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Manufacturing and physico-chemical characterization of new fruit spreads obtained from blackthorn, hawthorn and rosehip

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Abstract

The fruits of blackthorn (*Prunus spinosa* L.), hawthorn (*Crataegus monogyna*), rosehip (*Rosa canina*) are commonly used in food industry and phytotherapy. The aim of the paper was to obtain a functional product valorisation fruits from spontaneous flora of Romania, richs in biologically active principles with high availability for the human body. The contents of phenols, antioxidative activity in extracts of blackthorn, hawthorn, rosehip fruit and spreads from fruits were determined using spectrophotometric methods. Physicochemical methods have been used to determine moisture, acidity, vitamin C and mineral substances. In order to obtain a product that could be used as a dressing for food industry, a classical technological process was used, resulting in a nutritionally complex product with multiple therapeutic effects.

Keywords: blackthorn, hawthorn, rosehip, spreads, phenols

1. Introduction

Healthy aliments are the key to a healthy life and are representing one of the most important external factor influencing the human organism.

Fruits are the main raw material for jelly and jam production and they represent the organs of reproduction of plants. Those with a certain alimentary value, aroma, pleasant taste and attractive color are usually uded in food industry. Especially appreciated are those whose processing operations can be mechanized thus making the process economically efficient.

Today, consumer awareness and interest in nutritional value, mainly in healthy food, is observed in most societies. People are selecting aliments based not only on their taste, but also on the positive impact on their health. These force the food producers to adapt to a new market and to develop food products that will be attractive to potential consumers and become competitive in the market. Today, these actions can be divided into two categories: the first one is returning to natural, traditional products that are least processed, and the second one is a production of functional foods, frequently using unconventional constituents or additives. Such constituents can be wild grown fruits, which are often a reliable source of healthy compounds, as well as antioxidants [1].

Due to the complexity of the components in wild fruit species, antioxidative capacity and the content of biologically active compounds is still unknown. However, it seems that antioxidants play a major role in the protection of plants.

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The main property of an antioxidant is its capacity to trap free radicals which may oxidize nucleic acids, proteins, lipids [2, 3]. Fresh fruit extracts are an excellent source of polyphenolic compounds, as free radicals scavengers, which can significantly reduce the negative effect of free radicals in the organism. Consequently, they have an essential role in the prevention of neurodegenerative diseases, cardiovascular diseases and cancer [4].

There is an increasing interest in the measurement and use of wild fruits as antioxidants for research, as well as for industrial (dietary, pharmaceutics and cosmetics) purposes.

The blackthorn (*Prunus spinosa* L.) is part of the family Rosaceae and can be found from the plain to mountain areas (1400 m) in Europe, South-West Asia, Caucasus and North Africa. It is a perennial plant that can be found frequently in the lysing of the forests, along the roads, in the cultivated lands and in the limestone regions [4,5]. The blackthorn fruts are representing an important source of nutrients with a high content of sugars, organic acids, polyphenols, anthocyanins, punicunicin, vitamin C, tannins, calcium and magnesium salts.

Blackthorn is used in phytotherapy for the treatment of many respiratory diseases related to various forms of cough; it is a mild laxative, diuretic, spasmolytic and antiinflammatory agent. It has antibacterial (due to the presence of tannins) effect and shows activity against inflammation of the mucosal layer of the digestive system [6].

The hawthorn (*Crataegus monogyna*) is part of the Rosaceae family and cand be found in Central Europe but also in South-West Asia. It has a very wide spreading area, growing from the plain areas, where it forms bushes, to the hillside and the premontone regions.

Scientific evidence has showed that hawthorn fruit possesses powerful antioxidant and free radical scavenging activities, due to the presence of different bioactive compounds, such as epicatechin, hyperoside, and chlorogenic acid. These compounds are reported to have many pharmacological effects, including neuroprotective, hepatoprotective, cardioprotective and nephroprotective activity [7]. Furthermore, hawthorn fruit possesses tonic effects on the heart, as several studies have shown that it could reduce some cardiovascular risk factors, such as hypertension, hypercholesterolaemia, etc. [8]. Its chemical composition is particularly rich, being very complex, containing a series of compounds such as: triterpenic acids, flavonoid derivatives, sterols, glucosides, amigdaline, choline, vitamins, mineral salts, tannins, pectins [9]. Its small dark-red fruit (commonly called haw), which ripens in midautumn, is used for different culinary purposes, such as the preparation of jellies and syrups [10].

Rosehip (*Rosa canina*) is part of *Rosaceae* family, with over 150 species, is one of the most widespread members of the Rosacea family. This genus is widely distributed in Europe, Asia, the Middle East and North America. Petals are white to pale pink, rarely deep pink and fruit ripens late. The most important ingredients of dog rose are natural antioxidants, acids and phenolic compounds such as tannins [11].

Chemical compounds that are found in fruits are phenolic compounds, anthocyanin, flavonols, ascorbic acid, and galactolipid. Fruits are famous for high vitamin C, high antioxidant properties and also high amounts of carotenoid, lycopene, carotene and xanthophyll that are useful for treatment of patients with lung cancer [12,13,14]. Fruits (hips) have long been traditionally used in the prevention and therapy of common cold and other infections, as diuretic agent and for the treatment of various inflammatory diseases [15]. Generally, rose hips are used for the processing industry to obtain different products, such as jam, jelly and marmalade.

2. Materials and Methods

In order to obtain the three types of fruit paste, hawthorn fruits (67% w/w), blackthorn (67% w/w) and rosehip (67% w/w) from spontaneous flora of Romania, Cluj-Napoca region, were used. As a sweetener, comercial sugar (33% w/w) was included in composition.

The fruits were harvested at maturity, sorted, washed, subjected to mechanical machining and then boiled until a paste with a certain viscosity and texture was obtained, in order to remain stable for as long as possible (Figure 1).



Figure 1. Technological flow for obtaining spreads of blackthorn, hawthorn and rosehip fruits at laboratory scale

2.1. Chemicals and reagents

1,1-Diphenyl-2-picrylhydrazyl (DPPH), were purchased from Sigma Chemical Co (St Louis, MO, USA). Folin–Ciocalteu's phenol reagent and sodium carbonate were purchased from Merck Chemical Suppliers (Darmstadt, Germany), gallic acid purchased from Merck Chemical Suppliers. All other chemicals used, including solvents methanol, were of analytical grade. An Shimadzu 1700 UV-VIS spectrophotometer was used for absorbance measurements and spectra recording, using optical or quartz cuvettes with 0.5 cm of optical path.

2.1.1. The total phenolic assay: Total polyphenol content of hawthorn fruits was determined according to the method described by [16, 17]. An aliquot of 25µL sample was transferred into a glass test tube. Then, 1.8 mL of distilled water and 120 µL of Folin-Ciocalteu phenol reagent were added. After 5 min, 340 µL of sodium carbonate aqueous solution (7.5%, w/v) was added to the mixture. After incubation for 90 min at room temperature, in dark, the absorbance was read at 750 nm, using a Shimadzu UV-1700 PharmaSpec spectrophotometer, against the blank, in which the sample was replaced with methanol. Standard curve was performed using different concentration solution of gallic acid and the results were expressed as mg of GAE/100 g sample.

2.1.2. Antioxidant capacity assessment by DPPH method: The antioxidant activity was determined using the 2,2- diphenyl-1-picrylhydrazyl (DPPH) method according to [18, 19]. An amount of 30µl of the methanol extract was transferred into a glass test tube with a screw cap, then 270 µL of distilled water and 11.7 mL of DPPH solution in methanol (0.025 g/l) were added. The incubation of the test sample was carried out in dark, at room temperature for 30 min. The absorbance value was read at 515 nm against methanol with a double-beam UV-VIS spectrophotometer (Shimadzu 1700 UV-VIS). The positive control was prepared using a gallic acid solution (0.5 mg/mL). The negative control was prepared using methanol. Results were expressed as percent over standard DPPH absorbance according to Eq.(1).

$$RSA [\%] = \frac{A_{DPPH} - A_P}{A_{DPPH}} \times 100 \qquad \text{Eq. (1)}$$

where, A_{DPPH} is the absorbance of DPPH free radical in methanol and A_p – sample is the absorbance of DPPH free radical solution mixed with the sample.

2.1.3. Physicochemical analysis of fruit spreads

Ascorbic acid: The amount of ascorbic acid of the blackthorn, hawthorn and rosehip fruits was determined according to the methods of [20].

Titrable acidity: The total acidity was performed by neutralization with sodium hydroxide solution (0.1 N) in the presence of methylene blue as indicator Eq.(2).

Total acidity = m x 0,0067 x 2 x V g % acid malic Eq.(2)

where: m - the weight of the sample , V– volume of NaOH 0.1N used for titration; 0.0067 conversion factor: 1 ml 0.1 N sodium hydroxide corresponds to 0.0067 g malic acid

Ash Determination: The content of mineral substances was assessed by calcination at $550-600^{\circ}$ C Eq.(3).

Ash =
$$=\frac{G_1}{m} \cdot 100$$
 (g % ash) Eq.(3).

where: m - the amount of the sample under analysis [g]; G1 - the amount of ash after calcination [g]; [21].

Moisture Determination: Moisture content was determined by drying in an oven at $103^{\circ}C \pm 2^{\circ}C$ for 3 hours, the experiment being repeated until the weight was constant. The samples were cooled in a desiccator for one hour and weighed [22].

2.1.4. Sensory evaluation of fruit spreads: Sensory characteristics of samples were evaluated by a panel of 25 trained assessors (12 female and 13 male), with a mean age of 22. Fruit spreads samples were presented in a random order in plastic cups. The nine-point hedonic scale test (1 was the worst and 9 was the best) was used to evaluate all fruit spreads samples. Overall acceptability, aspect, smell, consistency, taste, aroma were the sensory attributes evaluated.

3. Results And Discussions

In agreement with previous studies of other fruits geographical, seasonal and ripening status variations

were expected to influence the chemical composition of the fruits as a result of differences in soil composition, sun exposition and climate; this expectation was observed from the results of our study. In general, we can consider that our results were coherent with those reported by other authors.

Moisture is an important parameter for the quality and stability of spreads of blackthorn, hawthornand and rosehip because high moisture content can lead to the alteration and instability of the spreads, hence it has to be at low levels, but suficient enough for showing the desired viscosity. As can be seen, the moisture content of the spreads of blackthorn is 61.10%, hawthorn is 58.20% and rosehip is 61.00% making this product stable, as well as showing the desired rheological properties.

The moisture content of the fruits is in line with that presented by the literature and is presented in Table 1.

Fruits of shrubs can be a good source of minerals. Their sum, determined as the residue after complete combustion of organic matter (ash) in the studied fruits was 2.60 g per 100 g for blackthorn fruits, 1.82 g per 100 g for hawthorn fruits and 2.36 g per 100 g for rosehip fruits.

These amounts are in the range of 0.3 - 2.72 g per 100 g, which is generally given for fruits [23, 24].

After fruit processing, a decrease in minerals content was observed (Table 1). The acidity represents a quality element that is part of spreads of blackthorn, hawthornand and rosehip quality. To keep balance acidity in the body, one must consume 4 times more alkaline foods than acidic. As can be seen in the table 1 the fruits blackthorn, hawthorn and rosehip from spreads of blackthorn, hawthornand and rosehip has a low acid fruits because it is made alkaline healthy human body.

Table 1. The content of moisture, mineral substances content, vitamin C, total acidity, total polyphenols and antioxidant capacity of fruits

·		Moisture %	Mineral substances %	Titrable acidity %	Vitamin C mg/100g	Total polyphenols mg GAE/100g	Antioxidant capacity RSA% DPPH
Fruits	of	33.0±0.15	2.60 ± 0.03	0.194±0.01	63.36±0.21	1210.31±54.21	89.99±0.32
blackthorn							
Fruits	of	27.38±0.12	1.82 ± 0.02	0.140 ± 0.02	49.28±0.29	1109.33±44.21	91.10±0.38
hawthorn							
Fruits	of	44.0±0.25	2.36±0.04	0.470 ± 0.01	35.20±0.19	1800.06 ± 61.45	98.65±0.47
rosehip							

antionaant euplicity of spreads										
	Moisture %	Mineral substances %	Titrable acidity %	Vitamin C mg/100g	Total polyphenols mg GAE/100g	Antioxidant capacity RSA% DPPH				
Spreads o	f 61.10±0.27	0.76 ± 0.07	0.170 ± 0.02	70.40±0.31	990.31±44.89	86.99±0.23				
blackthorn										
Spreads o	f 58.20±0.19	0.82 ± 0.05	0.101 ± 0.04	56.32±0.27	890.33±33.12	90.12±0.34				
hawthorn										
Spreads o	f 61.0±0.29	0.80 ± 0.04	0.198 ± 0.08	45.76±0.22	1200.06±41.23	95.65±0.24				
rosehip										

Table 2. The content of moisture, mineral substances content, vitamin C, total acidity, total polyphenols and antioxidant capacity of spreads

Vitamin C, also is known as ascorbic acid is one of the most important vitamins and essential for human and animal life. Vitamin C was determined at the level of 63.36 mg/100g for blackthorn fruits, 49.28 mg/100g for hawthorn fruits and 35.20 mg/100g for rosehip fruits. The differences that occurred after fruit processing were not significant differences, indicating as a result of fruit processing, the vitamin C content is quite high Table 1.

The Folin-Ciocalteu method measures the reduction of the reagent by phenolic compounds with the formation of a blue complex that can be measured at 750 nm against gallic acid as a standard. The total phenol content in the investigated samples of fruits of blackthorn, hawthorn and rosehip shown in Table 1 also phenol content in the spreads of blackthorn, hawthorn and rosehip shown in Table 2. The experimental results show that the content of total phenols in the investigated extracts was significant, ranging from 1210.31 mg GAE/100g for blackthorn fruits to 990.31mg GAE/100g for spreads of blackthorn, 1109.33 mg GAE/100g for hawthorn fruits to 890.33 mg GAE/100g for spreads of hawthorn and 1800.06mg GAE/100g for rosehip fruits and 1200.06 mg GAE/100g for spreads of rosehip.

The content in phenolic compounds of the fuits decreased after processing, but not so much that this product does not present benefits for the consumer.

The DPPH radical absorbs at 515 nm and this absorption is inhibited in the presence of antioxidants. This reduction in absorbance is related to the antiradical efficiency of the sample, extract or standard. The DPPH antiradical efficiency values of the fruit and spreads extracts analysed in this study are presented in Table 1, 2.

All tested extracts exhibited strong scavenging activity against DPPH radicals, which ranged from 89.99% fruits of blackthorn, 90.12% fruits of

hawthorn and 98.65% fruits of rosehip up to 86.99% spreads of blackthorn, 90.12% spreads of hawthorn and 95.65% spreads of rosehip.The high free radical scavenging capacity of the wild plants might be attributed not only to phenolic composition, but also to the presence of other bioactive compounds, such as vitamins (ascorbic acid, tocopherols) and pigments (anthocyanins), as well as the structural interaction among these compounds [25].

The hedonic scores for sensory attributes (aspect, aroma, taste, consistency, smell, and overall acceptability) of fruit spreads in Figure 2.



Figure 2. Hedonic scores of sensory attributes in fruit spreads

Sensory analysis reveals a very good acceptability in terms of appearance, flavor, consistency and aspect for all three fruit pastes.

4. Conclusion

The physical and chemical analysis of raw materials and finished products showed that the products obtained have a great antioxidant effect and are representing a rich source of antioxidant compounds, that may lead to many beneficial effects on the human body.

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Compliance with Ethics Requirements. Authors declare that they respect the journal's ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human / or animal subjects (if exist) respect the specific regulation and standards.

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