DOI : 10.33274/2079-4827-2024-48-1-5-12
UDC 664.8:543.42

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PERSPECTIVES OF USING THE MOUNTAIN ASH (SORBUS AUCUPARIA) IN THE FOOD PRODUCTION

УДК 664.8:543.42

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ПЕРСПЕКТИВИ ВИКОРИСТАННЯ ГОРОБИНИ ЗВИЧАЙНОЇ (SORBUS AUCUPARIA) У ВИРОБНИЦТВІ ХАРЧОВОЇ ПРОДУКЦІЇ

***Objective** is to study the possibility of using mountain ash as a potential raw material for food production.*

***Methods.** Chemical analysis of the total content of phenolic substances in mountain ash was carried out using a volumetric method, which is based on the principle of oxidation of phenols with potassium permanganate in the presence of indigo carmine. We determined the presence of phenolic substances in the rowan under study by IR spectroscopy, and the presence of polyphenolic structures in the plant's alcoholic extract – by UV spectroscopy. The study of the antioxidant effect of fruits was carried out using an accelerated method using a standard technique based on measuring the peroxide value – a conventional unit, the equivalent amount of iodine released from a sample with potassium iodide, from a given unit of mass of oil by peroxide compounds formed in it during oxidation with atmospheric oxygen. A more informative indicator of antioxidant activity is the peroxide value per unit time increase during the oxidation process (δ PV), equal to the difference in peroxide numbers of oxidized and non-oxidized oil samples.*

***Results.** A chemical analysis of the total content of phenolic substances in rowan fruits showed the content of phenolic substances in the substrate to be 1950 mg/100 g, which places these fruits in one of the first places in terms of the content of P-vitamin substances. They are second only to chokeberry, in which P-vitamin compounds sometimes reach 5000 mg/100 g. The presence of phenolic substances in the studied plant is confirmed by IR spectroscopy. UV spectra of a diluted alcoholic extract of the plant also confirm the presence of polyphenolic structures in them. Due to the complex structure of the various compounds they contain, they contain many characteristic bands.*

It has been experimentally established that rowan fruits (red-fruited) have a relatively powerful complex of polyphenolic substances, giving them high antioxidant properties. This fact makes the plant a promising raw material that can be used as an additive to fats and oils and various fat-containing products to preserve their quality and nutritional value for long periods.

Keywords: *mountain ash*, phenolic substances, antioxidants, extract, vegetable oil, spectra.

Formulation of the problem. Natural food products of plant origin that we consume daily are one of the elements of a healthy diet. Plants and plant products reliably occupy an important place in a properly balanced human diet. Plants used in nutrition contain a diverse set of vitamins, easily digestible carbohydrates, proteins, enzymes, amino acids, fats, minerals, aromatics and other valuable components that play an important role in metabolic processes in the body. They increase the ability to absorb protein and carbohydrates and help normalize the functioning of the digestive organs. Aromatic substances significantly improve the taste of food, increase appetite, and have a beneficial effect on digestive processes [1].

Eating plant foods in sufficient quantities helps normalize metabolism, prevent weight gain, and plays a vital role in preventing and treating cardiovascular diseases, salt metabolism disorders, etc. Humans have consumed many fruits and vegetables as food products from the deep past. In addition to food, they contain substances that have not been fully studied but have therapeutic and preventive value. Many so-called diseases of civilization are associated with a lack of plant products in modern man's diet [2].

Enriching the diet with fresh fruits and vegetables significantly prevents the insufficient supply of the body's various biogenic compounds. Still, their seasonal consumption only allows some of them to be used throughout the year.

A unique role in solving the problem of uniform provision of vegetables and fruits to the population belongs to the processing industries. Still, the technological means used in industry are distinguished by relatively strict processing parameters, which lead to the destruction of the share of vitamins, organic acids and other substances [3]. In addition, some of the most valuable fruits in terms of their chemical composition are practically not used in this area. Special attention is paid to non-traditional plants, which have long been used almost exclusively as medicines, and there is absolutely no experience in consuming them as complete raw materials rich in various nutritional and biologically active substances.

Analysis of the latest research and publications. Now, the processes taking place in Ukraine's national economy make the problem of providing the country's population with food products of high quality and nutritional and biological value very important. The solution to this problem closely depends on expanding the raw materials market and using new types of raw materials, mainly local and, most often, non-traditional. At the same time, it is possible to produce new types of products with increased nutritional and biological value, enriched with vitamins, minerals, protein, dietary fibre, antioxidants, and other valuable nutritional components. Many of these components perform therapeutic and prophylactic functions — they remove heavy metals and radionuclides from the body and increase its resistance under conditions of high anthropogenic load [3 – 7].

As a source of non-traditional raw materials, special attention is drawn to a widespread plant throughout Ukraine – the common or red-fruited rowan. This is a 15 m tall tree of the rose family. The berries are juicy and orange-red, with a diameter of up to 10 mm. They reach full ripeness in September.

In the food industry, this plant is almost never used as a raw material, although in medical practice, it is common to use it as a raw material for multivitamin tea to treat vitamin deficiencies, especially vitamin deficiency C. Multivitamin tea consisting of rowan and rose hips in a ratio of 1:1 [8] is often used.

Red rowan is a favourite medicinal plant in folk medicine. Its fruits are used as diuretics, hemostatics, and laxatives. Rowan, as a medicinal product, was widely used in official and folk medicine in Western countries. In Poland, rowan berries were used as medicine for diseases of the kidneys, urinary and gallbladder, and diabetes. In Hungary, they were used for dysentery, and in Norway, they were used as a means of helping wound healing [9].

The objective is to study the possibility of using mountain ash as a raw material for food production.

Presentation of the primary research material. The chemical composition of this plant has been studied in sufficient detail, albeit according to the traditional scheme – the vitamin composition of the berries, the content of minerals and essential nutrients in them have been found. The content of the main substances in mountain ash is given in Table 1.

Table 1 – Elemental chemical composition and energy value of rowan berries

№	The name of the indicators	Mass fraction, %
1	Water	81,0
2	Proteins	1,4
3	Carbohydrates, total	12,5
4	Mono- and disaccharides	8,5
5	Fiber	3,2
6	Organic acids	2,2
7	Ash	0,8
8	Energy value, kcal / 100 g	58,0
9	Energy value, kJ / 100 g	253,0

Rowan berries have long been used as a multivitamin, so the vitamin composition of the raw materials, shown in Table 2, has been studied in sufficient detail.

Table 1 – Vitamin composition of rowan berries (mg / 100 g)

Carotenoids	Vitamin B_1	Vitamin B_2	Vitamin C	Niacin
9,00	0,05	0,02	50-140	0,5

As seen from Table 2, the primary attention is drawn to the amount of vitamin C and carotenoids in berries, which exceeds the content of these biologically active substances in many vegetables and fruits. Regarding vitamin C content, the plant successfully competes with currants, tomatoes, and apples, and in terms of carotenoid content – with carrots and the best varieties of pumpkin [3]. However, there is no information in the literature about the presence of certain substances in mountain ash, which are now attracting special attention for their biological activity, thanks to which the raw material can be considered very valuable in manufacturing functional food products.

Plant organisms contain many substances that make up the physiological antioxidant system. Among them, phenolic compounds are primarily critical, including cyclic alcohols with an aromatic ring with one or more hydroxyl groups. If the benzene ring contains more than one hydroxy group, such compounds classify as polyphenols. Several thousand phenols are known and isolated from plant materials, and the largest group among them are flavonoids, molecules of which a chain of three carbon atoms interconnects benzene rings. Depending on the structure of this bridge and the degree of its oxidation, 10 groups of flavonoids can be counted, five of which are colourless substances with reducing properties (catechins, dihydrochalcones, flavonols, etc.). They are easily susceptible to oxidation, during which they acquire different colors. Thus, depending on the degree of oxidation, catechins in tea leaves acquire black, yellow or green color. The last five groups of natural flavonoids are the colored compounds that give color to leaves, flowers and fruits. The most important property of many phenolic compounds is their ability to reverse oxidation, that is, to transform from hydroxy to oxy form. Thanks to this transition, almost all phenolic compounds have pronounced antioxidant activity [10].

Using a volumetric method, We conducted a chemical analysis of the total content of phenolic substances in rowan fruits. This method is based on the principle of oxidation of phenols with potassium permanganate in the presence of indigo carmine. The analysis showed the content of phenolic substances in the substrate to be 1950 mg/100 g, which puts these fruits in one of the first places regarding the content of bioflavonoids. They are second only to chokeberry, in which bioflavonoids sometimes reach 5000 mg / 100 g.

The presence of phenolic substances in the fruits of the plant under study is also confirmed by IR spectroscopy; in the IR spectrum of dried and crushed berries, a characteristic intense diffuse absorption band with a maximum at 34885 $см^{-1}$ is observed, corresponding to stretching vibrations of one or more hydroxyl groups. Of course, the free hydroxyl group absorbs in the region of 3630 $см^{-1}$. Still, these groups very quickly form hydrogen bonds, significantly changing the spectrum's nature. Suppose the hydroxyl group participates in the formation of a hydrogen bond. In that case, the frequency of its stretching vibrations sometimes decreases by almost 170 $см^{-1}$, and the absorption band spreads considerably and becomes more intense. We observe the same thing — intermolecular hydrogen bonds predominate in the recorded IR spectrum, giving the spectrum this appearance. Along with the absorption band attributed to the hydroxyl group bound by hydrogen bonds, at 2852 and 2951 $см^{-1}$, two clear, unsmeared bands with slightly lower intensity are observed, which can be attributed to the stretching vibrations of CH groups associated with both the aromatic nuclei of polyphenolic compounds, in particular flavonoids, and with aliphatic fragments of their molecules — bands with a lower frequency relate to CH bonds of aromatic rings, and with a higher frequency — to CH fragments of aliphatic sections of the molecule. At around 1712 $см^{-1}$, the spectrum contains a clear band with a high frequency, which fully corresponds to the stretching vibrations of the flavone ring's carbonyl groups (C=O). Strength with them, a slight separation of double molecules can be observed with a maximum value at 1588 $см^{-1}$.

UV spectra of a diluted alcoholic extract of berries also confirm the presence of polyphenolic structures in them. They contain many characteristic bands due to the complex structure of the various compounds they contain. The spectra are characterized by a group of characteristic bands in the 180...700 nm wavelength range. The first absorption band with a maximum of 213 nm has high intensity. It corresponds to the excitation of lone electron pairs of the oxygen atom of the carbonyl group, which is not associated with the aromatic nucleus ($n \rightarrow \sigma^*$ transition) and, most likely, is not related to compounds of a phenolic nature. It also includes a weak, diffuse band in the region of 230 nm, which corresponds to the $n \rightarrow \pi^*$ transition of carbonyl oxygen electrons. A reasonably intense absorption band in the region of 274 nm and a slightly less intense one at 325 nm can be explained by the excitation of the same electron pairs of the oxygen atom of the carbonyl group but connected by a powerful chromophore to the aromatic ring, which is typical for flavonoid molecules. But in addition to absorption, which confirms the presence of a reasonably large amount of bioflavonoids in the fruits, two more intense bands with maxima at 454 and 479 nm are observed in the UV spectrum, related to electron $\pi \rightarrow \pi^*$ transitions of the carotenoid chromophore, consisting of a long chain of single and double bonds which are alternating and causing the bright colour of the compounds. It is not surprising because, as literature data indicate, the content of carotenoids in fruits is relatively high..

Polyphenolic substances of plant products mix in their structures into several hydroxyl groups with a mobile water atom. It can be done with the help of powerful antioxidants, such as the antioxidant reaction caused by the manifestation in their compositions of a mobile water atom or functional, active groups that actively react with a molecular organism. The primary function of oxidation inhibitors is the detection of radical molecules, adding a new carbohydrate radical in molecules according to the following scheme:

$$RH + O_2 \rightarrow R\cdot + \cdot OOH$$

This radical saturates with the hydrogen atom of the antioxidant by the following reaction:

$$R\cdot + AH \rightarrow RH + \cdot A$$

Consequently, antioxidants sharply reduce the possibility of forming free peroxide radicals:

$$R\cdot + O_2 \rightarrow ROO\cdot$$

As we see from these diagrams, antioxidants have an inhibitory effect due to sufficiently mobile active hydrogen. If hydrogen is not adequately reactive, the reaction occurs according to the scheme:

$$AH + O_2 \rightarrow A\cdot + \cdot OOH$$

and proceeds more quickly than the reaction according to this scheme:

$$RH + O_2 \rightarrow R\cdot + \cdot OOH$$

The easier free hydrocarbon radicals form, the less active they are. Therefore, the free hydrocarbon radical A·, formed from the antioxidant, should not react with molecular oxygen to form peroxide radicals. In this regard, the oxidation of the RH substrate does not occur, and the concentration of A· radicals constantly increases until their frequent collisions and recombination become possible.

The above interpretation schemes made it possible to search for antioxidant substances among products of natural origin purposefully. These compounds include polyphenolic structures with more than one hydroxyl group in the aromatic ring. Their most important property is the ability to reverse oxidation to quinone (3). Quinones are oxidized forms of many phenols that arise when phenol donates (1) two electrons and two hydrogen nuclei (protons). Oxidation to quinone occurs in steps by losing two electrons one after the other (Fig. 1).

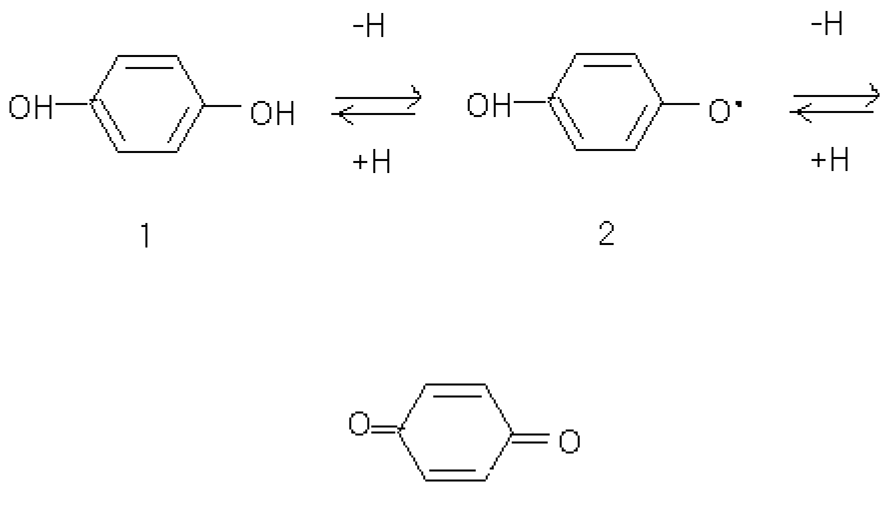

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Figure 1 – Ability of phenolic compounds to reverse oxidation to quinone
(1 – phenol, 2 – semiquinone radical, 3 – quinone)

In this case, an unstable intermediate compound forms – semiquinone radical (2). After the donation of the second electron and proton (the second hydrogen atom), the system of double bonds in the benzene ring rearranges, and carbonyl groups appear in place of hydroxyl groups. Such quinones, unlike reduced phenols, very easily attach hydrogen atoms and, if present, are converted back into the corresponding phenols through the intermediate semiquinone form.

The above diagrams show that the phenolic inhibitor molecule, which neutralizes and inactivates the free radical involved in the oxidative reaction, turns into an inhibitor radical – semiquinone. However, when, in contrast to one radical, another arises, the essence of the matter should not change. It is possible to observe natural antioxidant effect only when the newly formed inhibitor radical has low energy, is relatively unstable and does not continue the chain of oxidative processes. It is precisely what the semiquinone radicals of phenolic inhibitors are. These are relatively long-lived and low-active radicals. The formation of each of them when using phenolic inhibitors means the termination of one of the free radical oxidation chains and a general slowdown of the oxidation process. When a phenolic inhibitor is present from the beginning in a substrate that requires protection from oxidation, achieving the desired effect with just 0.01...0.02% additive becomes possible.

Since both flavonoids and tannins, as well as other representatives of phenolic compounds, have all the properties for identifying antioxidant activity, we decided to quantify their antioxidant effect in the studied raw materials. The study of the antioxidant effect of fruits was carried out by an accelerated method using a standard technique based on measuring the value of the peroxide number – a conventional unit equivalent to the amount of iodine that is released from a sample with potassium iodide from a given unit of mass of oil by the peroxide compounds that form in it. A more informative indicator of antioxidant activity is the increase in peroxide number per unit of time during the oxidation process (δ PV), equal to the difference in peroxide numbers of oxidized and non-oxidized oil samples.

To screen the new antioxidants, we added concentrations of 0.05. 0.1% of the additive to the reaction mixture. Concentrations less than 0.05% do not exhibit antioxidant activity, while concentrations exceeding 0.1% cause a pro-oxidant effect [4].

Therefore, taking into account the research methods for new antioxidant agents, studies were carried out on fruits in the process of oxidation of sunflower oil using a concentration in the form of powder (finely crushed dry berries) of 0.05. 0.1%. Data on the study of the antioxidant activity of rowan fruits are given in Table 3.

Table 3 – Influence of rowan berries on the oxidation process of sunflower oil (oxidation time - 5 hours, oxidation temperature – 150 °C, PV of unoxidized oil – 0.069)

№	Additive concentration, %	Peroxide value (PV), mmol ½ O / kg	Peroxide value (PV), mmol ½ O / kg	Coefficient of antioxidant effect, D, %
1	-	0,335	0,053	-
2	0,1	0,091	0,004	92,4
3	0,05	0,078	0,002	96,2

As evidenced by the experimental data in Table 3, rowan berries have a powerful complex of polyphenolic substances that give them high antioxidant properties.

Conclusions. We experimentally established that mountain ash berries have a fairly powerful complex of polyphenolic substances, which give them high antioxidant properties. This makes the plant a promising raw material that can be used as an additive to fats and oils and various fat-containing products to preserve their quality and nutritional value for long periods.

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Мета *– дослідження можливості використання горобини звичайної в якості потенційної сировини для виробництва харчової продукції.*

Методи. *Хімічний аналіз на загальний вміст фенольних речовин у плодах горобини проведений об'ємним методом, в основі якого лежить принцип окислення фенолів перманганатом калію в присутності індигокарміну. Наявність речовин фенольного характеру у складі плодів дослідженої рослини проводилося методом ІЧ-спектроскопії. Наявність структур поліфенольної природи в спиртовому екстракті плодів проводилося методом УФ-спектроскопії. Вивчення антиоксидантної дії плодів проводили прискореним методом з використанням стандартної методики, заснованої на вимірюванні значення перекисного числа – умовної одиниці, еквівалентної кількості йоду, який вивільнюється з проби з йодидом калію, з обумовленої одиниці маси олії перекисними сполуками, які утворюються в ній при окисленні киснем повітря. Більш інформативним показником активності антиоксиданту є така величина як прирощення перекисного числа в одиницю часу в процесі окислення (δ ПЧ), яке дорівнює різниці перекисних чисел окисленого та неокисленого зразків олії.*

Результати. *Проведений хімічний аналіз на загальний вміст фенольних речовин у плодах горобини показав вміст фенольних речовин у субстраті 1950 мг / 100 г, що виводить ці плоди на одне з перших місць за вмістом Р-вітамінних речовин. Вони поступаються лише горобині чорноплідній, у якій кількість Р-вітамінних сполук іноді досягає 5000 мг / 100 г. Наявність речовин фенольного характеру у складі плодів дослідженої рослини підтверджується методом ІЧ-спектроскопії. УФ-спектри розведеного спиртового екстракту плодів також підтверджують наявність в них структур поліфенольної природи. Вони вміщують багато характеристичних смуг завдяки складній структурі різноманітних сполук, що входять до їх складу. Експериментально встановлено, що плоди горобини звичайної (червоноплідної) мають достатньо потужний комплекс поліфенольних речовин, які надають їм високих антиокислювальних властивостей. Це робить рослину перспективною сировиною, яку можливо використовувати в якості добавок до жирів та олій, а також різних жировміщуючих продуктів з метою збереження їх якості та харчової цінності протягом довгих строків.*

Ключові слова: горобина звичайна, фенольні речовини, антиоксиданти, екстракт, олія, спектри.