OPTICAL PROPERTIES OF OIL EXTRACTS AND RESIDUES OF MEDICINAL AND AROMATIC HERBS

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ABSTRACT. The purpose of this work is to conduct a comparative study of attenuated total reflection infrared spectroscopy, diffuse-reflection electron spectroscopy and refractometry of the optical characteristics of a series of oil extracts, residues and dry-milled (<0.5 mm) aromatic and medicinal plant materials of different origin and anatomical localisation (roots, grass, flowers). Sunflower oil infusion was carried out in a water bath (90 °C) for one hour, followed by storage at room temperature for six months. For the studied series of extracts, the refractometry method allowed the linear dependency of the refractive index and iodine value to be obtained. This indicates that the extraction ability of the oil is determined not only by the fatty acid composition of the triglycerides of the samples, but also by the selectivity of the lipophilic components present in the extractant itself. The obtained data are consistent with the change in the intensity of the characteristic bands (320 nm) in the electronic spectra of extracts, residues and dry raw materials. The individual lipophilicity of oil extracts is confirmed by their IR spectra in the absorption region of C = C-bonds (1653 cm⁻¹), valency (3008 cm⁻¹) and deformation (722 cm⁻¹) vibrations of the CH-groups with a double bond (CH = CH) when compared with the spectra of residues and dry raw materials.

Keywords: oil extracts, oil residues, vegetable raw materials, infrared and electron reflection spectroscopy

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INTRODUCTION

Human beings began to use oil extracts of medicinal, aromatic plants and spices for various medical, therapeutic and food purposes in ancient times, thousands of years before the invention of technologies for their isolation in pure form. Today [1, 2], one of the traditional technologies used to increase the extractability of the lipophilic part of natural compounds is the infusion of crushed plant raw materials in oil heated to 70–90 °C. However only up to 5% of the lipophilic substances contained in the raw material, such as fatty acids, fat-soluble vitamins, pigments and other fat-soluble components [1, 3], are transferred to the extract. A number of biologically important substances do not dissolve in oils, including starch, sugars, proteins, water-soluble vitamins and metal salts. For this reason, the residual solid products of oil extraction processes are significant, since these residues almost completely retain the hydrophilic part of the substances, which have significant bioactive, preventive and therapeutic potential.

Biologically active and useful oil residues [4–7] can be used to enrich foods for human consumption including bakery, meat, fish, dairy, vegetable, etc. pro-ducts. Specially created compositions of oil extracts and powdered oil residues from medicinal plant materials are also used in pharmacopoeia, cosmetology, medical practice, including the development of coatings for wound and burn dressings [8–11]. Unlike synthetic products, the complex effect of products of natural origin on the systems of a living organism is based on the basic principle of the synergy of their components, which complement each other to enhance their overall effectiveness. However, in general these biological mechanisms either have not been studied or have yet to be studied in sufficient detail.

Since oil extraction is limited to lipophilic substances, it was necessary to use a complex of optical methods in order to obtain a positive confirmation of their presence: refractometry, widely used in laboratories of the oil extraction industry, attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy; and diffuse reflection electron spectroscopy (DRES). The lack of literature data on the study of the oil extracts and residues of plant materials by the ATR-FTIR and DRES methods predetermined the purpose of this work.

EXPERIMENTAL PART

The object of the study was the various anatomical parts of dry crushed medicinal and spicy aromatic plant materials of different types (Table), its oil extracts and residues obtained in the process of hot drawing (90 °C) in refined «Dary Kubani» sunflower oil. The volume of the liquid phase was 50 ml, while the mass of the crushed (<0.5 mm) raw material was 5 g. Extraction was carried out in a water bath for an hour. The obtained samples were stored for six months at room temperature with occasional stirring. Prior to the measurements being carried out, the extract was centrifuged.

Electronic diffuse reflectance spectra of the samples were recorded on a Specord M-200 spectrophotometer (AIZ Engineering GmbH, Germany) against the Spectron standard in the 200–700 nm wavelength range in the absorption format – A = f (λ), where A = log (100/R) is the absorption, R is the reflection coefficient and λ is the wavelength in nanometres (nm). When obtaining the spectra of the extracts, a fluoroplastic liner was used in the working cell, who-se reflection coefficient was close to the standard ref-lection coefficient. Vibrational spectra were obtained by the ATR-IR spectroscopy method using a Tensor 37 Fourier spectrometer (Bruker, Germany), with the OPUS software package in the frequency range 4000-600 cm⁻¹ also in the absorption format. Refractometry measurement of the refractive index (nD) of the sample under study for the sodium line of the spectrum λ = 589 nm, % (relative) fat content and iodine value (IV) was performed at 40 °C on a digital refractometer AVVEMAT-200 (Anton Paar GmbH, Austria) with automatic temperature control module. All three rapid methods are simple and do not require special sample preparation for analysis.

RESULTS AND DISCUSSION

The Table presents the results of the study of an experimental series of oil extracts from plant raw materials of different types by the method of refractometry following six months of storage.

Graphic processing of the data (Fig. 1) showed a linear relationship between the controlled refractometric parameters of oil extracts regardless of the anatomical part of the plant and its type. An increase in the iodine value in this series of samples clearly indicates an increase in the total content of unsaturated C=C bonds in the composition of extractable compositions. However, the sequence in the location of the studied samples on the resulting dependency may be due not only to the different content of extractable substances from the plant material in question, but also to the selectivity of the extractant oil relative to the lipophilic components present in it.
**Optical properties of oil extracts and residues of medicinal and aromatic herbs**

**Refractometric indices of experimental series of vegetable oil extracts**

| № in order | Vegetable raw materials       | Refractive index n\(_D\) | Iodine value IV | % fat (rel.) |
|------------|-------------------------------|---------------------------|----------------|-------------|
| 1          | Hypericum (herb)              | 1.4672                    | 106.6          | 61.3        |
| 2          | Chilli Pepper (pod)           | 1.4670                    | 105.6          | 61.1        |
| 3          | Sweet flag (root)             | 1.4669                    | 105.0          | 60.9        |
| 4          | Ginger (root)                 | 1.4668                    | 104.5          | 60.8        |
| 5          | Carnation (buds)              | 1.4668                    | 104.3          | 60.7        |
| 6          | Calendula (petals)            | 1.4667                    | 103.9          | 60.6        |
| 7          | Nettle (herb)                 | 1.4666                    | 103.3          | 60.5        |
| 8          | Chaga (mushroom)              | 1.4665                    | 102.7          | 60.3        |
| 9          | Base (sunflower oil)          | 1.4664                    | 102.1          | 60.1        |

![Graph](image.png)

**Fig. 1. Dependency – IV = f(n\(_D\)) for a series of oil extracts of vegetable raw materials; the numbering in the Figure corresponds to that of the Table**

**Рис. 1. Зависимость – ІЧ = f(н\(_D\)) для серии масляных экстрактов растительного сырья; нумерация на рисунке отвечает нумерации в таблице**

The sample of electronic spectra of oil extracts (Fig. 2, a) of the studied raw materials, which confirm the results of refractometric analysis, allows us to conclude that they differ not only in the content of extracted lipid components, but also in the composition of their mono- and polyunsaturated fatty acids (region 280–380 nm) [12, 13]. The bands in the spectra of nettle and calendula extracts in the long-wavelength range (≈430 and ≈680 nm) are due to pigment substances (chlorophylls, carotenoids), extracted by the oil to varying degrees, give the extract its characteristic colour.

A comparative study of the spectral characteristics of dry crushed vegetable raw materials, oil extracts and residues using the DRES method is illustrated by the example of the hypericum perforatum herb (Figure 2b), which showed the highest extractability of lipophilic components by the base oil. From the reduced spectrum of the residue (Curve 2), it can be seen that when the dry raw material swells (Curve 1) in the extractant oil, a rise in the spectral curve is observed in the wavelength region above 380 nm. However, a decrease in the intensity of a number of bands in the range of 280–340 nm, where lipid components usually manifest themselves, suggests a partial transition in the composition of the extractant.

This is indicated by an increase in the intensity in the spectrum of the extract (Curve 3) of the band at 320 nm as compared with the spectrum of the original extractant oil (Curve 4).
Fig. 3 and 4 show the IR spectra of three samples of calendula and nettle. Comparison of the data shows that the spectra of their oil extracts have no bands in three areas: 3294–3296 cm\(^{-1}\), where nitrogen containing functionals absorb, 1700–1500 cm\(^{-1}\); absorption of carbonyl groups of protein structures and 1030–900 cm\(^{-1}\) taking place in the region of manifestation of the absorption of carbohydrate components, but which are present in the spectra of samples of dry raw materials and oil residues [14–16].

Fig. 3. IR spectra of calendula samples: 1 – oil extract; 2 – residue; 3 – dry raw materials

Рис. 3. ИК-спектры образцов календулы: 1 – масляный экстракт; 2 – шрот; 3 – сухое сырье
This fact suggests that the protein and carbohydrate components of vegetable raw materials are virtually unaffected by the extraction process. In the spectra of oil extracts of all samples, there are narrow intense bands in the region of 2980–2830 cm⁻¹, due to fluctuations of CH₃ groupings and few intense bands (3008 cm⁻¹) of valence vibrations of CH groups having a double bond (=CH–). Their deformation fluctuations are observed in the position 722 cm⁻¹. The characteristic structured stripe in the form of a “trident” with a maximum at 1160 cm⁻¹, corresponding to the vibrations of C – O bonds in the composition of triglycerides of lipid components, is always very clearly visible in the spectra of oils and their extracts, almost overlapping each other. In the spectra of dry raw materials, this is represented by a shoulder on the left branch of the wide carbohydrate maximum (1060 cm⁻¹), which may indicate the spectral manifestation of glycolipid bonds in the sample structure. It should be noted [1] that the quality of the product produced from plant materials depends on many factors – type, variety, zoning, climatic conditions, collection time, drying and storage conditions, technological schemes of production and their parameters, as well as the quality of oil extractant.

CONCLUSION

The individual extractive capabilities of sunflower oil are shown with respect to plant raw materials of various kinds, manifested to a different degree in increasing absorption of oil extracts and a reduction in the intensity of bands in the spectra of oil residues in the area of manifestation of lipid components.

It is noted that the integrated use of optical methods that are consistent and complement each other in the study of biological tissues of plant origin, increases access to useful information, not only allowing the purposeful extraction of oil extracts with desired composition and properties, but also the possibility to enrich the necessary components of ingredients that are important for such branches of science and industry as food, pharmaceuticals, phytochemistry, medicine and phytotherapy.

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** Contribution **
Nechiporenko A.P., Melnikova M.I., Nechiporenko U.Yu., Plotnikova L.V., Uspenskaya M.V. carried out the experimental work, on the basis of the results summarized the material and wrote the manuscript. Nechiporenko A.P., Melnikova M.I., Nechiporenko U.Yu., Plotnikova L.V., Uspenskaya M.V. have equal author’s rights and bear equal responsibility for plagiarism.

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Нечипоренко А.П., Мельникова М.И., Нечипоренко У.Ю., Плотникова Л.В., Успенская М.В. выполнили экспериментальную работу, на основании полученных результатов провели обобщение и написали рукопись. Нечипоренко А.П., Мельникова М.И., Нечипоренко У.Ю., Плотникова Л.В., Успенская М.В. имеет на статью равные авторские права и несет равную ответственность за плагиат.
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