The prospects of using hawthorn fruits for the production of biologically active food additives and food products based on them

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Abstract. Due to the wide range of pharmacological properties and the presence of bioactive components with antioxidant action hawthorn fruits can be widely used as part of dietary supplements for the prevention or improvement of diseases associated with oxidation and (or) obesity, as well as concomitant cardiovascular diseases. An urgent task of the modern pharmaceutical and food industry in the development of biologically active food additives is the use of hawthorn varieties that are resistant to the accumulation of heavy metals and have increased resistance to excess toxic elements. The chemical composition and safety indicators of fresh hawthorn fruits have been studied and it has been established that the studied fruits of zoned hawthorn varieties in terms of safety indicators meet the requirements of the State Pharmacopoeia of the Russian Federation and can subsequently be used in the development of biologically active food additives. An analysis of the safety indicators of powders made from hawthorn fruits dried at different temperatures was carried out. It has been established that maximum preservation of ascorbic acid in hawthorn fruit processing products is facilitated by drying fresh fruits at 50ºC.

1 Introduction

Hawthorn belongs to the Pink family, a genus of hawthorns with more than 280 varieties. Deciduous shrubby tree with long and short prickly shoots. It grows in wooded and shrubby areas at an altitude of up to 1,500 meters above sea level [1]. The flowers are pink to white in color with 5 petals, short triangular sepals, stamens protruding around the nectary, and carpels in corymbs. Hermaphrodite flowers appear in late spring (from May to early June). In autumn, dark red fruits appear, small oval in shape, about 10 mm long, similar to berries, but in structure they represent a pome fruit [2].

Hawthorn grows throughout Europe, North America and Asia. For example, Crataegus pinnatifida is widespread in China, while C. monogyna and C. laevigata are mainly in Europe,

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Crataegus monogyna is a local species in Ireland. The main varieties of hawthorn are C. pinnatifida Bge, C. brettschneideri Scheneid, C. scabrifolia Recd and C. hupehensis Sarg [1].

The common hawthorn differs from the related but less common Midland hawthorn (C. laevigata) in more erect growth, leaves with spreading lobes, flowers have only one column, not two or three. However, they are interfertile, so hybrids are common.

The vast majority of published articles on the chemical composition of hawthorn are devoted to polyphenolic compounds, the biological value of which is due to hydroxy derivatives of flavones and phenols. Due to the active intensification of technologies for the industrial production of functional food products, the need for a more detailed study of the compounds presented is increasing everywhere [4]. In terms of their antioxidant activity, phenolic compounds surpass many natural and synthetic antioxidants, and, according to recent data, they also exhibit protective mechanisms against chronic diseases [3].

Oxidative stress, which occurs in the body due to an excess of free radicals, can provoke diseases of various etymologies, such as diabetes mellitus. At the same time, substances that can interfere with free radical oxidation reactions can mitigate inflammatory processes and restore a permanent environment of the body. Natural antioxidants (phenols, polysaccharides, alkaloids, as well as lecithins, carotene and phospholipid compounds), which are rich in hawthorn fruits [6], are becoming increasingly popular as an alternative to chemical preservatives in the food industry.

It is reported [7] that there is a linear correlation between the concentration of released phenols of hawthorn and its ability to absorb free radicals. The authors emphasize that the biological activity of phenolic compounds depends on the physical properties of hawthorn fruits. Thus, the concentration of phenol in the shell is higher when compared with the pulp, however, this trend may vary depending on the varieties of hawthorn [5].

When studying the bioavailability of substances that inhibit oxidation, the intracellular antioxidant activity of hawthorn was considered [8]. The research results demonstrated a significant number of phenolic compounds that prevented lipid peroxidation by activating endogenous enzymes [9].

Hawthorn is not only used for direct consumption, but has been used in medicine for centuries to have a therapeutic effect on strengthening lymphoid organs [10], stimulating appetite [9], regulating blood glucose levels and lipid metabolism [4]. First of all, a wide range of applications in therapeutic practice is associated due to the abundance of biologically active substances - flavonoids [12], phenols, terpenoids and pectins [2].

Many scientific studies have demonstrated that the occurrence of oncology and the development of diseases of the nervous system are mainly associated with the formation of excessive amounts of free radicals [11, 13]. However, antioxidants are not always able to suppress the process of aggressively produced radicals in the later stages, so it is important to take into account that the prevention of oxidative damage is possible only at the early stages of the development of diseases, in particular when natural foods of plant origin are included in the diet.

Dyslipidemia, steatohepatosis, cardiovascular diseases (hypertension, thrombophlebitis, angina pectoris) have become an acute problem of mankind in recent decades. As a result, diseases of the presented etymology cause disorders of lipid metabolism associated with an increase in the level of total cholesterol and lipoproteins, as well as total triglyceride. It has been reported that hawthorn extract reduces the concentration of lipids in the blood by reducing the content of the presented organic compounds [4, 14].

Thus, hawthorn can be widely used as a part of biologically active additives for the prevention or improvement of diseases associated with oxidation and (or) obesity, as well as concomitant cardiovascular diseases.

2 Materials and methods

The research was conducted at the Innovative Research and Testing Center for Collective Use of the Orel State Agrarian University named after N.V. Parakhin.

The object of the study was the fruits of the blood-red hawthorn (Crataegus sanguinea). The fruits were grown and obtained on the territory of the Orel region of the Russian Federation (52.976252 lat.; 36.033792 long.) in October 2023.

The determination of safety indicators of medicinal plant raw materials was carried out according to generally accepted methods: toxic elements (lead) were detected according to GOST 30538-97, arsenic – according to GOST 26930-86, cadmium – according to GOST 30538-97, mercury – according to GOST 26927-86, as well as in accordance with the requirements of the General Pharmacopoeia Article (hereinafter referred to as GPhA) "Determination of the content of heavy metals and arsenic in medicinal plant raw materials and medicinal herbal preparations". The content of residual amounts of pesticides was determined in accordance with the requirements of the GPhA "Determination of the content of residual pesticides in medicinal plant raw materials and medicinal plant preparations" and in accordance with GOST 30349-96. The determination of radionuclides (caesium–137 and strontium–90) was carried out in accordance with the requirements of the GPhA "Determination of the content of radionuclides in medicinal plant raw materials and medicinal herbal preparations" on the Progress-gamma Gamma scintillation spectrometer.

The characteristics and chemical composition of hawthorn fruits were studied in accordance with the pharmacopoeia article PhA.2.5.0061.18 Hawthorn fruits (characteristics of fruits, shredding of raw materials, humidity, total sol), the mass fraction of protein was determined by the Kjeldahl method on the KjeltecTM 2300 (Foss) device; the fiber content was established on the FibertekTM 1020 (Foss) device; the amount of ascorbic acid is determined by the iodometric method; the mineral composition was analyzed on an atomic emission spectrometer with inductively coupled plasma ICAP-6300 after sample preparation, which was carried out according to the methodological instructions for the device. The study of the acidity of fresh hawthorn fruits was carried out in accordance with GOST ISO 750-2013, including conversion to malic, oxalic, citric (monohydrate), tartaric, sulfuric, acetic, lactic and citric acids.

The degree of satisfaction of the recommended daily requirement for basic nutrients is determined in accordance with the Methodological Recommendations (MR) 2.3.1.0253-21 "Norms of physiological energy and nutritional needs for various population groups of the Russian Federation".

Hawthorn fruits were dried by convection in a CONTERM series drying unit while maintaining constant temperatures of 50, 60, 70 and 80°C. Laboratory samples of the dried material were divided into batches: 1 batch – 1 kg of fresh hawthorn fruits, subject to the thickness of the dried product layer 1-1.5 cm; batch 2 – 40 g of fresh hawthorn fruits in the appropriate weight of the container.

The separation of the dried material into batches was necessary to construct curves of the dynamics of the moisture evaporation process and control the weight reduction of the suspension during the drying process.

3 Results and discussion

An urgent task of the modern pharmaceutical and food industry in the development of biologically active food additives is the use of hawthorn varieties that are resistant to the accumulation of heavy metals and have increased resistance to excess toxic elements.

The safety indicators of fresh hawthorn fruits were studied (Table 1): toxic elements (lead, arsenic, cadmium and mercury), pesticides (hexachlorocyclohexane (HCH),

dichlorodiphenyltrichloroethane (DDT) and its metabolites), as well as radionuclides (caesium-137 and strontium-90).

Table 1. Safety indicators of fresh hawthorn fruits.

Name of indicators, units of measurement	**Acceptable levels in accordance with the State Pharmacopoeia of the Russian Federation (GPhA.2.5.0061.18 Hawthorn fruits), no more**	**The value of the indicators**
Toxic elements, mg/kg		
- lead	6.0	0.025
- arsenic	0.5	0.001
- cadmium	1.0	0.034
- mercury	0.1	0.001
Pesticides, mg/kg		
-hexachlorocyclohexane	0.1	
-(alpha isomer;		Less than 0.02
-beta isomer;		Less than 0.01
-gamma isomer)		Less than 0.02
- DDT and its metabolites	0.1	Less than 0.02
Radionuclides, Bq/kg		
caesium-137	400	1.4497
strontium-90	200	0.0326

The conducted studies presented in Table 1 showed that the content of toxic elements and pesticides in fresh hawthorn fruits does not exceed the permissible levels established by regulatory documents – the State Pharmacopoeia of the Russian Federation (GPhA.2.5.0061.18 Hawthorn fruits). The level of pesticides in hawthorn fruits was less than 0.01-0.02 mg/kg. The values of caesium-137 (Figure 1) and strontium-90 for the studied samples were 1.4497 and 0.0326 Bq/kg, respectively, which is also significantly lower than the permissible norm of the The State Pharmacopoeia of the Russian Federation.

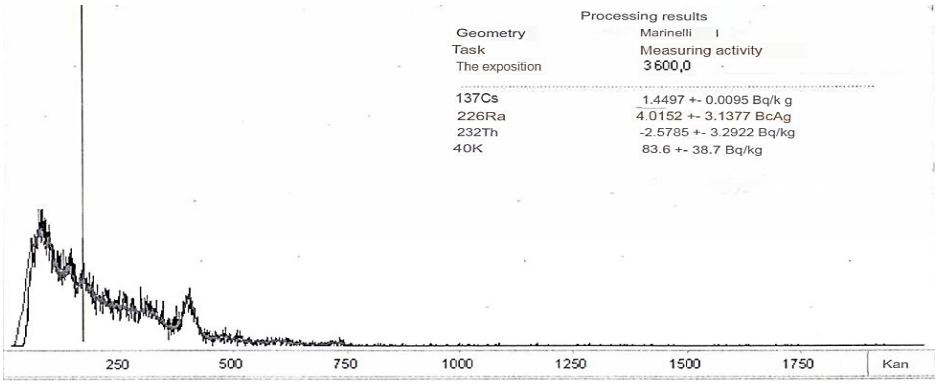

Fig. 1. Results of the detection of caesium-137 in fresh hawthorn fruits.

Thus, the studied fruits of the zoned hawthorn varieties meet the requirements of the State Pharmacopoeia of the Russian Federation in terms of safety and can further be used in the development of biologically active food additives.

Table 2 shows the average values of the basic chemical and mineral composition of fresh hawthorn fruits.

Table 2. Chemical composition of fresh hawthorn fruits.

Main substances of fresh hawthorn fruits	Values
Humidity, %	68.23±2.06
Protein in terms of dry matter, %	1.83±0.04
Total ash in terms of dry matter, %	3.91±0.01
Fiber in terms of dry matter, %	79.82±2.09
Mineral substances: - calcium, mg/g - iron, mg/kg - zinc, mg/kg	 3.09±0.03 94.0±0.3 7.1±0.1

The data presented in Table 2 on the chemical composition of hawthorn show a significant amount of fiber (79.82% in terms of dry matter with an actual fruit moisture content of 68.23%, which corresponds to 101.4 – 126.8% satisfaction of the recommended daily dietary fiber requirement (20-25 g) for adults of both sexes of all physical activity groups in terms of 100 g of the product). A high concentration of macronutrients in fresh hawthorn fruits was found in calcium – 3.09 mg/g, trace elements – in iron (94.0 mg /kg).

The results of the study of the acidity of fresh hawthorn fruits are presented in Table 3. It was experimentally determined that the average value of titrated acidity for fresh hawthorn fruits was 23.03 mmol H+ per 100 g of product.

Table 3. Acid content in fresh hawthorn fruits.

Name of the acid, g/100 g	The value of the indicator
malic acid	1.409
Oxalic acid	0.947
Citric acid (monohydrate)	1.472
Tartaric acid	1.578
Sulfuric acid	1.031
Acetic acid	1.262
Lactic acid	1.893
Citric acid	1.346

In order to concentrate biologically active substances of hawthorn and to eliminate the spoilage of fresh fruits, dried samples were obtained at temperatures from 50 to 80°C in increments of 10°C. In order to plot the dynamics, a sample of intact hawthorn fruits of the same size with a total weight of 40 g was dried in a separate glass container. The drying curves of hawthorn, reflecting the dependence of the mass of the dried product on the time of temperature exposure are shown in Figure 2.

When comparing the graphs of the dynamics of drying hawthorn fruits, it was found that with an increase in the drying temperature, the drying time required for samples to achieve the humidity required by the State Pharmacopoeia of the Russian Federation decreases (Pharmacopoeia article.2.5.0061.18 Hawthorn fruits) – no more than 14%.

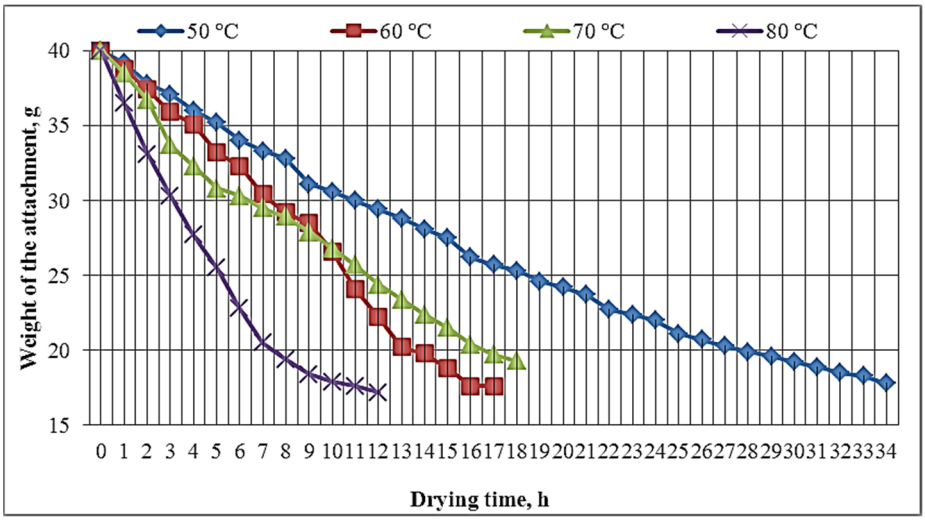

Fig. 2. Graph of convection drying of hawthorn fruits at different temperatures.

The results obtained demonstrate that, on average, the final moisture content of the dried samples was at the level of 5.52%, which meets the requirements of the State Pharmacopoeia. The conducted studies demonstrate that a more intensive decrease in the humidity of hawthorn samples occurred with an increase in the temperature of the drying process.

Dried hawthorn fruits were ground in a laboratory mill to a loose powdery state and sieved through a sieve made of polyamide sieve fabric 22.7H-150 with a cell size of 560 microns. Thus, a light brown powder with a characteristic taste and smell of hawthorn was obtained. The safety indicators of the fine powder obtained after grinding dried hawthorn fruits are presented in Table 4.

Table 4. Safety indicators of dried hawthorn fruit powder.

Name of indicators, units of measurement	**Acceptable levels in accordance with the State Pharmacopoeia of the Russian Federation (GPhA.2.5.0061.18 Hawthorn fruits), no more**	**The value of indicators for samples of powder from hawthorn fruits dried at different temperatures**			
		50°C	**60°C**	**70°C**	**80°C**
Toxic elements, mg/kg					
- lead	6.0	0.031	0.031	0.030	0.030
- arsenic	0.5	0.001	0.001	0.001	0.001
- cadmium	1.0	0.042	0.042	0.042	0.042
- mercury	0.1	0.001	0.001	0.001	0.001
Pesticides, mg/kg					
-hexachlorocyclohexane	0.1				
-(alpha isomer;		Less than 0.02			
-beta isomer;		Less than 0.01			
-gamma isomer)		Less than 0.02			
- DDT and its metabolites	0.1	Less than 0.02			
Radionuclides, Bq/kg					
caesium-137	400	2.8961	2.8959	2.8963	2.8962
strontium-90	200	0.0728	0.0725	0.0727	0.0723

As a result of the technological process of drying fresh hawthorn fruits, the concentration of substances responsible for the safety of the dried powder occurs. It was found that in terms of the content of toxic elements, pesticides and radionuclides, the powder from dried hawthorn fruits fully complies with the requirements of the State Pharmacopoeia of the Russian Federation. Thus, the obtained powder with proven safety proves its acceptability for inclusion in the formulation of biologically active additives and food products based on them.

To identify optimal drying modes in which the biological properties of hawthorn fruits are maximally preserved, studies were conducted to determine the content of ascorbic acid in fresh hawthorn fruits and dried powders (Figure 3).

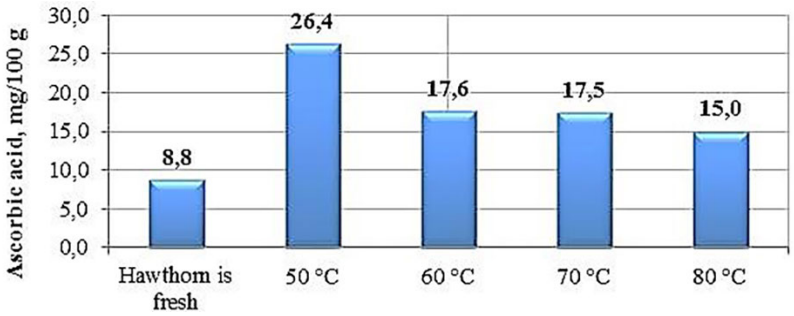

Fig. 3. Ascorbic acid content in fresh and processed (dried and crushed) hawthorn fruits.

According to the research results presented in Figure 3, a higher value of the mass fraction of ascorbic acid is observed in dried hawthorn fruits compared to fresh fruits, due to the concentration of dry substances in the dried samples due to moisture evaporation during drying. It is noted that an increase in the drying temperature of hawthorn fruits leads to a decrease in the mass fraction of ascorbic acid in the obtained powders. Thus, an increase in the drying temperature for every 10 0C (starting with a sample dried at 50 0C) leads to a decrease in the mass fraction of ascorbic acid by 33.3; 33.7%; 43.2%, respectively.

4 Conclusion

The conducted studies of the safety indicators of fresh hawthorn fruits, such as toxic elements, residual amounts of pesticides and radionuclides, have established their full compliance with the requirements of the State Pharmacopoeia of the Russian Federation (Pharmacopoeia article.2.5.0061.18 Hawthorn fruits).

To concentrate biologically active substances of hawthorn and exclude spoilage processes of fresh fruits– drying of samples at temperatures of 50-80°C is proposed. The powder obtained by grinding and sieving from dried hawthorn fruits meets the requirements of the State Pharmacopoeia of the Russian Federation in terms of quality and safety. Hawthorn fruit powder is characterized by a high content of ascorbic acid and can be used in the development of biologically active food additives and food products based on them.

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