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EIGHT OLD CULTIVARS OF APPLE TREES – AN EVALUATION OF THEIR POTENTIAL FOR USE BY THE PROCESSING INDUSTRY

S u m m a r y

Background. Fruit of old cultivars may contain more micro- and macronutrients and polyphenols than modern tree cultivars. This paper presents the results of a study on eight old cultivars of apple trees. The fruit was gathered in the Wolin National Park (Woliński Park Narodowy) from old uncultivated trees.

Results and conclusions. Despite the lack of tree care, the fruit of all the cultivars studied contained small amounts of harmful heavy metals and nitrates. Different criteria are used to evaluate fruit by consumers and the processing industry. For consumers, taste is important, and a low sugar-to-acid ratio makes fruit much tastier. The Roter Herbstkalvill cultivar, despite containing the least sugar of all the cultivars tested, has the lowest sugar-to-acid ratio (3.3). The highest content of health-promoting polyphenolic compounds was found in the fruit of the following cultivars: Roter Herbstkalvill (734 mg/100 g DM) and Kaiser Alexander (701 mg/100 g DM). Due to their high dry matter content, the Geflammter Kardinal and Boikenapfel cultivars will be the best choice for the processing industry. Whereas cultivars with a low sugar content, which caramelizes at high temperatures - Roter Herbstkalvill and Weisser Winterkalvill - will be useful for flour production and baking.

Key words: polyphenolic compounds, color, mineral content, sugars, acids

Introduction

Apple trees for a long time have been a valued part of town, country, field and home garden landscapes. They enrich people's diets and provide refuge and food for animals. They occur as cultivated forms, wild trees or can be found in abandoned human settlements as feral forms of once cultivated trees. There are several thousand cultivars of apple trees, but industrially cultivated ones are mainly disease-resistant and

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the most prolific cultivars. Their fruit is usually characterized by high weight [1]. Nowadays, when it comes to the industry, the economic result is the most important [12, 18]. Historically, fruit has had several uses in the kitchen, ripening at different times and being stored even until spring. It was used for a range of culinary purposes. Apple cultivars came to Poland from various parts of the world. This is due to historical conditions. In the west, there are numerous cultivars imported from Western Europe, mainly of German origin. In the eastern part of the country, there are cultivars of Russian provenance [31].

In forests and national parks, it is still possible to find abandoned human settlements together with old orchards or domestic plantings. Often, only the foundations of houses have remained and there is no trace of the vegetation of the time, but trees can survive for many years even competing with the successional vegetation. In such places, old apple cultivars can be found. The Wolin National Park (Woliński Park Narodowy), from which the samples for this study were taken, is one of such locations. Apple trees found in such places have not only been able to survive for many years in a feral form, but also still bear fruit.

It is an excellent object for a study on old cultivars that are not yet as severely genetically mixed as in modern crops, while not being fertilized. This indicates the high resistance of these cultivars. Studying old apple cultivars can be useful in the process of improving the quality of modern food by producing apples of this type or creating new cultivars with them. It has been shown that the fruit of old apple cultivars has often a better taste, aroma and nutritional qualities compared to contemporary mass-grown cultivars [6, 8]. Apples are a source of carbohydrates, micro and macronutrients, vitamins and fiber [11, 32]. Apples can enrich our daily diet with micro and macronutrients that are essential for the proper functioning and development of the human body. They are characterized by a great variability in the abundance of micro and macronutrients. However, by selecting the right cultivars for diets, we can choose the most beneficial ones [7, 23].

There are some micro and macronutrients that play an important role in the body. For example, iron, copper, zinc or manganese have antioxidant effects. In addition, zinc can prevent certain diseases and disorders of the human body. It ensures a good balance of minerals. Many people are found to be deficient in calcium or iron, among others, which proves that more attention should be paid to a balanced diet and functional foods [2, 3, 17]. A large group of plant metabolites are polyphenols, with high health-promoting qualities [13, 18]. Some compounds can increase the disease resistance of apples, which is particularly important with a today's economic approach to cultivation [4, 40].

The present study aims to determine the content of micro and macronutrients, sugars, acidity, pectins and phenolic compounds of fruit from eight old apple cultivars.

In this way, it can be determined which of the studied cultivars would be potentially suitable for industrial or local use in food processing.

Material and methods

Characteristics of the area of research and plant material

The fruit was harvested in the Wolin National Park located at the mouth of the Oder River, in the north-western Poland (Zachodniopomorskie Province), close to the border between Poland and Germany. It protects the highly valuable north-western part of Wolin Island. The Park was established in 1960, coveringan area of 4,844 ha. It was extended in 1996 by incorporating one nautical mile broad belt of Baltic coastal waters in the north and delta of the Świna River. The inclusion of the part of the Pomeranian Bay and the inner salt waters of the Szczecin Bay has made the Wolin National Park the first maritime park in Poland. The total area of the Park today is 10,937 ha, of which forests cover 4,530 ha (41 %). Six forest communities of the total area of 165 ha (1.5 %) are under strict protection. Within the Park and in the neighboring areas, one can find the remnants of strongholds and other places of historic settlements, which are both subject to scientific research and tourist attractions.

Plant materials

The fruit of eight old apple cultivars collected in the Wolin National Park was used in the study: Weihnachtsapfel (Wapnica), Weisser Winterkalvill (Wapnica), Boikenapfel (Międzyzdroje - Biała Góra), Geflammter Kardinal (Obręb Wodny), Roter Herbstkalvill (Wicko), Lausitzer Nelkenapfel (Wicko), Riesenboiken (Warnowo), Kaiser Alexander were (Warnowo).

The cultivars were initially identified on the basis of fruit and leaf characteristics, based on catalogues and comparative material taken from the collection. Their affinities were confirmed using ISSR. Fruit samples (~5.0 kg each) were collected from trees growing in abandoned human settlements and buildings that are now located within the Wolin National Park.

Determination of color

The pigment measurement (color) of the fruit (skin and pulp) was analyzed in a transmitted mode evaluated by the spectrophotometer Konica Minolta CM-700d method tested in CIE L*a*b* system, as described by Chełpiński et al. [5]. Measurements were taken with an aperture diameter of 8 mm, through a 10º observer type and D65 illuminant. The *a** value showed the place of appearing in the color gamut, in the range from green to red (+a* means redness; −a* means greenness) on the surface of dried fruits of analyzed genotypes. The *b** parameter described the color in the range from yellow to blue (+b* means yellow; −b* means blue) on the skin and pulp of the tested cultivars. Measurements were taken on fresh fruit in 50 replicates for skin and flesh for each cultivar.

General fruit parameters

Nitrate content was measured with an RQflex 10 requantometer (Merck, Darmstadt, Germany) [19]. Measurements were taken on fresh fruit in five repetitions Pectin content was analyzed using the Morris method described by Pijanowski et al. [28]. Measurements were taken on dried fruit in three repetitions.

Drying conditions

Fruit was cut into 5 mm thick slices and dried in PROMIS-µLAB's microwave-convection drying (MW-CD) with microwave power of 220 W and a maximum temperature of 60 °C. The air flow was perpendicular to the material layer, with a velocity of approximately 3.5 m/s. Homogeneous powders from dried fruit were prepared in a closed laboratory mill to avoid hydration. Then the water content of the fruit was examined. Dry fruit according to PN-90/A- 75101/03 [29] was determined in fresh and dried fruit.

Chemical analysis

Identification of mineral contents

The contents of elements in fruit were determined after mineralization: N, P, K, and Ca were determined after wet mineralization in H_2SO_4 (96 %, Chempur, Poland) and $HClO_4$ (70 %, Chempur, Poland), whereas Cu, Zn, Mn, Fe, P b, Cd and Al were determined after mineralization in HNO_3 (65 %) and $HClO_4$ (70 %) in the ratio of 3:1 (IUNG, 1990). The total N concentration was determined by the Kjeldahl distillation method, and $N\text{-}NO_3$ and $N\text{-}NH_4$ were determined potentiometrically. The K content was measured using atomic emission spectrometry, whereas the content of Mg, Ca, Cu, Zn, Mn, and Fe was measured using flame atomic absorption spectroscopy. Phosphorus (P) was assessed by the colorimetric method with a Specol 221 apparatus (Carl Zeiss, Germany). The concentration of selenium in the apples was determined using Watkinson's spectrofluorometric method [38], modified by Grzebuła and Witkowski [15]. Dry fruit was digested in HNO_3 at 230 ºC for 180 minutes and in $HClO_4$ at 310 ºC for 20 minutes. Subsequently, the samples were hydrolyzed with 9 % HCl. Selenium was derivatized with 2,3-diaminonaphtalene (Sigma-Aldrich) and the complex was extracted into cyclohexane. Se concentration was measured fluorometrically using an RF-5001 PC Shimadzu spectrophotofluorometer (Japan). The excitation wavelength was 376 nm, and the fluorescence emission wavelength was 518 nm. Measurements were taken on dry fruit in three repetitions.

Identification of phenolic compounds, sugar and acidity

The materials were extracted with methanol acidified with 2.0 % formic acid (phenolic compounds) or redistilled water (sugar and acidity). The separation was conducted twice by incubation for 20 minutes at 20 °C under sonication (Sonic 6D, Polsonic, Warsaw, Poland) followed by shaking from time to time (a few times or rarely). Subsequently, the suspension was centrifuged MPW-251 (MPW MED. INSTRUMENTS, Warsaw, Poland) at 19,000×g for 10 minutes. Before analysis, the supernatant was additionally purified with a Hydrophilic PTFE 0.20 μm membrane (MillexSamplicity Filter, Merck). All extractions were carried out in triplicate.

Qualitative (LC–Q-TOF–MS, Waters, Manchester, UK) and quantitative (ACQUITY Ultra Performance LC system equipped with a photodiode array detector with a binary solvent manager (Waters Corporation, Milford, MA, USA) analyses of polyphenols were performed as described previously by Oszmiański et al. [25]. Separations of individual polyphenols were carried out using a UPLC BEH C18 column (1.7 μm, 2.1 × 100 mm, Waters Corporation, Milford, MA) at 30 °C. The samples (10 μL) were injected, and the elution was completed in 15 minutes with a sequence of linear gradients and isocratic flow rates of 0.45 cm^3/min. The mobile phase consisted of solvent A (2.0 % formic acid, v/v) and solvent B (100 % acetonitrile). The program began with isocratic elution with 99% solvent A (0 ÷ 1 min), and subsequently, a linear gradient was used until 12 minutes, lowering solvent A to 0 %; from 12.5 to 13.5 minutes, the gradient returned to the initial composition (99 % A), and subsequently, it was held constant to re-equilibrate the column. All measurements were repeated three times. The results were expressed as mg per 100 g of dry matter (DM).

An analysis of sugar by the HPLC-ELSD method was performed according to the protocol described by Oszmiański and Lachowicz [24]. The samples of apple fruit (1 ÷ 2 g) were diluted with redistilled water (50 cm^3). The extraction was performed by incubation for 15 minutes under sonication (Sonic 6D, Polsonic, Warsaw, Poland) and with occasional shaking, and then incubation at 90 °C for 30 minutes. Next, the slurry was centrifuged at 19,000*g* for 10 minutes, and the supernatant was filtered through a Sep-Pak C-18 Cartridges (Waters Milipore), and through a Hydrophilic PTFE 0.20 mm membrane (Millex Samplicity Filter, Merck) and used for analysis. All extractions were carried out in triplicate. Organic acids were analyzed using high-performance liquid chromatography (LC-20AT; Shimadzu, Kyoto, Japan), a UV–Vis detector, and a data acquisition system fitted with a CAPECELL PAK MG S5 C_{18} column. The results were expressed as g per 100 g of dry matter (DM).

Statistical analysis

All statistical analyses were performed with Statistica 12.5 (StatSoft Polska, Cracow, Poland). The statistical significance of differences between means was established by testing the homogeneity of variance and normality of distribution followed by ANOVA with Tukey's *post hoc* test, significance was set at $p < 0.05$. The results are expressed as means. A multivariate analysis was performed by applying a principal component analysis (PCA). The data was auto-scaled during pre-processing.

Results and discussion

Quality of fresh fruit

Fruit chemical composition is a cultivar feature. Tests carried out showed that the content of individual mineral elements in the tested fruit varied greatly. Nitrogen was the element with the smallest variation in content among the fruits of the studied cultivars. The least amount of nitrogen was contained in the fruit of the Roter Herbstkalvill cultivar, while the highest content, by 37 %, of this element was in the fruit of Kaiser Alexander. Of the macronutrients, the greatest differences, by 78 %, were in the content of P. Much greater variation was in the content of micronutrients. In the case of Mn, it was as high as 160 %. However, in the content of harmful Cd, the differences were as high as 200 %.

Analyzing individual components, the tested cultivars were divided into those accumulating minerals and those with lower mineral content. Among the tested apple cultivars, the following stand out due to their high contents of micro and macro elements: Boikenapfel (P – 0.16 g/100 g, Zn – 5.58 mg/1000 g, Mn – 2.13 mg/100 g), Geflammter Kardinal (N – 2.44 g/100 g, K – 0.87 g/100 g), Riesenboiken (Ca – 1.35 g/100 g, Se – 1.12 μg/100 g, Cu – 0.50 mg/100 g) and Kaiser Alexander (N – 2.38 g/100 g, Mg – 0.23 g/100 g, Fe – 15.8 mg/100 g). The fruit of the cultivars Weihnachtsapfel and Weisser Winterkalvill proved to be the least rich in micro and macro elements. Roter Herbstkalvill and Lausitzer Nelkenapfel (Table 1).

The apples of these cultivars are rich in minerals, but despite having been harvested from long-abandoned settlements in the Wolin National Park, they are not free of heavy metals. In terms of heavy metal content, the highest concentrations of heavy metals were detected in the fruit of the following cultivars: Weihnachtsapfel (Pb – 0.021 mg/100 g, Cd – 0.0027 mg/100 g, Boikenapfel (Pb – 0.019 mg/100 g), Riesenboiken (Al – 0.73 mg/100 g) and Kaiser Alexander (Pb – 0.020 mg/100 g). The detected values exceed the dietary standards for cadmium: in Weihnachtsapfel fruit by 35 %, Lausitzer Nelkenapfel by 10 %, and Boikenapfel by 5 %. Lead content was exceeded in all the cultivars. However, it should be noted that the heavy metal content depends on the substrate on which trees are grown and this factor can be eliminated in the case of cultivation [9, 10].

Table 1. Macro- and microelements and heavy metals composition of all old apple cultivars (macroelements g/100 g; microelements and heavy metals mg/100 g DM)

Tabela 1. Skład makro- i mikroelementów oraz metali ciężkich wszystkich starych odmian jabłoni (makroelementy g/100 g; mikroelementy i metale ciężkie mg/100 g DM)

Cultivar / Odmiana	Weihnachtsapfel	Weisser Winterkalvill	Boikenapfel	Geflammter Kardinal	Roter Herbstkalvill	Lausitzer Nelkenapfel	Riesenboiken	Kaiser Alexander
N	2.11^{c} ±0.09	2.23^{cd} ±0.11	1.95^{b} ±0.08	2.44^{e} ±0.10	1.78^{a} ±0.07	2.08^{c} ±0.08	2.27^{d} ±0.10	2.38^{e} ±0.11
P	$0.12b^{c}$ ±0.004	0.13^{c} ±0.004	0.16^{d} ±0.005	0.10^{ab} ±0.003	$0.12b^{c}$ ±0.004	0.09^{a} ±0.003	0.11^{abc} ±0.004	0.13^{c} ±0.004
K	0.61^{a} ±0.03	0.67^{ab} ±0.03	0.73^{b} ±0.03	0.87^{d} ±0.04	0.83^{cd} ±0.04	0.72^{b} ±0.02	0.75^{bc} ±0.03	0.69^{ab} ±0.02
Ca	1.02^{b} ±0.04	0.88^{a} ±0.03	1.15^{c} ±0.05	1.09^{bc} ±0.04	0.94^{a} ±0.03	1.24^{d} ±0.05	1.35^{e} ±0.04	1.12^{c} ±0.04
Mg	0.17^{a} ±0.06	0.19^{bc} ±0.05	0.16^{a} ±0.04	0.15^{a} ±0.04	0.21^{cd} ±0.04	0.20^{c} ±0.05	0.17^{a} ±0.03	0.23^{e} ±0.04
Fe	11.2^{b} ±0.06	8.8^{a} ±0.03	12.6^{c} ±0.06	9.2^{a} ±0.05	10.7^{b} ±0.04	8.9^{a} ±0.04	13.3^{c} ±0.06	15.8^{d} ±0.06
Cu	0.41^{d} ±0.02	0.32^{b} ±0.01	0.36^{bc} ±0.01	0.44^{de} ±0.01	0.47^{ef} ±0.02	0.39^{cd} ±0.02	0.50^{f} ±0.03	0.22^{a} ±0.01
Zn	4.52^{bcd} ±0.14	3.26^{a} ±0.11	5.58^{f} ±0.17	4.04^{bc} ±0.15	4.79^{de} ±0.16	3.53^{a} ±0.12	4.56^{de} ±0.13	5.01^{e} ±0.15
Mn	0.82^{a} ±0.03	1.67^{e} ±0.05	2.13^{f} ±0.07	0.79^{a} ±0.03	1.24^{c} ±0.04	0.98^{b} ±0.04	1.41^{d} ±0.05	1.04^{b} ±0.04
Al	0.55^{c} ±0.02	0.34^{a} ±0.01	0.61^{d} ±0.02	0.42^{b} ±0.01	0.39^{b} ±0.01	0.51^{c} ±0.02	0.73^{e} ±0.03	0.59^{cd} ±0.02
Pb	0.021^{d} ±0.001	0.017^{c} ±0.001	0.019^{cd} ±0.001	0.012^{a} ±0.001	0.015^{b} ±0.001	0.011^{a} ±0.001	0.013^{ab} ±0.001	0.020^{d} ±0.001
Cd	0.0027^{e} ±0.0001	0.0016^{b} ±0.0001	0.0021^{cd} ±0.0001	0.0009^{a} ±0.0000	0.0018^{bc} ±0.0001	0.0022^{d} ±0.0001	0.0015^{b} ±0.0001	0.0012^{a} ±0.0001
Se (µg/100 g)	0.97^{e} ±0.04	0.92^{de} ±0.04	0.58^{b} ±0.02	0.88^{d} ±0.03	0.46^{a} ±0.02	0.76^{c} ±0.03	1.12^{f} ±0.05	0.54^{b} ±0.02

Explanatory notes / Objaśnienia:

a–f mean ± SD followed by different letters within the same line represent significant differences ($p < 0.05$)

średnia a–f ± SD, po której następują różne litery w tej samej linii, oznacza istotne różnice ($p < 0,05$)

Not only basic micronutrients and macronutrients such as iron and magnesium are worth noting. Selenium and zinc also deserve attention. They have antioxidant properties, have a positive effect on glucose metabolism and blood sugar levels and regulate pancreatic function. They also support the body in the fight against many diseases [22]. By far, the highest level of selenium was found in the fruit of the Riesenboiken cultivar – 1.12 µg/100 g (Tab. 1). Its high levels were also observed in Weihnachtsapfel and Weisser Winterkalvill fruit, 0.92 ÷ 0.97 µg/100 g. The highest amounts of selenium are found in mushrooms and garlic [16]. These were concurrent with the results reported by Pezzarossa et al. [27] for peach and pear leaves and fruit. The analytical results of all apple cultivars for dry weight, pH, pectins, nitrates, sugars and titratable acidity are given in Table 2. Dry matter, pH and pectin content are very important parameters of the fruit that are relevant for processing. Fruit for drying średnia a–f ± SD, po której następują różne litery w tej samej linii, oznacza istotne różnice (*p* < 0,05)
should have a high dry matter content. This shortens the drying process and increases the amount of product. The dry matter concentration in the fruit of the analyzed old apple cultivars ranged from 13.6/100 g FM in the Riesenboiken cultivar to 16.7/100 g FM in the case of the Geflammter Kardinal cultivar. These results are similar to those obtained in the studies by Mitre et al. [20] and Oszmiański et al. [25]. In contrast, the cultivar Geflammter Kardinal with its high dry matter content had little pectin (7.13 g/100 g). Only the 'Roter Herbstkalvill' fruit had less pectin (5.08 g/100 g). Boikenapfel and Lausitzer Nelkenapfel apples contained more than twice as much pectin: >12 g/100 g. Pectin occurs naturally in fruit and has health-promoting effects on humans. Apples are fruits that contain high amounts of pectin, which increases their attractiveness [37].

Nitrates influence human health negatively, their excess can cause various diseases [14, 39]. The tested cultivars contain a low amount of nitrates and they mostly meet the strict standards for children's products according to: the European Commission's Commission Regulation (EC) No 1881/2006 of 19 December 2006 setting maximum levels for certain contaminants in foodstuffs [10]. The permissible amount of nitrates according to the aforementioned standard is 20 mg/100 g fruits. Only the cultivars Lausitzer Nelkenapfel and Riesenboiken did not meet these requirements, containing 25.2 mg/100 g and 23.7 mg/100 g respectively. However, it is important to note that these are still within the dietary standards for adults. Furthermore, a study from 2020 showed that old apple cultivars, including Riesenboiken, can have much lower levels of nitrate [34].

Table 2. Chemical composition of all old apple cultivars
Tabela 2. Skład chemiczny wszystkich starych odmian jabłoni

Cultivar / Odmiana	Weihnachtsapfel	Weisser Winterkalvill	Boikenapfel	Geflammter Kardinal	Roter Herbstkalvill	Lausitzer Nelkenapfel	Riesenboiken	Kaiser Alexander
Dry weight / Sucha masa (g/100 g FM)	14.0^{a} ±0.4	15.4^{bc} ±0.4	16.2^{d} ±0.3	16.7^{e} ±0.5	15.6^{c} ±0.4	14.9^{b} ±0.3	13.6^{a} ±0.4	15.1^{bc} ±0.5
pH	3.69^{e} ±0.15	3.26^{b} ±0.11	3.04^{a} ±0.16	3.48^{cd} ±0.09	3.65^{de} ±0.12	3.57^{cde} ±0.13	3.37^{bc} ±0.12	3.05^{a} ±0.10
Pectines / Pektyny (g/100 g DM)	7.19^{b} ±0.32	6.82^{b} ±0.29	11.32^{d} ±0.39	7.13^{b} ±0.35	5.08^{a} ±0.27	11.84^{d} ±0.37	9.92^{c} ±0.30	7.69^{b} ±0.31
Nitrates / Azotany (mg/100 g DM)	19.3^{d} ±1.7	11.0^{a} ±1.2	11.1^{a} ±1.5	14.6^{b} ±1.2	15.8^{bc} ±1.6	25.2^{e} ±1.8	23.7^{e} ±2.1	18.0^{cd} ±1.5
	Sugar / Cukry g/ 100 g DM							
Fructose /Fruktoza	33.6^{f} ±0.63	20.9^{b} ±0.57	30.7^{e} ±0.59	27.7^{d} ±0.44	10.7^{a} ±0.29	29.7^{de} ±0.42	20.2^{b} ±0.39	24.8^{c} ±0.38
Glucose / Glukoza	9.35^{d} ±0.21	5.90^{a} ±0.19	7.30^{b} ±0.24	5.25^{a} ±0.17	5.95^{a} ±0.20	14.80^{f} ±0.35	12.25^{e} ±0.33	8.69^{d} ±0.22
Sorbitol / Sorbitol	6.64^{d} ±0.13	3.71^{b} ±0.09	1.73^{a} ±0.06	4.04^{b} ±0.12	4.20^{b} ±0.10	9.68^{e} ±1.07	6.43^{d} ±0.15	5.18^{c} ±0.14
Sucrose / Sacharoza	0.93^{e} ±0.02	0.59^{b} ±0.01	0.73^{c} ±0.02	0.52^{a} ±0.01	0.59^{b} ±0.01	1.48^{g} ±0.03	1.22^{f} ±0.03	0.87^{d} ±0.02
Total / Razem	50.52^{d}	31.15^{b}	40.46^{c}	37.56^{c}	21.40^{a}	55.71^{e}	40.15^{c}	39.55^{c}
	Acids / Kwasy (g/100 g DM)							
Shikimic / Szikimowy	0.16^{e} ±0.003	0.15^{e} ±0.003	0.20^{f} ±0.004	0.04^{b} ±0.001	0.07^{c} ±0.002	0.01^{d} ±0.000	0.02^{a} ±0.000	0.09^{d} ±0.002
Citric / Cytrynowy	0.53^{c} ±0.012	0.60^{d} ±0.011	0.20^{a} ±0.009	0.67^{e} ±0.013	0.62^{d} ±0.014	0.22^{a} ±0.008	0.96^{f} ±0.015	0.31^{b} ±0.009
Tartaric / Winowy	0.11^{b} ±0.004	0.14^{c} ±0.004	0.75^{g} ±0.011	0.20^{e} ±0.007	0.17^{d} ±0.006	0.24^{f} ±0.008	0.16^{cd} ±0.005	0.07^{a} ±0.004
Malic / Jabłkowy	6.24^{c} ±0.18	6.18^{bc} ±0.19	2.74^{a} ±0.06	6.95^{cd} ±0.10	5.60^{b} ±0.09	7.84^{d} ±0.12	5.57^{b} ±0.10	9.92^{e} ±0.15
Succinic / Bursztynowy	0.09^{e} ±0.002	0.01^{a} ±0.000	0.05^{c} ±0.001	0.07^{d} ±0.001	0.07^{d} ±0.001	0.03^{b} ±0.000	0.08^{e} ±0.001	0.03^{b} ±0.000
Lactic / Mlekowy	0.06^{c} ±0.001	0.09^{de} ±0.001	0.05^{a} ±0.001	0.08^{d} ±0.001	0.05^{b} ±0.000	0.04^{a} ±0.000	0.09^{e} ±0.001	0.04^{a} ±0.000
Total / Razem	7.19^{c}	7.17^{c}	3.99^{a}	8.01^{d}	6.58^{b}	8.38^{d}	6.88^{bc}	10.46^{e}
Sugars/acids ratio Stosunek cukry / kwasy	7.0	4.3	10.1	4.7	3.3	6.6	5.8	3.8

Explanatory notes / Objaśnienia:

a–f mean ± SD followed by different letters within the same line represent significant differences ($p < 0.05$)

The range of sugars and acid contents determined in old apple cultivars is shown in Table 2. The food industry prefers sweeter fruit for its taste and processing properties. The acid content of the fruit is equally important. They affect the taste of the apples, but also the preserves obtained from them. Due to the need for a balance between sweetness and acidity, the processing industry prefers sour apples [21]. Among the cultivars tested, Roter Herbstkalvill (3.25) and Kaiser Alexander (3.80) have the most favorable sugar/acid ratio. The cultivars with the most unfavorable acid-to-sugar ratio are Weihnachtsapfel (7.03), Boikenapfel (6.76) and Lausitzer Nelkenapfel (6.57).

Fructose, glucose, sorbitol and sucrose, in that order, occurred in the analyzed apples. The sugar content ranged from 21.4 to 55.7 mg/100 g and fructose from 10.7 to 33.6 mg/g (50-76 % sugars) (Fig. 1). The cultivar with the highest glucose content was Riesenboiken (30.51 %), with the least glucose content being found in Geflammter Kardinal (13.98 %). The smallest sucrose content was found in the fruit: 0.52-1.48 mg/g. Similar proportions of sugars were found in a study by Oszmiański et al. [25].

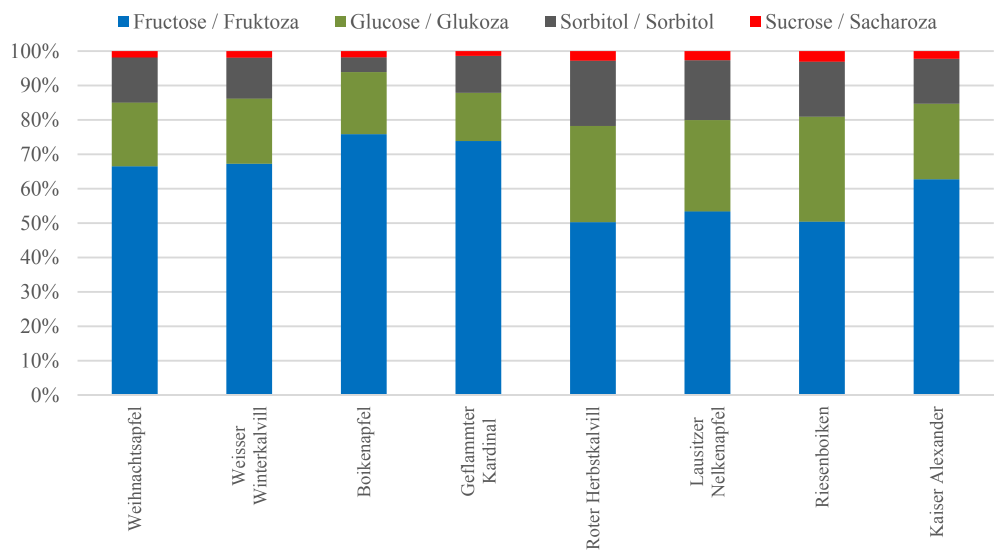

Fig. 1. Percentage of sugars in the old apple cultivars
Ryc. 1. Procentowa zawartość cukrów w starych odmianach jabłek

The amount of sucrose present is significantly influenced by the degree to which the fruit ripens. Glucose is a more preferred sugar than fructose and sucrose for health reasons; it is the most important source of energy for the brain and neurons. The efficient functioning of the nervous system is largely dependent on it [26]. When glucose is metabolized in the liver, the high-energy compound ATP is formed. Out of 120 kcal of glucose, only 0.5 kcal is converted into fat. In contrast, out of every 120 kcal of fructose, as much as 40 kcal (that is up to 80 times more) will be converted into fat tissue [33].

Phenolic compounds in fruit are responsible for its disease resistance, but also for its taste and health-promoting properties such as antiviral, anticancer, anti-inflammatory or anti-diabetic effects [24]. On average, in apples, the contents of the compounds assigned to each group were: flavan-3-ols (39.37 %), phenolic acids (39.35 %), dihydrochalcones (10.55 %) flavonols (7.09 %) and anthocyanins (3.64 %). The proportion of individual phenolic groups and individual compounds varies significantly between cultivars (Fig. 2).

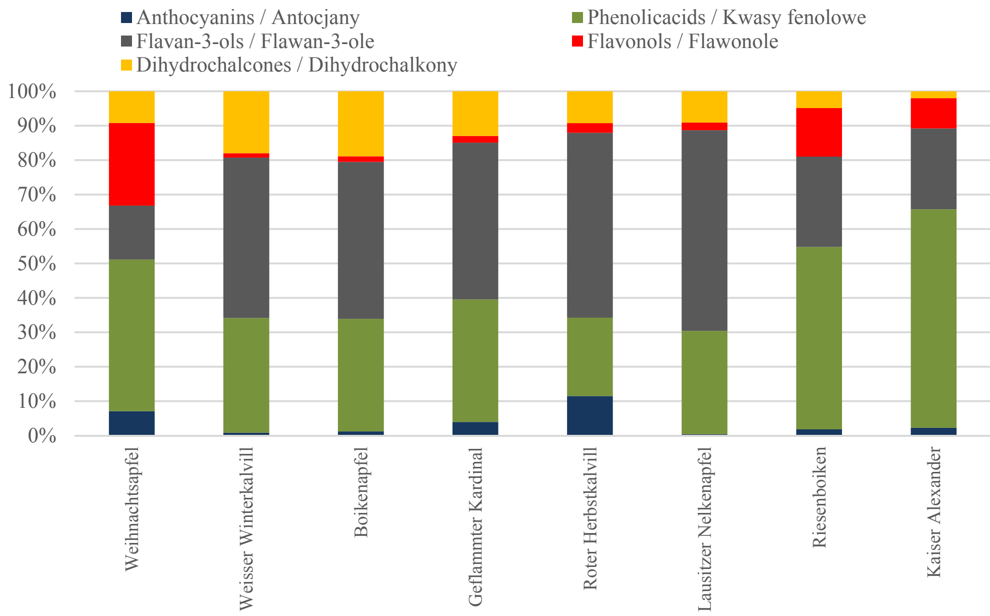

Fig. 2. Percentage concentration of phenolic compounds of old apple cultivars
Ryc. 2. Procentowe stężenie związków fenolowych w starych odmianach jabłek

The highest amount of flavan-3-ols was found in the Roter Herbstkalvill cultivar (394.18 mg/100 g DM), while the lowest was found in the Riesenboiken cultivar (124.62 mg/100 g DM) and the Weihnachtsapfel cultivar (129.05 mg/100 g DM). (+)catechin was predominant in each cultivar, ranging from 106 to 312 mg/100 g (Table 3). The most polyphenolic acids were found in the Kaiser Alexander cultivar (444.58 mg/100g DM), while the least in Boikenapfel (115.09 mg/100 g DM). Among the seven compounds determined in each cultivar, chlorogenic acid predominated (111 ÷ 434 mg/100 g).

Table 3. Concentration of phenolic compounds of all old apple cultivars (mg/100 g DM)

Tabela 3. Stężenie związków fenolowych wszystkich starych odmian jabłek (mg/100 g s.m.)

Compound / Składnik	Weihnachtsapfel	Weisser Winterkalvill	Boikenapfel	Geflammter Kardinal	Roter Herbstkalvill	Lausitzer Nelkenapfel	Winter Goldparmane	Kaiser Alexander
Anthocyanins / Antocyjany								
Cyanidin 3-O-glucoside	6.41^{c} ±0.16	0.00	0.00	4.89^{a} ±0.14	9.03^{d} ±0.21	0.00	0.00	5.52^{b} ±0.13
Cyanidin 3-*O*-galactoside	47.81^{g} ±1.19	2.75^{b} ±0.07	3.72^{c} ±0.10	11.30^{f} ±0.27	68.36^{h} ±1.58	1.94^{a} ±0.05	7.37^{d} ±0.15	9.84^{e} ±0.20
Cyanidin 3-*O*-arabinoside	1.77^{e} ±0.04	0.32^{a} ±0.01	0.45^{ab} ±0.01	2.07^{f} ±0.06	3.91^{g} ±0.10	0.65^{bc} ±0.02	1.16^{d} ±0.03	0.74^{c} ±0.02
Cyanidin 3-*O*-xyloside	2.30^{d} ±0.06	0.00	0.14^{a} ±0.01	1.18^{c} ±0.04	3.21^{e} ±0.08	0.00	0.19^{a} ±0.01	0.77^{b} ±0.02
Total / Razem	58.29^{f}	3.07^{ab}	4.31^{b}	19.44^{e}	84.51^{g}	2.59^{a}	8.72^{c}	16.87^{d}
Phenolic acids / Kwasy fenolowy								
3-*O*-(4'-*O*-Caffeoylglucosyl)quinic acid	0.63^{e} ±0.02	0.32^{b} ±0.01	0.40^{c} ±0.01	0.21^{a} ±0.01	0.70^{e} ±0.02	1.86^{f} ±0.04	0.49^{d} ±0.02	1.89^{f} ±0.05
5-*O*-(3'-*O*-Caffeoylglucosyl)quinic acid	0.87^{d} ±0.02	0.38^{c} ±0.01	0.30^{b} ±0.01	0.40^{c} ±0.02	1.37^{f} ±0.03	1.72^{g} ±0.04	0.10^{a} ±0.00	1.00^{e} ±0.02
Chlorogenic acid	360^{g} ±7.2	119^{b} ±2.4	111^{a} ±2.2	172^{d} ±4.4	162^{c} ±3.9	182^{e} ±4.2	249^{f} ±5.5	434^{h} ±9.5
Cryptochlorogenic acid	0.09^{a} ±0.00	0.09^{a} ±0.00	0.63^{e} ±0.01	0.30^{c} ±0.01	0.28^{bc} ±0.01	0.24^{b} ±0.01	0.42^{d} ±0.01	2.01^{f} ±0.05
Caffeoylglucoside acid	0.77^{a} ±0.02	0.97^{d} ±0.02	0.91^{c} ±0.02	0.86^{b} ±0.02	0.90^{c} ±0.02	0.83^{b} ±0.02	0.87^{bc} ±0.02	0.77^{a} ±0.01
Coumaroylquinic acid	0.51^{c} ±0.01	0.67^{e} ±0.01	0.79^{f} ±0.02	0.58^{d} ±0.01	0.38^{a} ±0.01	0.54^{cd} ±0.01	0.57^{d} ±0.01	0.45^{b} ±0.01
Coumaroylquinic acid	0.02^{a} ±0.00	0.47^{d} ±0.01	0.81^{f} ±0.02	0.31^{c} ±0.01	0.64^{e} ±0.01	0.15^{b} ±0.01	0.67^{e} ±0.02	3.91^{g} ±0.12
Total / Razem	363.04^{e}	122.38^{a}	115.09^{a}	174.33^{bc}	166.76^{b}	187.71^{c}	252.18^{d}	444.58^{f}
Flavan-3-ols / Flawon-3-ole								
(+)-Catechin	106.60^{a} ±2.71	134.08^{c} ±2.43	132.14^{c} ±2.09	196.71^{d} ±4.31	310.56^{e} ±6.42	312.91^{e} ±6.74	116.99^{b} ±2.87	136.15^{c} ±1.95
(-)-Epicatechin	22.02^{b} ±0.49	36.80^{d} ±0.72	27.46^{c} ±0.55	25.59^{bc} ±0.57	82.94^{f} ±1.93	50.84^{e} ±1.34	7.22^{a} ±0.17	27.76^{c} ±0.71
Total / Razem	128.6^{a}	170.9^{b}	159.6^{b}	222.3^{c}	393.5^{e}	363.8^{d}	124.2^{a}	163.9^{b}
Flavonols / Flawonole								
Quercetin 3-*O*-rutinoside	14.79^{g} ±0.30	0.32^{b} ±0.01	0.37^{c} ±0.01	0.47^{d} ±0.01	0.27^{a} ±0.01	0.31^{b} ±0.01	1.12^{f} ±0.02	1.00^{e} ±0.02
Quercetin 3-*O*-galactoside	16.6^{e} ±0.33	1.40^{a} ±0.03	1.30^{a} ±0.03	3.00^{b} ±0.07	13.62^{d} ±0.29	9.22^{c} ±0.21	50.19^{g} ±1.42	34.87^{f} ±0.68

Quercetin 3-*O*-glucoside	$5.18^{e} \pm 0.13$	$0.61^{a} \pm 0.02$	$1.23^{b} \pm 0.03$	$3.40^{c} \pm 0.08$	$4.74^{d} \pm 0.10$	$0.64^{a} \pm 0.02$	$8.67^{f} \pm 0.19$	$16.69^{g} \pm 0.38$
Quercetin 3-*O*-pentoside	$2.15^{h} \pm 0.04$	$0.18^{c} \pm 0.01$	$0.03^{a} \pm 0.00$	$0.34^{d} \pm 0.01$	$0.11^{b} \pm 0.00$	$0.40^{e} \pm 0.01$	$1.03^{f} \pm 0.03$	$1.14^{g} \pm 0.03$
Kaempferol 3-*O*-rutinoside	$0.58^{a} \pm 0.02$	$1.05^{bc} \pm 0.03$	$1.04^{bc} \pm 0.03$	$1.09^{c} \pm 0.03$	0.00	$0.99^{b} \pm 0.02$	$0.96^{b} \pm 0.02$	$1.03^{bc} \pm 0.03$
Quercetin 3-*O*-pentoside	$3.62^{e} \pm 0.09$	$0.13^{a} \pm 0.00$	$0.51^{c} \pm 0.01$	$0.09^{a} \pm 0.00$	$0.41^{b} \pm 0.01$	$0.37^{b} \pm 0.01$	$1.54^{d} \pm 0.03$	$3.80^{f} \pm 0.08$
Kaempferol 3-*O*-pentoside	$0.63^{a} \pm 0.01$	$0.87^{c} \pm 0.02$	$1.01^{de} \pm 0.02$	$0.95^{d} \pm 0.02$	$0.75^{b} \pm 0.02$	$1.04^{e} \pm 0.03$	$1.00^{de} \pm 0.03$	$1.01^{de} \pm 0.02$
Quercetin 3-*O*-rhamnoside	$3.98^{f} \pm 0.11$	$0.05^{a} \pm 0.00$	$0.22^{b} \pm 0.01$	$0.21^{b} \pm 0.01$ b	$0.76^{c} \pm 0.02$	$0.81^{c} \pm 0.02$	$2.56^{e} \pm 0.08$	$2.04^{d} \pm 0.07$
Total / Razem	47.53^{e}	4.61^{a}	5.71^{a}	9.55^{b}	20.66^{d}	13.78^{c}	67.07^{g}	61.58^{f}
Dihydrochalcones / Dihydrochalkony								
Phloretin 2'-*O*-xyloglucoside	$50.81^{f} \pm 1.05$	$19.37^{c} \pm 0.42$	$37.40^{e} \pm 0.78$	$37.74^{e} \pm 0.70$	$18.25^{c} \pm 0.36$	$23.20^{d} \pm 0.62$	$11.37^{b} \pm 0.23$	$4.13^{a} \pm 0.12$
Phloretin 2'-*O*-glucoside	$25.27^{c} \pm 0.44$	$46.68^{f} \pm 0.94$	$29.13^{d} \pm 0.63$	$25.88^{c} \pm 0.56$	$49.61^{g} \pm 0.89$	$33.70^{e} \pm 0.75$	$11.99^{b} \pm 0.27$	$10.11^{a} \pm 0.25$
Total / Razem	76.08^{e}	66.05^{d}	66.53^{d}	63.62^{d}	67.86^{d}	56.9^{c}	23.36^{b}	14.24^{a}
Total / Razem	673.6^{D}	367.0^{A}	351.2^{A}	489.2^{B}	733.3^{F}	624.7^{C}	475.5^{B}	701.2^{E}

Explanatory notes / Objaśnienia:
a–f mean ± SD followed by different letters within the same line represent significant differences ($p < 0.05$)
średnia a–f ± SD, po której następują różne litery w tej samej linii, oznacza istotne różnice ($p < 0,05$)

The content of the other compounds classified as phenolic acids did not exceed 4 mg/100 g. Another group of compounds are dihydrochalcones, which exhibit antioxidant activity, have anti-cancer effects and influence glucose transport [40]. The highest number of dihydrochalcones was found in Weihnachtsapfel (76.08 mg/100 g DM), while the lowest was found in Kaiser Alexander (14.24 mg/100g DM). The highest amount of flavonols characterized the Riesenboiken cultivar (67 mg/100 g DM), while the least flavonols were found in the Weisser Winterkalvill cultivar (4.61 mg/100 g DM).

The highest anthocyanin content was found in the fruit of the cultivar Weihnachtsapfel (58.29 mg/100 g DM), which is characterized by an intense red skin color (Fig. 3). The least amount of anthocyanins was in the poorly colored fruit of Lausitzer Nelkenapfel (2.59 mg/100 g DM) and in the green, blush-free fruit of Weisser Winterkalvill (3.07 mg/100 g DM) (Fig. 2, Fig. 3). Depending on the study, the content of polyphenolic compounds in old apple tree cultivars may be between1.4 and even 3.0 times higher than that of contemporary cultivars [30, 35, 36, 40]. These results indicate that there is a wide variability in the results of the studies, but it depends mainly on the cultivar chosen. Not every study deals with the same cultivars, but rather distinguishes only between old cultivars and modern mass-bred ones. Moreover, the fruit polyphenol content can be significantly influenced by the weather in a given year, geographical location, genetic variability, growth period and conditions, fruit storage conditions, and cultivation methods [35, 36, 40].

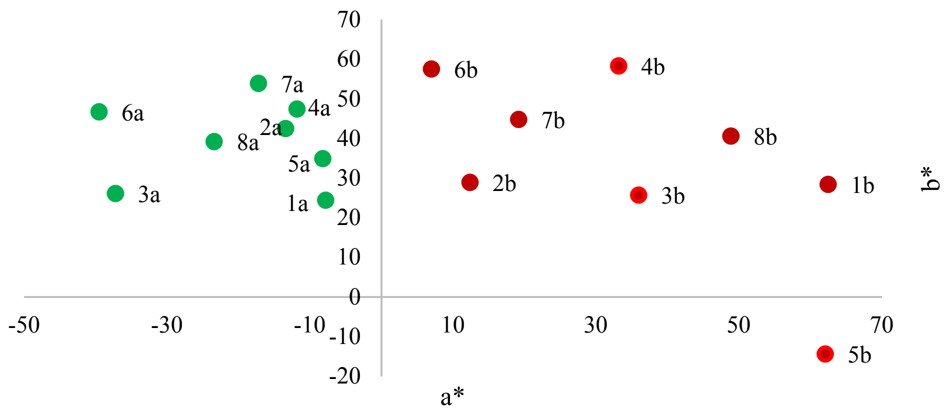

Fig. 3. The color of the skin and the colored part of the fruit of the old apple cultivars tested; a – skin color, b – pulp color

Ryc. 3. Barwa skórki i wybarwienie owocu badanych starych odmian jabłek; a – kolor skórki, b – kolor miąższu

Explanatory notes / Objaśnienia:
1 – Weihnachtsapfel; 2 – Weisser Winterkalvill; 3 – Boikenapfel; 4 – Geflammter Kardinal; 5 – Roter Herbstkalvill; 6 – Lausitzer Nelkenapfel; 7 – Riesenboiken; 8 – Kaiser Alexander

Conclusions

1. The fruit of the Riesenboiken and Kaiser Alexander cultivars was rich in micro- and macronutrients. The fruit of all cultivars contained low amount of harmful heavy metals. The lowest sugar content among the tested cultivars is found in Roter Herbstkalvill, although it has the best sugar-to-acid ratio (3.25). For consumers, a low sugar-to-acid ratio makes the fruit tastier. A low sugar content is important for consumers, especially as fructose is predominant, which is not the healthiest sugar form.
2. The Weihnachtsapfel cultivar had the highest content of polyphenolic compounds. The following cultivars: Roter Herbstkalvill and Kaiser Alexander also need to be mentioned. For health-promoting reasons, these cultivars should be popularized. Their rich chemical composition could have a positive impact on human health.
3. The cultivars which are the best for use in the processing industry are Geflammter Kardinal and Boikenapfel due to their high dry matter content. The low-sugar cultivars Roter Herbstkalvill and Weisser Winterkalvill are suitable for drying and producing flour for baking.
4. If the fruit size and disease resistance allow an efficient yield, these cultivars can be successfully used instead of or in addition to the currently popular apple cultivars.

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OSIEM STARYCH ODMIAN JABŁONI - OCENA MOŻLIWOŚCI ICH WYKORZYSTANIA PRZEZ PRZEMYSŁ PRZETWÓRCZY

S t r e s z c z e n i e

Wprowadzenie. Inne kryteria oceny owoców stosowane są przez konsumentów i przemysł przetwórczy. Dla konsumentów ważny jest smak, a niski stosunek cukru do kwasu sprawia, że owoce są znacznie smaczniejsze.Niniejsze badania mają na celu określenie zawartości mikro- i makroelementów, cukrów, kwasowości, pektyn i związków fenolowych w owocach 8 starych odmian jabłoni. Owoce zbierano na terenie Wolińskiego Parku Narodowego. Określono jakość 8 odmian jabłoni - ich barwę i skład chemiczny.

Wyniki i wnioski. Owoce odmian Riesenboiken i Kaiser Alexander były bogate w mikro- i makroelementy. Owoce wszystkich odmian zawierały niewielkie ilości szkodliwych metali ciężkich. Najniższą zawartością cukrów spośród testowanych odmian charakteryzuje się odmiana Roter Herbstkalvill, choć ma najlepszy stosunek cukrów do kwasów (3,25). Dla konsumentów niski stosunek cukrów do kwasów sprawia, że owoce są smaczniejsze. Niska zawartość cukru jest ważna dla konsumentów, zwłaszcza że dominuje fruktoza, która nie jest najzdrowszą formą cukru. Odmiana Weihnachtsapfel miała najwyższą zawartość związków polifenolowych. Na wyróżnienie zasługują również odmiany Roter Herbstkalvill i Kaiser Alexander. Ze względów prozdrowotnych odmiany te powinny być popularyzowane. Ich bogaty skład chemiczny może mieć pozytywny wpływ na zdrowie człowieka. Do wykorzystania w przemyśle przetwórczym najlepsze będą odmiany Geflammter Kardinal i Boikenapfel, ze względu na wysoką zawartość suchej masy. Odmiany o niskiej zawartości cukru Roter Herbstkalvill i Weisser Winterkalvill nadają się do suszenia i produkcji mąki do wypieków. Jeśli wielkość owoców i odporność na choroby pozwalają na wydajne plony, odmiany te mogą być z powodzeniem stosowane zamiast lub jako dodatek do obecnie popularnych odmian jabłoni.

Słowa kluczowe: cukry, kolor, związki polifenolowe, zawartość minerałów, kwasy organiczne