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STUDY OF THE CHEMICAL COMPOSITION OF THE FRUITS OF Crataegus orientalis L. AND USE

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ИССЛЕДОВАНИЕ ХИМИЧЕСКОГО СОСТАВА ПЛОДОВ Crataegus orientalis L. И ИСПОЛЬЗОВАНИЕ

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Abstract. The article presents a phytochemical study of the fruits of Crataegus orientalis L. and, based on the results obtained, a comprehensive scheme for their use was developed. The main components of oriental hawthorn fruits (flavonoids, carotenes, water-soluble polysaccharides, etc.) were sequentially isolated from the same sample and studied using modern physicochemical methods. The characterization of these compounds was achieved by chemical, as well as various chromatographic and spectroscopic (UV/VIS, 1h- and 13c-nmr) methods. The scheme presented in the research work is dedicated to solving a very important and important problem in the direction of waste-free or low-waste complex processing of plant raw materials. A scheme for complex processing of fruits is proposed, including stage IV and allowing the extraction of carotenoids, flavonoids, water-soluble polysaccharides, pectin substances of hemicellulose, α-cellulose and fatty oil from seeds.

Представлено фитохимическое исследование боярышника Аннотация. плодов восточного (Crataegus orientalis L.) и на основании полученных результатов разработана комплексная схема их использования. Основные компоненты плодов боярышника восточного (флавоноиды, каротины, водорастворимые полисахариды и др.) последовательно выделены из одного образца и изучены с использованием современных физико-химических методов. Характеристика этих соединений проведена химическими, а также хроматографическими и спектроскопическими (УФ-видимая область, 1Н- и 13С-ЯМР) методами. Представленная схема посвящена решению весьма важной и актуальной проблемы в направлении безотходной или малоотходной комплексной переработки растительного сырья.

Keywords: environment, Crataegus orientalis, polysaccharides, complex use, spectrophotometric.

Ключевые слова: окружающая среда, Crataegus orientalis, полисахариды, комплексное использование, спектрофотометрия.

Identifying plant species rich in biologically active substances and studying their phytochemical composition are currently one of the pressing problems of modern science. Currently, there is a great need for natural compounds of plant origin in various sectors of the national economy, and research is expanding towards the complex use of plant-based raw materials [10].

Many natural compounds have irreplaceable properties and are in dire need in various sectors of the national economy, including medicine, pharmacy, and the food industry. The plant flora of the Nakhchivan Autonomous Republic, which can be renewed every year and therefore has an inexhaustible reserve and a very diverse species composition, is a source of natural biologically active substances [2].

The chemical composition, flavonoids, polysaccharide complex and other compounds of the eastern hawthorn fruits, which are widely distributed in the territory of the Nakhchivan Autonomous Republic, have not been studied previously. Therefore, conducting a phytochemical analysis of hawthorn fruits and determining the methods of their complex processing based on the results obtained is of scientific and practical importance. According to the experimental findings, the ethanol extract of C. orientalis displays remarkable antinociceptive, antiinflammatory, and antioxidant activities [3].

Biological features. The genus Crataegus L. (hawthorn) belongs to the Rosaceae family and has 280 species distributed in temperate regions of the world. It is known that 19 species of hawthorn are distributed in the territory of the Nakhchivan Autonomous Republic [6, 7].

Pharmacological properties. Some species of the genus Crataegus L. have been used in folk medicine in various countries since ancient times. Pharmacological and toxicological studies have shown that various extracts of the hawthorn plant have a positive effect on cardiovascular diseases [1].

Extracts from hawthorn flowers and fruits have also been found to have antiviral and antioxidant activity. Hawthorn extracts are also known to significantly inhibit thromboxane A2 synthesis and platelet adhesion, thereby reducing the rate of atheromas and thrombosis formation [4; 11].

The main pharmacological effects of hawthorn are associated with the presence of flavonoidtype compounds in their composition. Many flavonoids have been found to have a wide range of They exhibit antibacterial, antiviral, anti-inflammatory, effects. antithrombotic activities, and have the ability to dilate capillaries and increase their elasticity [5; 9].

Material and methods

The fruits of the Eastern hawthorn were collected in the ripening phase from the Batabat area of the Shahbuz district of the Nakhchivan Autonomous Republic. The fleshy part of the fruits was separated from the seeds, dried at room temperature, and then ground. The ground plant sample (570 g) was sequentially extracted with diethyl ether, ethyl alcohol, water, and alkaline solutions of water (1% ammonium oxalate, 5 and 10% NaOH) to obtain carotenoids, flavonoids, and a polysaccharide complex (water-soluble polysaccharides, pectin substances, A- and Bhemicelluloses, α-cellulose) [2; 10].

Spectrophotometric and chromatographic methods were applied, UV spectra of the substances were obtained on a UV-2900 spectrophotometer. Separation of individual substances from the extracts and their purification were carried out using paper, thin layer and column chromatography methods. Paper chromatography was performed on Filtrak FN-7 and FN-11 papers, thin layer chromatography on Silufol UV254 plates, and column chromatography on alumina, silica gel (Silica Gel, 70-140 µ) and Sephadex LH-20 columns. The determination of the obtained substances in pure form was performed using chemical and physicochemical methods [4; 8].

Results and discussion

Fractionation of the total carotenoids extracted from the fruits of Eastern hawthorn was carried out using column chromatography, quantitative analyses were carried out using paper and thin layer chromatography, and quantitative analyses were carried out using UV-spectrometric methods.

As a result of the analyses, it was determined that the carotenoid composition of hawthorn fruit consists of α-carotene, β-carotene, lutein, phytoin and phytofluin. The percentage amounts of individual carotenes were determined as: α-carotene (37.5%), β-carotene (30.3%), lutein (15.5%), phytoin (2.3%), phytofluin (3.8%).

The residue of the plant sample was extracted with 80% ethyl alcohol (60°C, 3 hours), the extract was filtered through filter paper and concentrated under vacuum (40°C). The ethanol extract was treated sequentially with ethyl ether and chloroform. The chloroform extract was chromatographed on a silica gel column. The obtained substances were purified by Sephadex LH-20 column. The pure substances were determined as quercetin, rutin, hyperoside, isoquercitrin and catechin based on the results of chemical transformations (complete and partial hydrolysis in acidic medium, enzymatic and alkaline hydrolysis), as well as the analysis results of UV- and 1H-NMR spectra and comparison of these results with literature data. The total amount of flavonoids in oriental hawthorn was determined to be 1.05%.

After extraction with ethyl alcohol, the solvent was removed from the residue of the plant sample and extracted with water to obtain water-soluble polysaccharides (WSP). After dialyzing the water-soluble polysaccharides, it was precipitated with ethanol. The precipitate was washed sequentially with ethanol and acetone, and dried under vacuum at 40oC. The yield was 6.90%.

The qualitative and quantitative characteristics (%) of water-soluble polysaccharides were determined by the titrimetric method: free carboxyl groups — 4.62, esterified carboxyl groups — 6.75%, total carboxyl groups — 11.37, methoxyl groups — 4.65 and the degree of methoxylation — 59.37. The content of galacturonic acid in SHOK was determined to be 37.5%. The high content of galacturonic acid indicates that SHOK is of pectin nature.

The residue of the sample was extracted with a 1% aqueous solution of ammonium oxalate, yielding 6.60% pectin substances (PS). The total content of WSP and PS in the fruits of Eastern hawthorn was determined to be 13.50%. WSP and PS were completely hydrolyzed in an acidic medium and their monosaccharide composition was analyzed by paper chromatography. As a result of the analysis, it was determined that the characteristic monosaccharide composition of both polysaccharides is the same, consisting of arabinose, galactose, xylose and rhamnose.

Analysis of the complete hydrolysis products of WSP showed that it contains a high amount (37.5) of galacturonic acid, equal to neutral sugars. The high content of galacturonic acid in WSP indicates that it is a polysaccharide with acidic properties and pectin character.

Pectin was partially hydrolyzed to obtain galacturone (40%). Chromatographic analysis of the products of hydrolysis of galacturone in an acidic environment and by enzymatic method showed that this substance consists mainly of galacturonic acid.

One of the main reasons for the increased interest in studying the chemical composition, properties and structure of plant-derived polysaccharides is the recent discovery that some polysaccharides exhibit physiological activity. These compounds have the ability to remove heavy metal ions and radionuclides from the body. They have a gastroprotective effect and have a positive effect on the endocrine and immune systems. Pectic substances are also widely used for technical purposes. They are used in the production of D-galacturonic acid, in geological drilling, in the textile industry, and in printing. Pectic substances are irreplaceable natural compounds due to a number of specific properties (gelling, complexing, etc.).

Currently, the development direction of chemical technologies is directed towards the complex use of plant-based raw materials. For these purposes, priority is given to the application and development of continuous and waste-free processes, while protecting the safety of the environment. Therefore, the development of waste-free or low-waste complex processing schemes for plant raw materials is very important and is the demand of the day.

The results of the conducted research allow us to propose a complex processing scheme for hawthorn fruits, consisting of the following stages:

Obtaining total carotenes by extraction of fruits with diethyl ether. Separation of individual carotenes by chromatographic methods.

- 2. Obtaining the total flavonoids from the sample residue by extraction with ethyl alcohol. Separation of individual flavonoids by chromatographic methods.
- 3. Sequential extraction of water-soluble polysaccharides, pectin substances, A- and Bcelluloses from the sample residue.
 - 4. Oil was obtained from hawthorn berries by extraction method (1.86%).

The physicochemical constants of the obtained oil (acid number -11.1, free fatty acid content 5.5, saponification number 238, peroxide number 1.04, iodine number 82.4, and nd - 1.4735) were determined.

Conclusion

As a result of the research, natural compounds belonging to various chemical classes were obtained from the fruits of oriental hawthorn by sequential extraction method: carotenoids, flavonoids, water-soluble acidic polysaccharides, pectin substances, A- and B-hemicelluloses. A method of complex processing of hawthorn fruits was proposed for the first time. The wide range of applications of carotenes, flavonoids and polysaccharides, as well as the inability to replace these substances with adequate other substances in most cases, allow us to characterize hawthorn fruits as an indispensable source of raw materials for obtaining food additives, medicines and technical means. The scheme presented in the research work is dedicated to solving a very important and urgent problem in the direction of waste-free or low-waste complex processing of plant raw materials.

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