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ASSESSMENT OF THE CONTENT OF POLYPHENOL AND THE ANTIOXIDATING POTENTIAL IN DRIED FRUITS POPULATED ON THE MARKET

Summary

Dried fruits are available to consumers all year round. Their regular consumption may contribute to the improvement of health and reduce the development of many diet-related diseases. The aim of the study was to determine the content of total polyphenols, the ability to scavenge the DPPH radical, ABTS cation radical and the ability to chelate iron (II) ions in selected dried fruits available and consumed in Poland. It was found that dried fruit shows the ability to inactivate the DPPH radical and the ABTS cation, and also have chelating properties. It was shown that the content of polyphenols in the tested dried fruits was varied, however, the highest content of phenolic compounds and anti-radical activity were characteristic of dried strawberries. The obtained results indicate that, thanks to the anti-free radical properties, the consumption of dried fruit may play an important role in the nutrition of health-conscious people.
***Key words**: dried fruits, polyphenols, antioxidant properties*

OCENA ZAWARTOŚCI POLIFENOLI ORAZ POTENCJAŁU PRZECIWUTLENIAJĄCEGO W POPULARNYCH NA RYNKU OWOCACH SUSZONYCH

Streszczenie

Owoce suszone są dostępne dla konsumentów przez cały rok. Ich regularne spożywanie może wpłynąć na poprawę zdrowia człowieka oraz na ograniczenie rozwoju wielu chorób dietozależnych. Celem pracy było oznaczenie zawartości polifenoli ogółem, zdolności do zmiatania rodnika DPPH, kationorodnika ABTS oraz zdolności do chelatowania jonów żelaza (II) w wybranych suszonych owocach dostępnych i spożywanych w Polsce. Stwierdzono, że suszone owoce wykazują zdolność do dezaktywacji rodnika DPPH oraz kationorodnika ABTS, a także mają właściwości chelatujące. Wykazano, że zawartość polifenoli w badanych owocach suszonych była na zróżnicowanym poziomie, jednak najwyższą zawartością związków fenolowych i aktywnością antyrodnikową charakteryzowały się suszone truskawki. Uzyskane wyniki wskazują, że dzięki właściwościom antyrodnikowym spożywanie suszonych owoców może odgrywać istotną rolę w żywieniu osób dbających o zdrowie.
***Słowa kluczowe:** owoce suszone, polifenole, właściwości antyoksydacyjne*

1. Introduction

Fresh fruits are characterized by seasonal availability, and when kept fresh, it causes a rapid deterioration in quality and promotes spoilage. Drying is a good way to preserve fruit. Dried fruit is a source of fiber, vitamins and minerals [1]. They are characterized by a high content of potassium, iron, magnesium, calcium and phosphorus [1]. They contain fractions of soluble and insoluble fiber with functional properties [2]. The fractions of insoluble fiber affect the intestinal peristalsis, thus effectively preventing diseases of the digestive system, while soluble fiber contributes to the reduction of blood cholesterol levels [3]. Many studies show the benefits of consuming dried fruit. Dried plums are said to have mild laxative properties, and dried apricots and peaches have similar properties [4]. In most dried fruits, the carbohydrate content is from 50 to 70%, therefore they can be an excellent source of a quick and high-energy snack for people who lead an active lifestyle and practice sports, especially endurance sports. Frequent consumption of dried fruit may have a positive effect on the maintenance of the acid-base balance of the body, which is the result of the appropriate proportions of the content of minerals and low protein content [5]. Dried fruits also contain polyphenolic compounds, among them the two main groups are flavonoids, phenolic acids and other phenolic compounds, eg. tannins [6].

Flavonoids (bioflavonoids) constitute the largest group of polyphenols, which can be divided into: flavones, flavanones, flavanols, phlaownols, isoflavones, anthocyanins and proanthocyanins. Phenolic acids include: gallic, salicylic, hydroxybenzoic, chlorogenic and vanillic acids. Other phenolic compounds include natural plant tannins, i.e. tannins. Polyphenols contain at least two hydroxyl groups attached to an aromatic ring. The number and location of these groups determine the strength of their antioxidant activity. The greater the number of hydroxyl groups in the molecule, the stronger the antioxidant properties [6]. Studies show a relationship between the incidence of ischemic heart disease and the consumption of food containing polyphenols [6]. Flavonoids inhibit the effects of phosphodiesterase and cytoxygenase, and are more effective than aspirin in reducing platelet aggregation, which is why they are recommended in the prevention of atherosclerosis

[7]. Polyphenols are also credited with preventing the formation of gastric or duodenal ulcers, which are a consequence of taking medications, alcohol, and a stressful lifestyle [8]. It is recommended to systematically consume fruit and vegetables that are a source of polyphenols. It has been shown that polyphenols can act as reducing substances, as compounds blocking free radicals, forming complexes with metals catalyzing oxidation reactions, preventing reactions caused by a single active oxygen atom, inhibiting the activity of oxidizing enzymes [9]. The quality and quantity of phenolic compounds varies depending on the type of fruit. The content and antioxidant activity also depend on the degree of ripeness and storage after harvest, and the pretreatment and proper processing of the fruit also have a decisive influence. Literature data indicate that drying processes may reduce the content of polyphenols in raw materials [10]. There are reports that fruit drying, during which hydrolysis of polyphenols in glycosidic bonds with other components may take place, increases the antioxidant activity [11]. As a result, the total antioxidant potential of the fruit depends not only on the total content of individual groups of compounds, but also on their relative proportions (Table 1) [12].

Table 1. Occurrence of polyphenolic compounds in fruits [13]
Tab. 1. Występowanie związków polifenolowych w owocach [13]

Ingredient	Raw material
flavonols quercetin kempferol	dark grapes, apples, elderberry, wild rose, cherries, black currant, strawberry, cranberry, chokeberry, blueberry, raspberry
flavonols luteolin apigenin	apples, cherries, grapes, lemons
flavanones hesperidin naringenin	oranges, grapefruits
flavanols catechin epicatechin epigallocatechin proanthocyanidins	apples, peaches, red grapes
anthocyanins cyanidin dolphinidine	aronia, blackcurrant, strawberry, grapes, cherries, elderberry, bilberry, blackberries, raspberry, wild strawberry, pomegranate fruit, cranberry
phenolic acids coffee acid chlorogenic acid ellagic acid	white grapes, apples, cherries, peaches, pears, bilberry, strawberry, grapes, apples, blackberries, cranberries, chokeberry, black currant, raspberry, pomegranate

Scientific research confirms the high activity of fruits containing anthocyanins. Chokeberry and blueberry fruits are characterized by significant antioxidant activity and concentration of active substances. Apples, cherries, strawberries, blackberries, elderberries and rosehips contain a large amount of flavone monomers and oligomers (19-30% of polyphenols) [14, 15]. Chokeberry fruits, among the anthocyanins, contain cyanidin-3-galactose with the highest antioxidant activity among all known anthocyanins, while strawberries contain pelagronidin-3-glucoside [16]. Cranberry fruits are characterized by a significant content of peonidin-3-galactoside. Strawberries contain ellagic acid, constituting 35-40% of the total content of polyphenols, and cranberries, blueberries and lingonberries contain significant amounts of quercetin. In grapes, especially red ones, the presence of 10 phenolic acids in free and bound form, 16 anthocyanin glucosides, 12 flavonoids (derivatives of quercetin and kaempferol), 5 flavanols monomers, including three with special antioxidant activity: galactocatechin, epigalactocatechin and epigalactocatechin gallate, six dimers and two trimers of proanyocyanidins and tannins with a higher degree of polymerization [17]. Numerous studies show that berries and stone fruits, in terms of antioxidant activity, have a higher antioxidant potential compared to citrus fruits, and vitamin C, and to a lesser extent carotenoids, are responsible for antioxidant properties [18]. Grape, blackberry, raspberry, strawberry, cherry and blueberry extracts show the ability to inhibit the oxidation of LDL cholesterol, liposomes, free radical binding and inhibit the formation of NO radicals [14, 15]. Therefore, the aim of the study was to assess the total phenolic compounds content and antioxidant activity in popular dried fruit available and consumed in Poland.

2. Material

In the study the following dried fruits were tested: bananas, grapes (raisins), apples, pineapple, apricots, figs, strawberries, cranberries, white mulberry, mangoes, dates, California plums. Fresh raw materials were purchased in a retail network, they were cleaned and seeds and seed cores were hollowed out. Sliced or whole small fruits were convection dried. The drying took place at the temperature of 65°C for 240 minutes. Before drying, the fruits were not sulfurized. Dried raisins, plums and figs were purchased from a distributor.

3. Research methods

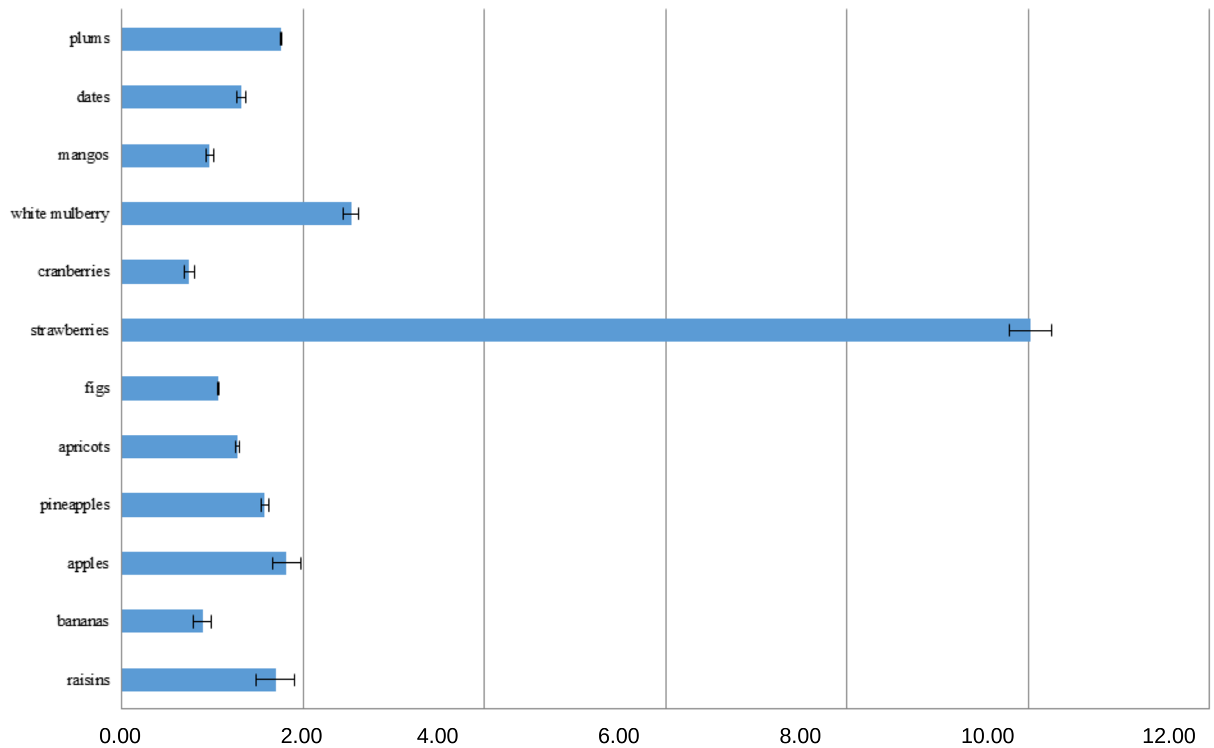
The fruit was ground in a Grindomix GM 200 from Retsch (Haan, Germany) for 15 seconds at a speed of 500 rpm and a temperature of 21°C. The fruit was subjected to water extraction. The three-fold extraction method was used to obtain the extract, the process was carried out under the following conditions: a quantity of 50 g of dried material was poured over 1000 ml of water (400, 300 and 300 ml consecutively) at a temperature of 80°C and extracted for 15 minutes each time. The extraction was repeated three times, each time the extract was centrifuged (2697 x g, 15 min) and decanted (Whatman 1:11 μm) each fraction, and the resulting supernatants were pooled and analyzed. The total phenolic compounds content was determined using the Folin-Ciocalteu reagent [19]. The principle of the method was based on the spectrophotometric (Metertek SP-830, Taiwan) measurement of the absorbance of a colored complex formed as a result of the reaction of phenolic groups in a given extract with a reagent - the Folin-Ciocalteau reagent, at a wavelength of 765 nm. The results are presented as the concentration equivalent of mg gallic acid / 1 g dry weight of the extract. The method with the DPPH • radical (1,1-diphenyl-2-pyrrylhydrazyl) was used to determine the antioxidant properties of the extracts. [20]. The principle of the method was based on the spectrophotometric (Metertek SP-830, Taiwan) measurement of the color of the reaction mixture, in which, depending on the antioxidant capacity of the tested extract, free azo radicals generated by the methanolic DPPH solution were swept away. Measurement of absorbance at a wavelength of 517 nm was made after incubation for 30 minutes at room temperature and protected from light. The ability to deactivate the radical ABTS • + was also determined during the research. The antiradical activity was expressed in µM of Trolox per 1 g of dry matter of the extract [21]. Aqueous solutions of ABTS (7 mM) and potassium persulfate (140 mM) were prepared and mixed to a final concentration of 2.45 mM potassium persulfate. The mixture was left in the dark at room temperature for 12-16 hours. On the day of analysis, the solution of the radical ABTS • + was diluted with ethanol until the absorbance was 0.70 ± 0.02 at 734 nm. All measurements were performed as follows: 100 µl of the extract was supplemented with 2.0 ml of the radical ABTS • + solution, the absorbance values were recorded after 6 minutes versus the corresponding reagent blank. The results of triplicate analyzes, derived from the calibration curve for this standard (100–1000 µM), were expressed in µM Trolox / g d.m. extract. The principle of the chelating activity assessment method was based on the formation of an antioxidant complex with iron (Fe2 +) through the attachment of an antioxidant molecule containing a free pair of electrons to a metal ion by a coordination bond [22]. The color change of the reaction system was recorded spectrophotometrically at a wavelength of 562 nm, and the chelating activity was calculated from the formula, taking into account the absorbance value using the determined iron chelating ability (ChA), specific sample absorbance (E_p), blank absorbance (E_0) and control absorbance (E_k).

4. Results and discussion

The antioxidant activity of raw materials depends on the presence of active ingredients, which include, among others polyphenolic compounds often showing a stronger effect than antioxidant vitamins. The mechanism of action of polyphenols is varied and concerns the chelating and reducing properties as well as the ability to break free radical reactions by creating stable and little reactive radicals. The tested dried fruits were compared in terms of the content of polyphenolic compounds and anti-radical activity. The obtained results allowed to rank the assessed dried fruit according to the total polyphenol content in the following order: strawberries > white mulberry > apples > plums > raisins > pineapple > dates > apricots > figs > mango > bananas > cranberries. In dried fruits extracts, the total polyphenol content ranged from 0.74 to 10.02 mg/g of the product (Fig. 1).

Among the tested dried fruits, strawberries had the highest content of polyphenols, of the order of 10.02 mg/g of product, and the lowest content of cranberries - 0.74 mg/g of product.

The result of determining the ability to deactivate stable DPPH • radicals was a discoloration of the dark purple solution and a decrease in absorbance, which was measured at a wavelength of 517 nm. The results are presented in µM Trolox/g of product (Fig. 2). The obtained results allowed to rank dried fruits according to their anti-free radical activity in the following order: strawberries > apples > white mulberry > plums > cranberries > apricots > mangoes > dates > pineapple > raisins > figs > bananas.

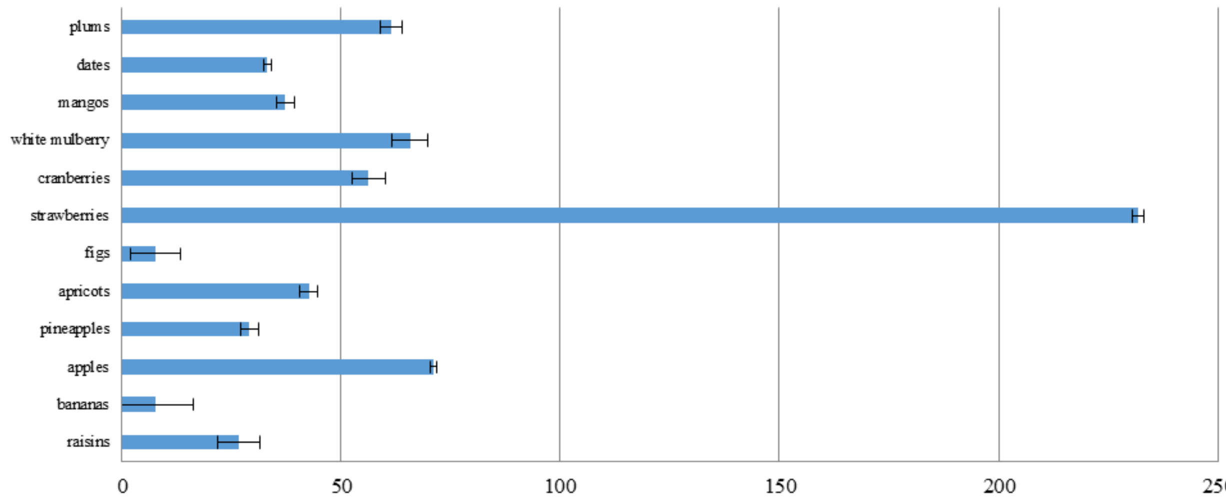


	raisins	bananas	apples	pineapples	apricots	figs	strawberries	cranberries	white mulberry	mangos	dates	plums
Serie 1	1.69	0.8	1.82	1.58	1.27	1.07	10.02	0.74	2.53	0.97	1.32	1.76

mg/g product

Source: own work / Źródło: opracowanie własne

Fig. 1. Total polyphenol content in different dried fruits
Rys. 1. Zawartość polifenoli ogółem w wybranych owocach suszonych



	raisins	bananas	apples	pineapples	apricots	figs	strawberries	cranberries	white mulberry	mangos	dates	plums
Serie 1	26.66	7.52	71.16	29.06	42.60	7.64	231.93	56.28	65.74	37.25	33.12	61.43

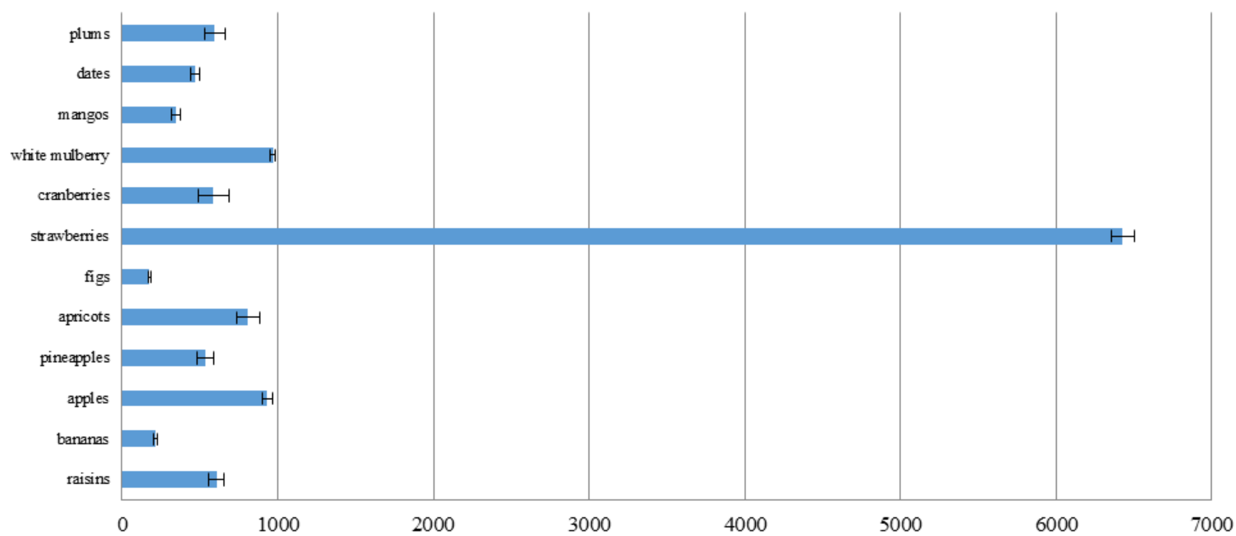
µM Trolox/g product

Source: own work / Źródło: opracowanie własne

Fig. 2. The ability to scavenge free radicals DPPH•
Rys. 2. Zdolność zmiatania wolnych rodników DPPH•

The anti-free radical activity of the tested dried fruit extracts against DPPH • ranged from 7.52 to 231.93 µM Trolox/g of product. The highest antioxidant activity was found for strawberries, 231.93 µM Trolox/g of product, and the lowest for bananas, 7.52 µM Trolox/g of product.

Many methods are used in the research on the assessment of the antioxidant potential. The method with the radical ABTS • + is often used to assess the activity of a mixture of compounds, eg. extracts. The antioxidants present in the analyzed sample reduce the radical cation to a degree depending on the duration of the reaction, the concentration of the antioxidant and its activity. The color of the solution disappears, the color intensity decrease is proportional to the antioxidant content in the solution. Taking into account the strict influence of polyphenols, including flavonols, on the antioxidant activity, the ability to bind ABTS • + free radicals by dried fruit extracts was measured. The antioxidant properties assessed in this method are presented in µM Trolox/g of product (Fig. 3). The obtained results allowed to rank the dried fruits according to their anti-radical activity in the following order: strawberries > white mulberry > apples > apricots > raisins > plums > cranberries > pineapple > dates > mangoes > bananas > figs.



	raisins	bananas	apples	pineapples	apricots	figs	strawberries	cranberries	white mulberry	mangos	dates	plums
Serie 1	606.45	215.32	934.23	536.77	810.72	175.74	6428.92	588.99	969.07	343.58	468.68	595.36

µM Trolox/g product

Source: own work / Źródło: opracowanie własne

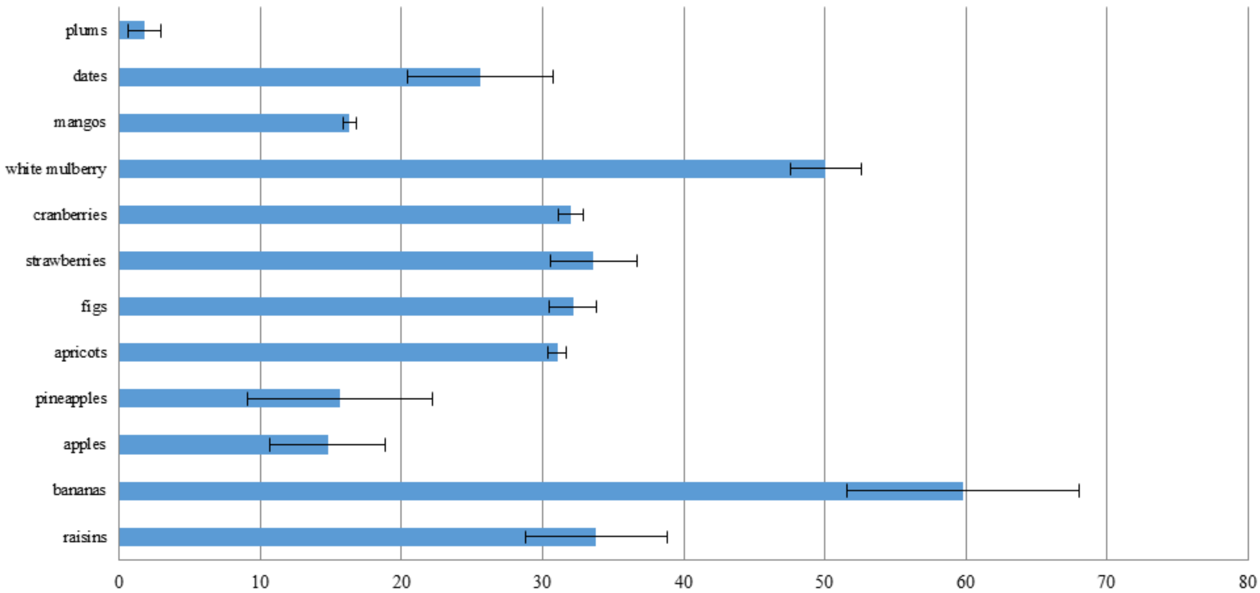
Fig. 3. The ability to deactivate ABTS•+ radicals
Rys. 3. Zdolność dezaktywacji rodników ABTS•+

The anti-free radical activity of the tested dried fruit extracts against ABTS • + ranged from 175.74 to 6428.92 μM Trolox/g of product. The highest antioxidant activity, expressed as the scavenging level of the radical ABTS • +, was recorded for strawberries, 6428.92 μM Trolox/g of product, and the lowest for fig fruit 175, 74 μM Trolox/g of product.

Transition metal ions such as copper and iron play a key role in the oxidation of fat in food as they catalyze the breakdown of lipid hydroperoxides. As a result of the reduction of hydrogen peroxide, the most reactive hydroxyl radicals are generated. Binding of ions in stable complexes called chelates significantly influences the course of lipid oxidative processes, limiting adverse changes, which is an antioxidant effect. The chelating activity is an important test in assessing the antioxidant activity of foods. It was found in the study that all tested extracts showed chelating activity dependent on the tested raw material (Fig. 4). The obtained results allowed to rank dried fruit according to the ability to chelate iron ions in the following order: bananas > white mulberry > raisins > strawberries > cranberries > figs > apricots > dates > mango > pineapple > apple > plums.

The ability to chelate iron (II) ions in the tested dried fruit extracts ranged from 1.78% to 50.06%. The highest chelating activity was recorded for dried bananas (59.79%) and the lowest for plums (1.78%).

The conducted research has shown that strawberries are the product with the highest total phenolic compounds content and the highest anti-free radical activity. Many publications confirm that berries are a particularly rich source of antioxidants due to the high content of phenolic compounds and vitamin C [23]. The obtained results are analogous to those observed by Szajdek et al., where strawberries were characterized by both a higher total polyphenol content and a higher ability to bind the DPPH radical than cranberries [14]. Processing and processing of fruit can significantly affect the content of antioxidants due to their sensitivity to light, high temperature and oxygen, on the other hand, processing often promotes bioavailability and digestibility, allowing more antioxidants to be delivered to the body [24]. Drying allows for a significant extension of the shelf-life and protection of the product, mainly by reducing the water activity [25]. However, drying parameters can significantly affect the quality and content of nutrients and antioxidants in the finished product. The study showed that the content of polyphenols in dried fruit was at a different level. The availability of dried fruit throughout the year suggests that they should be included in the daily diet. Samotich et al. compared the impact of 5 different drying methods, i.e. freeze drying, vacuum drying, vacuum, convection drying, microwave and combined method, on the quality of chokeberry fruit [26]. The highest quality was characterized by freeze-dried fruit, but all samples retained a significant amount of antioxidants in relation to fresh fruit [26]. Similar observations were made by Wojdyło et al., who investigated the influence of various drying methods on the quality of strawberries [27]. The studies showed a significant decrease in antioxidant activity under the influence of drying, however, it was observed that modern vacuum-microwave methods can minimize these losses, similarly to freeze drying [27]. There are also reports showing that drying can positively affect antioxidant activity. Piga et al. showed that drying plums at 85°C can significantly increase the antioxidant activity. It is concluded that the mechanism responsible for this effect is the formation of new compounds with high antioxidant potential in the Maillard reaction [28].



	raisins	bananas	apples	pineapples	apricots	figs	strawberries	cranberries	white mulberry	mangos	dates	plums
Serie1	33.78	59.79	14.75	15.62	31.02	32.15	33.61	31.99	50.06	16.33	25.61	1.78

[%]

Source: own work / Źródło: opracowanie własne

Fig. 4. The ability do chelate iron ions (II)

Rys. 4. Zdolność do chelatowania jonów żelaza (II)

5. Summary

Dried fruits can provide a good source of polyphenols with antioxidant properties. The study showed that strawberries had the highest polyphenol content among the tested dried fruit. Strawberries also showed the highest antioxidant activity measured in tests with DPPH and ABTS. All tested fruits chelated iron (II) ions. The highest chelating activity was found for bananas, 59.79%, and the lowest for plums, 1.78%. In view of the above, it can be concluded that dried fruit can be a good source of biologically active compounds with antioxidant properties, diversifying the daily diet. The proper processing of the fruit, such as drying, may enable the use of seasonal ingredients such as strawberries in the diet.

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