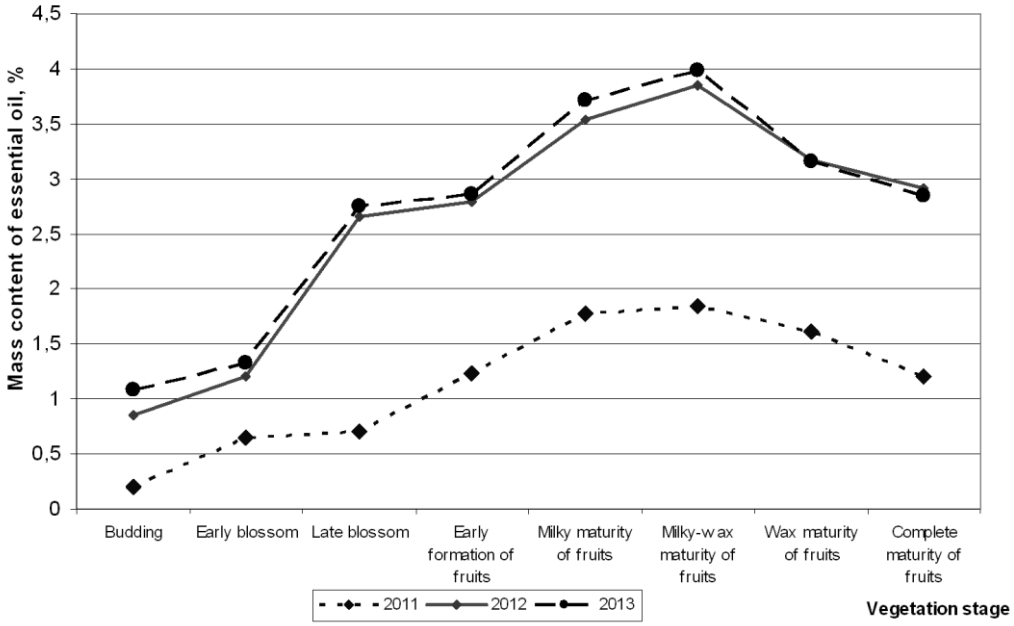


Fig. 1. Content of essential oil in fennel plants at different vegetation stages.

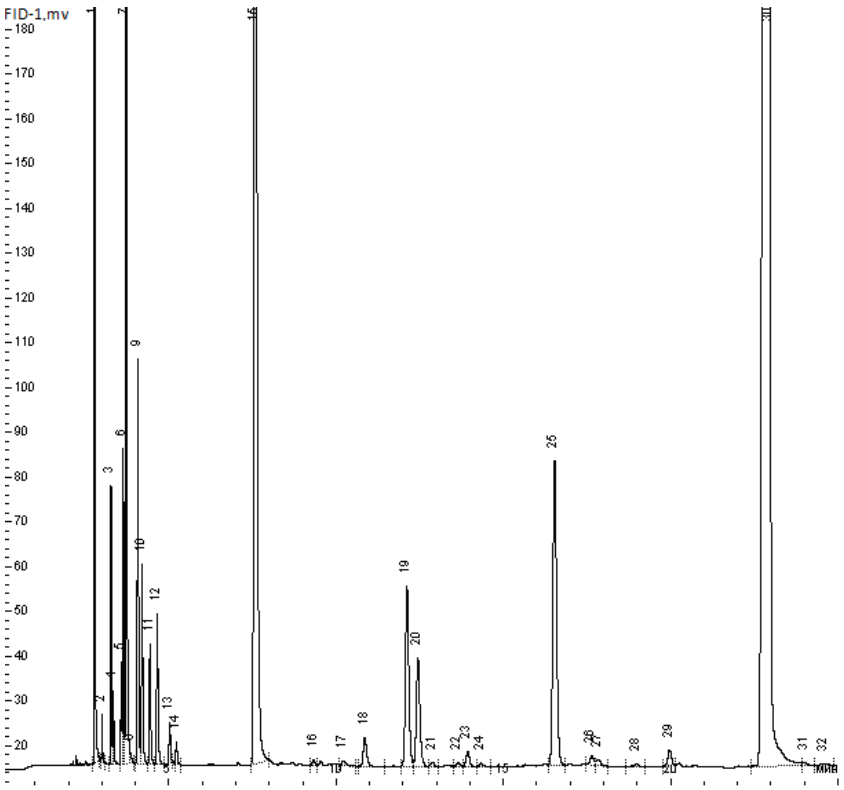


Fig. 2. Typical chromatographic pattern of fennel essential oil.

Table 1. Component composition of fennel essential oil at different vegetation stages (average over the period of 2011−2013)

Component	Mass content of components in essential oil, %				
	Budding	Blossom of central umbrels	Milky maturity of fruits on the central umbrel	Milky-wax maturity of fruits on the central umbrel	Complete maturity of fruits on the central umbrel
α-Pinene	3.17	9.24	8.20	7.41	6.44
Camphene	0.04	0.02	0.04	0.05	0.10
β-Pinene	0.11	0.92	0.94	0.72	0.17
β- Phellandrene	7.17	1.30	2.42	4.27	0.96
1,8-Cineole	1.23	1.33	1.06	0.91	1.37
Fenchone	4.84	2.84	2.99	4.94	10.09
Linalool	0.05	0.05	0.09	0.11	1.43
Methylchavicol	2.49	2.36	2.41	2.83	2.73
Anethol	68.12	67.32	68.52	69.60	63.91

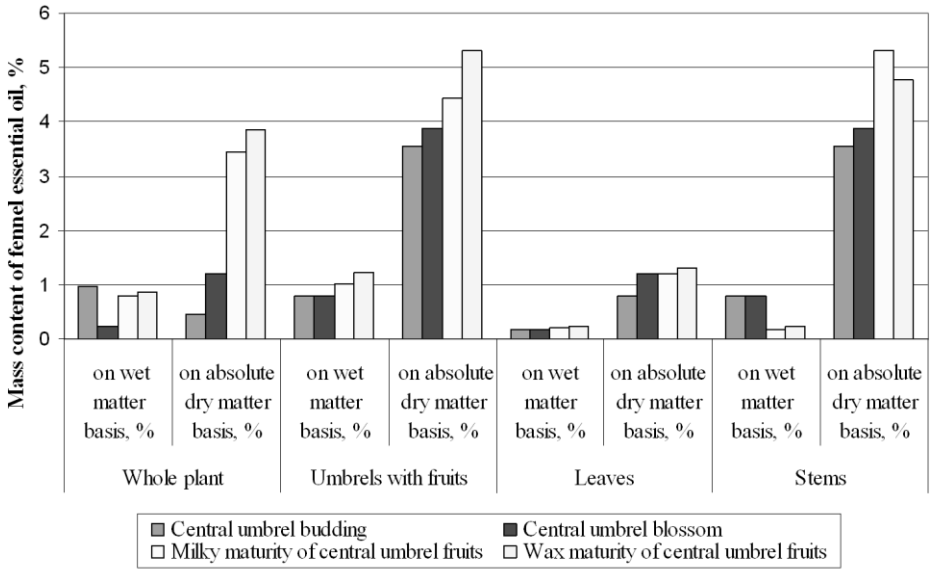


Fig. 3. Content of fennel essential oil in the plant organs at different vegetation stages.

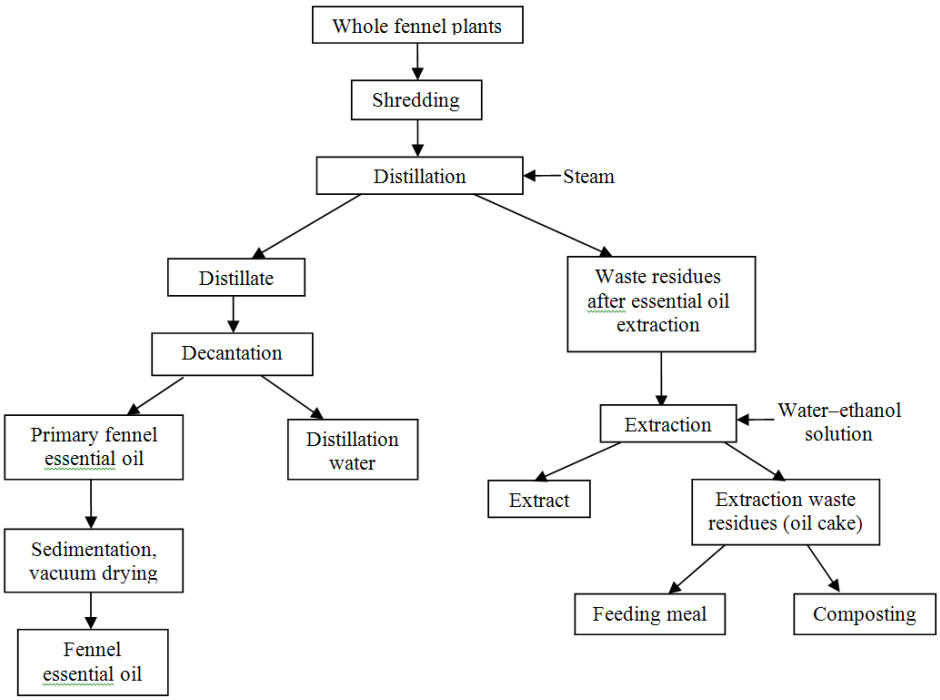


Fig.4. Scheme of the complex technology for the processing of fennel plants.

Industrial fennel raw materials are shredded to a size of 3–5 cm on a shredder, thereupon essential oil is obtained via steam distillation. The process is recommended to be performed for 120 min at a distillation rate of 0.5 kg/(kg h) and a steam pressure of 0.5 MPa. The curve of the extraction of essential oil depending on the time of the process is plotted in Fig. 5. From the curve it can be seen that 64.8% of the essential oil obtained from the raw materials throughout the entire period of experiment is distilled for first 30 min of the process, 84.1% for 60 min, 90.9% for 90 min, and 95.5% for 120 min, thereupon its amount increases almost uniformly until the end of experiment. Within a range of 150–300 min, the curve demonstrates an almost imperceptible ascent corresponding to 0.2% of the distilled product, so it is possible to say about the complete extraction of essential oil from the raw materials for 120 min under the conditions of the performed experiment.

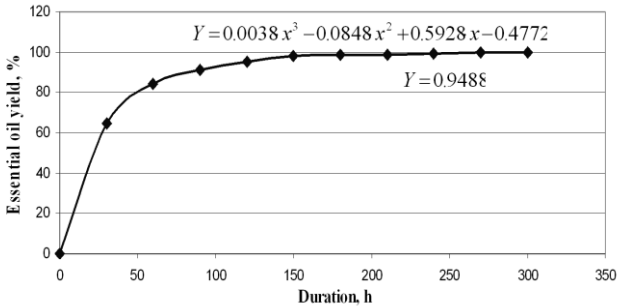


Fig. 5. Dynamics of the exhaustive extraction of fennel essential oil.

The liquid and solid waste residues formed in the process of distillation are not utilized, but subjected to recycling. Liquid wastes are distillation water (distillation fraction water) obtained in the steam distillation of volatile organic components from fennel plants. In the essential oil production, distillation water is a distillation process waste and amounts more than 70% of the weight of processed raw materials; it is not recycled in the technological process, but disposed into sewers [6]. However, distillation water contains a variety of biologically active components, which are so necessary in the pharmaceutical, perfume and cosmetic, and food industries. It is known that some fennel components are water-soluble. For this reason, it is possible to say that distillation water is a saturated aqueous extract.

The obtained distillation water is a colorless slightly opaque finely fennel-scented liquid, on the surface of which the formation of small essential oil drops is observed after sedimentation. The component composition of fennel water is given in Table 2 and in the chromatographic pattern (Fig. 6a).

Anethol is the dominant component of distillation water, and its concentration is 87.68%. The value of distillation water consists not only in the possibility of obtaining some additional amount of components, but also in its biological activity. It is historically known that fennel tinctures and decoctions are used in folk medicine and included into pharmaceutical drugs as an invigorant, expectorant, anti-inflammatory, bactericidal, disinfectant, diuretic, mild laxative, and tonic remedy [12].

Table 2. Component composition of essential oil in the distillation water of fennel*

Principal components	Retention time, min	Mass content, %
Fenchone	7.310	7.00
Camphor	10.694	0.47
Linaool	12.026	0.49
Methylchavicol	16.294	1.47
Anethol	22.708	87.68

*Mass content of essential oil in the distillation water was 0.05%.

Hence, distillation water is a commercial product and can be used in the perfume and cosmetic industry as an aqueous fennel extract and as a flavor in the alcoholic beverage industry or for the separation of anethol.

Solid residues are subjected to extraction with aqueous alcoholic solutions to obtain the target products. Extraction waste residues are washed with water and used to obtain feeding meal for farm animals or composting.

Fennel essential oil usually composes a small portion of all the biologically active components accumulated inside a plant, so fennel waste residues obtained after essential oil extraction contain valuable organic components (extractive substances) of interest. Extractive substances are represented by a great number of components of different classes [13]. The study of the extraction of extractive substances from fennel waste residues shows that the application of the obtained product is advantageous.

The content of extractive substances is one of the important quality characteristics of an extract obtained from fennel waste residues. It is known that the process of their extraction depends on a number of factors, such as the size of particles and the concentration of a solvent [6, 13]. In view of this, there occurs the necessity for studying the effect of technological factors on the yield of extractive substances from raw materials to select the most suitable regime of extraction.

Ethanol, which is widely applied for the extraction of biologically active components from plant raw materials, was used as an extragent. Ethanol as an extragent has a number of advantages [6]: it does not form hazardous components with extracted raw materials and does not provoke the corrosion of equipment, has a relatively low boiling temperature (78°C), is environmentally friendly, and represents a very good preservative. This enables the use of obtained extracts in the perfume and cosmetic, food, and pharmaceutical industries. For this reason, the secondary raw materials remaining after the extraction of essential oil are extracted with aqueous alcoholic solutions of different concentration.

In our studies it has been established that the total yield of extractive substances depends on the concentration of a solvent [13]. The content of extractive substances extracted with aqueous alcoholic extragents with a concentration varied from 20 to 90% is less than 7%. Their yield grows with increasing ethanol concentration, attains a maximum (9.17%) for a 60-% aqueous alcoholic solvent, and then decreases to 6.94% for a 90-% aqueous alcoholic solvent (Fig. 6).

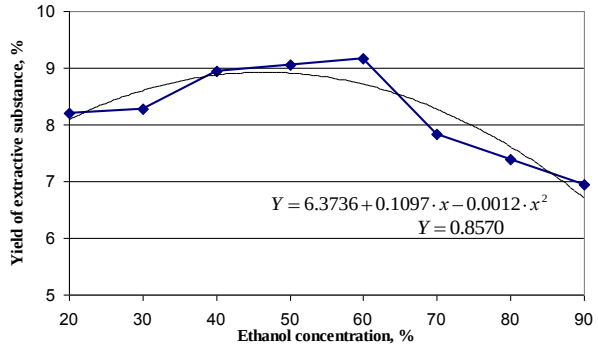


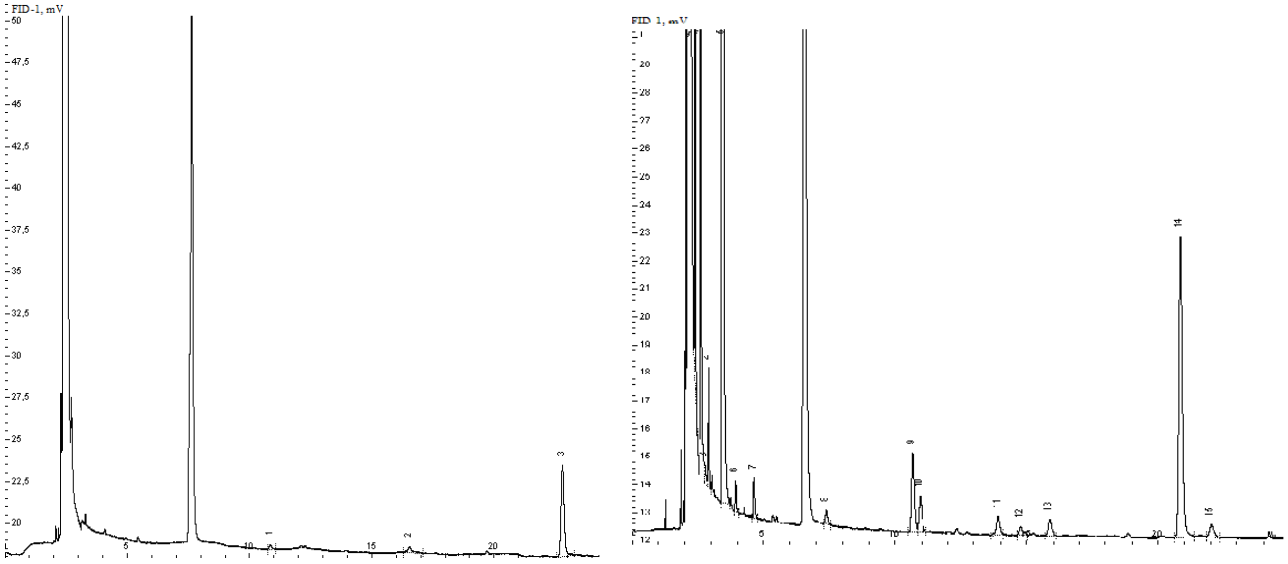
Fig. 6. Yield of extractive substances versus ethanol concentration.

The obtained aqueous alcoholic extract of fennel waste residues (ethanol concentration, 60%) is a transparent light-yellow finely fennel-scented liquid. The refractory index of the aqueous alcoholic extract is 1.5010, and its density is 0.9651 g/cm^3.

The component composition of the aqueous alcoholic extract obtained at an ethanol concentration of 60% and a temperature of 20ºC is presented in the chromatographic pattern (Fig. 7b) and Table 3.

Table 3. Component composition of the aqueous alcoholic extract of fennel waste residues

Principal components	Retention time, min	Mass content, %
α-Pinene	2.352	9.8
Camphene	2.594	40.2
Limonene	3.420	39.5
Camphor	10.663	1.1
Anethol	20.852	6.4



(a) (b)

Fig. 7. Chromatographic pattern of (a) distillation water and (b) aqueous alcoholic extract of fennel waste residues.

Among the fennel extract components, camphene and limonene are of special interest [13]. Camphene is used in the production of fragrances and insecticides and represents an intermediate in the synthesis of camphor, which is a valuable product for many chemical industries. Limonene is included into many perfumery products, shampoos, washing and cleaning products, and household and industrial solvents and used to degrease metals before industrial painting and in household chemicals, e.g., for the cleaning of wooden coverings and the removal of grease from hands. It is a perfect environmentally-friendly alternative to toxic and hazardous solvents and petrochemicals [14].

In our studies, it has been established that the aqueous alcoholic extract of fennel waste residues contains 8.1% of flavonoids, 1.2% tannins, 0.1% of coumarins, and 0.1% of ascorbic acid on absolute dry matter basis.

CONCLUSIONS

Hence, the performed studies have shown that fennel (*Foeniculum vulgare Mill.*) is a promising crop, the complex processing of which enables the production of new natural biologically active products.

Some regularities of the change in the quantitative and qualitative composition of fennel essential oil and

its distribution between the plant organs depending on a vegetation stage and weather have been shown for the first time. The optimal time period for the harvesting of raw materials has been determined. The epigeal fennel part cut at a level of 50 cm from the ground surface at the stage of milky-wax maturity of fruits on the central umbrel is recommended for industrial processing. A project of the National Standard of Ukraine on industrial fennel raw materials has been developed.

The developed technology for the extraction of new natural biologically active products from primary and secondary raw materials (essential oil, natural perfume water, aqueous alcoholic extract) results in the rational use of the valuable plant material, and its products contain a wide variety of biologically active components typical for the given plant. The proposed technology for the processing of fennel raw materials has been put into industrial practice at TRIA Ltd. (Simferopol) in September–October 2013.

REFERENCES

1. Gorbunova, E.V., Obosnovanie ispol'zovaniya *Foeniculum vulgare Mill.* dlya polucheniya tselevykh productov (Substantiating the use of *Foeniculum vulgare Mill.* for the production of target products), *Naukovi pratsi Krims'kogo agrotekhnologichnogo universiteta (tekhnichni nauki)* (Proceedings of the Crimean Agrotechnological University: Engineering Sciences), 2011, no. 138, pp. 128–134.

2. Anubhuti, P., Rahul, S., and Kant, K.C., Standardization of fennel (*Foeniculum vulgare*), its oleoresin and marketed ayurvedic dosage forms, *Journal of Pharmaceutical Sciences and Drug Research,* 2011, vol. 3, no. 3, pp. 265–269.

3. Gorbunova, E.V. and Timasheva, L.A., Izuchenie dinamiki nakopleniya efirnogo masla v protsesse vegetatsii rastenii fenkhelya (Studying the dynamics of the accumulation of essential oil during the vegetation of fennel plants), *Naukovi pratsi Krims'kogo agrotekhnologichnogo universiteta (tekhnichni nauki)* (Proceedings of the Crimean Agrotechnological University: Engineering Sciences), 2012, no. 146, pp. 164–170.

4. Gorbunova, E.V., Ekstragirovanie otkhodov fenkhelya posle izvlecheniya efirnogo masla (Extraction of fennel waste residues after the recovery of essential oil), *Naukovi pratsi Krims'kogo agrotekhnologichnogo universiteta (tekhnichni nauki)* (Proceedings of the Crimean Agrotechnological University: Engineering Sciences), 2013, no. 153, pp. 153–158.

5. Kapás, Á., András, C.D., Dobre, T.G., Vass, E., Székely, G., Stroescu, M., Lányi, S., and Ábrahám, B., The kinetic of essential oil separation from fennel by microwave assisted hydrodistillation (MWHD), University Politehnica of Bucharest Scientific Bulletin, *Series B: Chemistry and Materials Science,* 2011, vol. 73, no. 4, pp. 113–120.

6. Gorbunova, E.V., Tekhnologicheskie osobennosti kompleksnoi pererabotki tselykh rastenii fenkhelya obyknovennogo (Engineering peculiarities of the complex processing of whole fennel plants), *Tekhnika i tekhnologiya pishchevykh proizvodstv* (Technics and Technology of Food Industry), 2013, no. 3, pp. 9–15.

7. *Quality Control Methods for Medicinal Plant Materials,* Geneva: World Health Organization, 1998.

8. *European Pharmacopoea,* Strasbourg: Maisonneuve, 1998.

9. Karnick, C.R., *Pharmacopoeial Standards of Herbal Plants,* Delhi: Sri Satguru Publications, 1994, vol. 1, pp. 139–141; vol. 2, p. 71.

10. Goryachev, M.I. and Pliva, I., *Metody issledovaniya efirnykh masel* (Methods of Studying Essential Oils), Alma-Ata: Izdatelistvo akademii nauk Kazakhskoi SSP, 1962.

11. Chaouche, T., Haddouchi, F., Lazouni, H.A., and Bekkara, F.A., Phytochemical study of the plant *Foeniculum vulgare Mill., Der Pharmacia Lettre,* 2011, vol. 3, no. 2, pp. 329–333.

12. Radulović, N.S. and Blagojević, P.D., A note on the volatile secondary metabolites of *Foeniculum vulgare Mill.* (Apiaceae), *Facta Universitatis Series: Physics, Chemistry and Technology,* 2010, vol. 8, no. 1, pp. 25–37.

13. Patel, J.B, Patel, B., Patel, R.K., and Patel, B.H., Comparative evaluation of extraction methods for extraction of essential oil from *Foeniculum vulgare, Journal of Pharmaceutical Science and Bioscientific Research,* 2012, vol. 2, no. 4, pp. 176–178.

14. Coşge, B, Kiralan, M, and Gürbüz, B., Characteristics of fatty acids and essential oil from sweet fennel (*Foeniculum vulgare Mill. var. dulce*) and bitter fennel fruits (*F. vulgare Mill. var. vulgare*) growing in Turkey, *Natural Product Research,* 2008, vol. 22, no. 12, pp. 1011–1016.