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ANTIOXIDANT PROPERTIES OF DIFFERENT FRUIT SEEDS AND PEELS

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Abstract. The objective of the investigations performed was to assess the antioxidant properties of the seeds and peels of selected fruits. The antioxidant activity as well as total polyphenol and tannin content were determined. The results obtained revealed essential diversities of the analysed parameters among the material examined. The peels were characterized by higher ability to scavenge free radicals and higher polyphenols concentration than the seeds, particularly those of citrus fruits imported to Poland. The highest antioxidant activity was observed in the peels of the Šampion cultivar of apples and white grapes, and in the seeds of the Idared cultivar apples and oranges. Tannins play a meaningful role as antioxidants in grape, apple and goosberry fruits. The peels and seeds of various fruits, which are waste products in fruit and vegetable industry, may be a potential source of antioxidants.

Key words: antioxidant activity, polyphenols, tannins, fruit, peels, seeds

INTRODUCTION

The oxidative reactions proceeding in food are the main cause of its deterioration. They are responsible for the nutritional value losses, as well as aroma, taste and texture degradation. Moreover, the products of biological compounds oxidation, by interaction with important for organism function molecules, can upset cell homeostasis, and act cytotoxically resulting in different diseases like tumours, heart failure, cataract, brain dysfunction [Maniak and Targoński 1996].

Antioxidants are the substances able to prevent or inhibit oxidation processes in human body as well as in food products. The natural antioxidants are a stable part of nutrition as they occur in almost all edible plant products. Polyphenols are the most numerous group of antioxidant components, and they are present in fruits and vegetables, their products, leguminous plants, grains, teas, herbs, spices and wines [Horubała 1999, Borowska 2003].

Consumption of food containing a lot of polyunsaturated fatty acids raised the significance and usage of substances that protect them against oxidation.

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The antioxidant supplementation is a generally accepted method of prolonging the stability and storage life of food products, in particular the ones including fat. However, the artificial compounds with antioxidant properties, like butylated hydroxyanisol (BHA) and butylated hydroxytoluene (BHT), have a limited allowance for food due to their potential cancerogenicity [Jayaprakasha et al. 2003].

The growing demand for natural antioxidants observed in food and cosmetic industries forces the search for new sources of these compounds. Numerous scientific investigations point at consecutive rich sources of antioxidants, especially among fruits, but only few of them involve waste parts of fruits, i.e. seeds and peels.

Fruits and vegetables wastes and by-products, which are formed in great amounts during industrial processing, represent a serious problem, as they exert an influence on environment and need to be managed and/or utilized. On the other hand, they are very rich in bioactive components, which are considered to have a beneficial effect on health. For the last decade, efforts have been made to improve methods and ways of re-using fruits and vegetables wastes. The important purpose is the valorization of the antioxidants and other biocomponents in by-products from fruit and vegetable industries. It has been attempted to discuss which plants and their by-products can be considered as a rich source of natural antioxidants and what methods should be used for their efficient extraction. The competition between natural and synthetic antioxidants, in terms of consumer acceptance, legal needs for market access, toxicity and thermal stability, is a big problem.

The objective of the investigation performed was to determine the antioxidant properties of peels and seeds of different domestic and imported fruits, that are commonly available and readily consumed in Poland, and to indicate which of them can become a new source of natural antioxidants for food, cosmetic and pharmaceutical industries.

MATERIALS AND METHODS

Seeds and peels of commercially available domestic (gooseberry, apples, plums) and imported (watermelon, lemon, grapefruit, kiwi fruit, melon, orange, grapes) fruits were used in the investigation.

The fruits were gathered either directly from trees and shrubs or bought at local markets and were stored in cold conditions until the moment of analysis. For examination only healthy looking fruits were chosen (without mechanical damages and bacterial infection), mature, with declared place of origin (seller declaration). The antioxidant activity and total polyphenol and tannin contents were determined in methanol extracts.

Methanol extracts

The seed cores were cut out and individual seeds were separated from flesh. In case of goooseberry and kiwi fruit the seeds were sieved, then rinsed with distilled water and dried out on absorbent paper. Peels were cut of with a stainless steel knife.

The prepared material was weighed, frozen at a temperature of –18°C and lyophilized. Freeze-dried parts of fruits were weighed once more and stored in a closed container in nitrogen atmosphere until the analysis.

A portion of the lyophilized sample was placed in a container of the laboratory mill and ground (2 × 12 s). An amount of 25 ml 80% (v/v) methanol was poured over a 0.500 g ground lyophilisate and mixed for 2 h by a magnetic stirrer (500 rpm). The whole mixture was filtered and centrifuged for 10 min (1467 × g, 20°C), and the supernatants obtained were collected into twisted test-probes. Those methanol extracts were then stored in a freezer (–20°C).

Assessment of the antioxidant activity

The antioxidant activity was assayed on the basis of a protocol represented by Re et al. [1999] with some modifications incorporated. The ABTS radical was generated during a chemical reaction between the 7 mM aqueous solution of diammonium salt of the 2,2'-azino-bis (3-ethylbenzothiazoline-6-sulfonic) acid and the 2.45 mM potassium persulfate. The extract ability to scavenge the radical was determined spectrophotometrically by an absorbance measurement, at a wave length of 734 nm, in the 6th minute after adding the sample to the ABTS radical. The antioxidant capacity of extracts under study was calculated using a standard curve drawn up for solutions of the synthetic vitamin E (Trolox) and expressed as mg Trolox × 100 g^{-1} of dried weight.

Quantitative determination of tannin by vanillin method

The tannin content in the samples investigated was assessed on the basis of modified methods by Price et al. [1978]. The vanillin method involves the reaction of an aromatic aldehyde, vanillin, with meta-substituted ring of flavanols to yield a red coloured adduct measured spectrophotometrically at 500 nm. The tannins content in extracts examined was calculated using a standard curve drawn up for methanol solutions of catechin and expressed as mg catechin × 100 g^{-1} dried weight.

Quantitative determination of total polyphenols

Total polyphenols content was assayed by Folin-Ciocalteau method on the basis of a protocol represented by Swain and Hillis [1959]. Total polyphenols content was calculated using a standard curve drawn up for catechin methanol solutions and expressed as mg catechin × 100 g^{-1} dried weight.

Dry matter determination

The sample was dried at 105°C till the constant weight was obtained, cooled in dessicator and weighed in analytical scale. The dry matter was calculated by formula:

$$\text{dry matter} = \frac{c - a}{b - c},$$

where:

a – the weight of empty weighing bottle, g,
b – the weight of weighing bottle with fresh sample, g,
c – the weight of weighing bottle with dried sample, g.

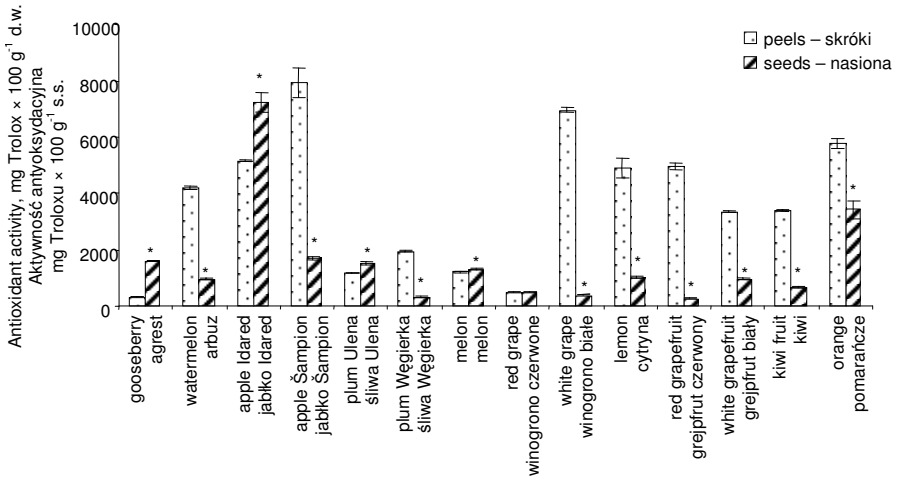
Statistical analysis

The results were shown as an arithmetic mean (± standard deviation). A single-factor Analysis of Variance test (ANOVA) with a *post hoc* Tukey's test were applied to perform a statistical analysis. A Kołmogorov-Smirnov test was applied to examine the normality of distribution.

RESULTS AND DISCUSSION

The investigations results revealed a considerable diversity of the antioxidant properties and polyphenol and tannin contents among the materials examined. The assays performed pointed out the seeds and the peels of fruits to be a rich source of natural antioxidant components. The peels of the fruits examined were in the majority of cases characterized by a significantly higher antioxidant capacity in comparison to the seeds. Antioxidant properties depend on the polyphenol components presence, primaly phenolic acids and flavonoids. One of the numerous flavonoid classes are tannins, which are responsible for astringent flavour of some plant materials and products.

Among the fruits' parts examined, the highest antioxidant activity was found in the peels of the Šampion cultivar (7925 mg Trolox × 100 g^{-1} d.w.) and white grapes (6944), and the seeds of the Idared cultivar and orange, respectively 7230 i 3423 mg Trolox × 100 g^{-1} d.w. (Fig. 1).



*Means seeds and peels are significantly different at $p < 0.05$.
*Oznacza istotne statystycznie różnice ($p < 0,05$) między skórkami i nasionami tego samego owocu.

Fig. 1. Antioxidant activity of fruit seeds and peels evaluated by free radical ABTS assay
Rys. 1. Aktywność antyoksydacyjna nasion i skórek badanych owoców oznaczana metodą z rodnikiem ABTS

According to the research outcomes published in other papers, epicatechin and its polymers, chlorogenic acid with isomers, quercetin, phloretin, phloridzin, cyanidin and their glycosides, as well as antocyanins, are confirmed to be the key polyphenols in apples [Kondo et al. 2002, Boyer and Liu 2004]. Based on the results achieved, it can be concluded that both peels and seeds of the Idared cultivar of apples are characterized by high antioxidant properties, and activity of these seeds was the highest among the fruit seeds examined. It was demonstrated that polyphenols, with tannins included, are the main agent responsible for antioxidant properties. In case of the Šampion cultivar of apples, the free radicals scavenge capacity of the peels components was much more higher in comparison with the ones from the seeds. The peels of this apple cultivar were characterized by a very high tannins concentration (1053 mg catechin × 100 g^{-1} d.w.). Robards et al. [1999] proved that up to 90% of polyphenol components of apple constitute flavanols, with (-)epicatechin and procyanidin B_2 being dominant.

In the experiments accomplished, the highest polyphenol concentration was found in seeds and peels of grapes (9207 mg catechin × 100 g^{-1} d.w. in red grape seeds and 8220 in white grape seeds, and respectively 5129 and 3794 in their peels). Much lower amount of the polyphenol compounds was detected in peels of apples (1613 in Šampion cultivar and 1790 in Idared one), kiwi fruit (1161) and lemon (966), and in seeds of watermelon (969) and gooseberry (801; Table 1).

The pertinent literature references available [Robards et al. 1999, Montealegre et al. 2006, Pinelo et al. 2006] proved very high antioxidant properties of grapes, which contain up to 5 polyphenols groups, with flavonols representing the main fraction in the peels, and flavan-3-ol in the seeds. It was demonstrated that tannins concetration correlated with polyphenol content in the seeds and peels of both types of grapes examined, and, that the significantly higher amounts of that compounds were found in seeds (Table 1).

The results achieved comply with the research outcomes published in other papers, the content of high-molecular flavanols, as well as concentration of procyanidins, anthocyanins, flavonoids and total polyphenols were much higher in grape seeds than in grape peels [Negro et al. 2003, Montealegre et al. 2006].

Antioxidant properties of red grapes were unexpectedly low in relation to the total polyphenol and tannins contents. However, it should be stressed that tannin polymers are not the substances with high antioxidant potential. So, even if they are present in high concentrations in the extracts, the capacity to scavenge ABTS radical by the extract can be lower than that of extracts abounding with quercetin glycosides, catechin or epicatechin.

Based on the results achieved from tannin content assessment in peels and seeds of mature fruits, it can be concluded that only in 5 of 14 samples examined, tannins played an important role as antioxidants (Table 1). The highest concentrations of tannins were revealed in the peels and the seeds of red grapes (respectively, 1410 and 5577 mg catechin × 100 g^{-1}), white grapes (937 and 3860), Idared apples (742 and 647) and gooseberries (937 and 3860), also in the Šampion peels (1053). There were no tannins in kiwi fruit seeds, nor in the peels of watermelon, Ulena plum and red grapefruit, and in any part of investigated: melon, orange or lemon.

Very interesting is a relatively high antioxidant activity of the gooseberry seeds. Based on the results obtained it can be admitted that the polyphenols, with tannins as their fraction, are, to a high level, responsible for the antioxidant properties. It is worth to highlight that antioxidant properties of the gooseberry seeds are of the order of Ulena

Table 1. Total polyphenols and tannin content in fruits' seed and peel (mean ± SD)
Tabela 1. Zawartość polifenoli ogółem i tanin w skórkach i nasionach owoców (średnia ± SD)

Fruit – Owoc (variety – odmiana)	Total polyphenols mg catechin × 100 g^{-1} d.w. Polifenole ogółem mg katechiny × 100 g^{-1} s.s.		Tannins mg catechin × 100 g^{-1} d.w. Taniny mg katechiny × 100 g^{-1} s.s.	
	seeds – nasiona	peels – skórki	seeds – nasiona	peels – skórki
Gooseberry (Biały Plenny) Agrest	800.7 ± 3.0	698.7 ± 11.9*	260.5 ± 4.1	282.5 ± 32.5
Watermelon Arbuz	969.3 ± 16.4	335.3 ± 20.8**	11.0 ± 10.0	0
Apple (Idared) Jabłko	345.0 ± 32.9	1 790.5 ±27.5**	647.3 ± 14.8	742.0 ± 90.2
Apple (Šampion) Jabłko	702.5 ± 8.3	1 613.7 ± 11.3**	20.5 ± 0.7	1 053.5 ± 20.4**
Plum (Renkloda Ulena) Śliwka	436.8 ± 4.2	334.0 ± 8.7**	24.0 ± 0.5	0**
Plum (Węgierka zwykła) Śliwka	147.3 ± 3.0	578.8 ±13.8**	13.25 ± 0.4	41.5 ± 17.0*
Melon (Galia) Melon	57.2 ± 2.6	466.5 ±8.8**	0	0
Red grapes (Alphonse Lavallee) Winogrono czerwone	9 207.5 ± 46.0	5 159.2 ±19.6**	5 577.2 ± 26.1	1 410.3 ± 88.0**
White grapes (Uva da Tavola) Winogrono białe	8 220.2 ± 60.3	3 794.5 ±32.9**	3 860.0 ± 367.0	937.2 ± 35.0**
Lemon (Primofiori) Cytryna	158.8 ± 0.7	966.2 ± 16.5**	0	0
Red grapefruit (Star Ruby Citra) Grejpfrut czerwony	222.5 ± 14.5	557.7 ± 10.9**	70.25 ± 26.5	0**
White grapefruit (Apemar) Grejpfrut biały	205.5 ± 6.1	528.8 ± 12.5**	77.3 ± 26.5	61.25 ± 17.3
Kiwi fruit (Hayward) Kiwi	102.0 ± 2.5	1161.0 ±13.1**	0	136.0 ± 4.0**
Orange (Midnight) Pomarańcze	212.0 ± 8.4	849.3 ± 21.8**	0	0

*Means seeds and peels are significantly different at $p < 0.01$.
**Means seeds and peels are significantly different at $p < 0.001$.
*Oznacza różnice między nasionami i skórkami istotne statystycznie przy $p < 0,01$.
**Oznacza różnice między nasionami i skórkami istotne statystycznie przy $p < 0,001$.

plum seeds antioxidant capacity, but are much higher than the values obtained for seeds of grapefruits, lemons and grapes. In the hitherto literature references there are no data on antioxidant properties of gooseberry, indicating wide area for scientific research on this domestic fruit.

SUMMARY

Perspectives of utilization of fruits and vegetables wastes-originated antioxidants are relatively big, but up to now little recognized. The research accomplished indicated the fruit peels and seeds as potential source of natural substances with antioxidant properties. It was demonstrated that among numerous already identified polyphenols compounds, tannins constitute an essential fraction in the peels and seeds of apples and grapes. In many cases, the fruit seeds and peels are the waste products of technological processes, hence their re-using as the antioxidant source, could bring measurable economical profits and contribute to reduction of pollutions introduced by fruit and vegetable industries into the environment. It is necessary to consider both environmental (waste management, protection against pollution) and economical aspects (extraction profitability).

Concluding, it should be stressed that the peels and seeds of many fruits can be considered as a potential source of different antioxidant components, which are not exploited at the moment, but could find practical application in many industrial branches. The fruits commonly cultivated in Poland – in particular Idared and Šampion cultivars of apples – are characterized by antioxidant properties which are comparable with citrus fruit.

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WŁAŚCIWOŚCI ANTYOKSYDACYJNE NASION I SKÓREK WYBRANYCH OWOCÓW

Streszczenie. Celem pracy była ocena właściwości antyoksydacyjnych nasion i skórek wybranych owoców. Badano aktywność przeciwutleniającą i określano zawartość polifenoli ogółem oraz tanin. Uzyskane wyniki wskazują na duże zróżnicowanie badanych parametrów w materiale badawczym. Silniejsze zdolności neutralizowania wolnych rodników oraz dużą ilość polifenoli zaobserwowano w skórkach badanych owoców, zwłaszcza wśród importowanych owoców cytrusowych. Największą aktywność antyoksydacyjną wykazały skórki jabłek odmiany 'Šampion' oraz winogron białych, a także nasiona jabłek odmiany 'Idared' i pomarańczy. Taniny odgrywają znaczącą rolę jako antyoksydanty w owocach winogron, jabłek oraz agrestu. Nasiona i skórki wielu owoców, jako materiał odpadowy przemysłu owocowo-warzywnego, mogą być potencjalnym źródłem substancji o właściwościach antyoksydacyjnych.

Słowa kluczowe: aktywność antyoksydacyjna, polifenole, taniny, owoce, skórki, nasiona

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