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BASIC CHEMICAL COMPOSITION, CONTENT OF MICRO- AND MACROELEMENTS AND ANTIOXIDANT ACTIVITY OF DIFFERENT VARIETIES OF GARLIC'S LEAVES POLISH ORIGIN

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

The aim of this study was to comparison of chemical components and antioxidant activity in leaves of winter and spring varieties of garlic, obtained from POLAN Company; Krakow, Poland) as well as in leaves of wild (bear's) garlic. The content of basic chemical components were determined according to the AOAC methods. Selected minerals content was determined according to the PN procedure. Vitamin C and polyphenols were determined using the Tillman's and Folin-Ciocalteau's methods, respectively. The ability to scavenging of the $ABTS^{\bullet +}$ was analyzed by Re et al. method.

Leaves of wild garlic had the significantly lowest amount of dry matter (79.0 $g \cdot kg^{-1}$), proteins (13.7 $g \cdot kg^{-1}$), total carbohydrates (50.8 $g \cdot kg^{-1}$), dietary fiber (26.9 $g \cdot kg^{-1}$), ash (8.9 $g \cdot kg^{-1}$), vitamin C (956.1 $mg \cdot kg^{-1}$), and antioxidant activity (25.0 mmol $TEAC \cdot kg^{-1}$), but the highest level of crude fat (5.6 $g \cdot kg^{-1}$), potassium (34.6 $g \cdot kg^{-1}$), magnesium (1.72 $g \cdot kg^{-1}$), iron (230.3 $mg \cdot kg^{-1}$) and zinc (58.8 $mg \cdot kg^{-1}$) as compared to winter and spring varieties. At the same time, there was no unambiguous differences in the level of basic chemical components (proteins 20.9 ÷ 35.7 $g \cdot kg^{-1}$, fat 1.6 ÷ 2.8 $g \cdot kg^{-1}$, total carbohydrates 61.3 ÷ 116.5 $g \cdot kg^{-1}$, fibre 33.7 ÷ 57.0 $g \cdot kg^{-1}$, ash 8.9 ÷ 14.1 $g \cdot kg^{-1}$), antioxidants (vitamin C 75.4 ÷ 459.7 $mg \cdot kg^{-1}$, polyphenols 335.3 ÷ 1895.1 $mg \cdot kg^{-1}$), antioxidant activity (27.0 ÷ 30.1 mmol $TEAC \cdot kg^{-1}$) and the amount of minerals (calcium 7.55 ÷ 28.9 $g \cdot kg^{-1}$, potassium 15.9 ÷ 28.0 $g \cdot kg^{-1}$, magnesium 0.85 ÷ 1.32 $g \cdot kg^{-1}$, sulphur 2.41 ÷ 6.22 $g \cdot kg^{-1}$, iron 34.4 ÷ 85.7 $mg \cdot kg^{-1}$, zinc 9.32 ÷ 13.8 $mg \cdot kg^{-1}$) between winter and spring varieties, as well as between winter varieties.

Słowa kluczowe: garlic leaves, wild garlic, chemical composition, phenolic compounds, vitamin C

Introduction

Garlic (*Allium sativium* L.) contains many bioactive substances, mainly organo-sulphur derivatives, but also flavonoids as well as vitamins (C, E), which have strong

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antioxidant activity. Several studies showed that garlic and it's bioactive compounds may be used in prevention of many diseases. This vegetable may be used in the prevention and treatment of cardiovascular diseases (atherosclerosis, heart attack, blood pressure control), cancer, bacterial, viral and fungal infections. What is more garlic improves the elasticity of blood vessels. Additionally, epidemiological studies indicate, that in areas where garlic is consumed regularly, the incidence of cardiovascular diseases are lower [4, 7, 10, 32]. It has been well reported that this plant reduces many risk factors, which play a key role in the formation and development of atherosclerosis (anti-inflammatory properties, lowers total and low density lipoproteins cholesterol, increases high density lipoproteins cholesterol, reduces triglycerides and fibrinogen levels) [13, 20, 21].

Some data suggested that bioactive compounds of garlic may decrease body gain and affect adipose tissue metabolism as well as decreased mRNA gene expression involved in adipogenesis [12].

It has been also reported that garlic, its products (fermented garlic, garlic oil) and isolated from it bioactive compounds have the ability to reduce blood glucose levels and modulate insulin secretion. What is more experimental and epidemiological studies provide evidence between garlic consumption and reduced risk of various types of the cancer (i.e. esophagus, stomach, liver, colon, bladder, brain, skin, prostate, breast and lung) [12, 27, 39]. For anticarcenogenic properties are probably responsible sulphur compounds, but also soluble dietary fibre (pectins, inulin), phenolic compounds also can reduce risk of various types of cancer [4, 9, 12, 13, 27, 37, 40]. It is well known that the consumption of garlic during antibiotic therapy enhances its effectiveness. Garlic also activates antioxidant enzymes such as catalase, superoxide dismutase and glutathione reductase. On the other hand some studies reported that garlic supplementation could cause interactions between food and drugs as well as change the therapeutic efficacy of any drugs administrated [3, 5].

Wild garlic (*Allium ursinum* L.), called also ramson or bear's garlic, is very often used as a traditional medicine [17]. Bear's garlic can be found in Northern and Central Europe and North Asia. It is adapted to humid temperate climate, grows best in shady, rich in humus forests near streams. Wild garlic frequently grows in large groups, forming extensive meadows in nature. From all white, narrow, onion grows two leaves. Wild garlic acts upon in the body generally improving strengthens and regenerates. It also helps in the treatment of diseases of the cardiovascular system, gastrointestinal tract or skin infections. Its flavour is more delicate compared to agriculture-garlic. Culinary uses of the wild garlic are limited mainly to use the leaves. They can be used as raw, pickled, salted or in brine with oil. They are added to salads, soup, potatoes, cabbage, stewed vegetables and meat dishes [1, 16].

The cloves of garlic are commonly used, but there is no habit of using garlic's leaves. The development and introduction of new products containing leaves of garlic could significantly increase its consumption. Leaves mainly are the waist product of this plant. Few published paper suggested that leaves have the same, and even richer than the cloves content of sulphur compounds (allicin), chlorophylls, carotenoids, phenolic compounds, and vitamin C [2, 8, 32].

The objective of this study was the assessment of chemical composition of leaves of winter and spring varieties of garlic as well as wild garlic.

Materials and methods

Fresh leaves of garlic (*Allium sativum* L.) varieties 'Harnaś', 'Ornak', 'Mega', 'Arkus', 'Huzar', 'Zawrat' (winter varieties) and 'Jankiel' (spring variety), have been purchased in 2011 from the Krakowska Hodowla i Nasiennictwo Ogrodnicze (KHNO POLAN PLC) (Kraków, Poland). Garlic has been cultivated for the production of bulbs. Wild garlic has been obtained from Poręba Wielka, Malopolska Region (cultivated on the private area). The winter varieties have been harvested at the beginning of July and the Jankiel variety at the end of July (during the final period of the variety vegetation). Wild garlic has been harvested at the end of May, 2011.

Chemical composition of fresh and dry garlic leaves

In fresh leaves of garlic the level of dry matter (AOAC method No. 934.06 [32]), vitamin C (ascorbic acid and dehydroascorbic acid; Tillman's method; [36]) was determined. Additionally fresh leaves were used for preparation of methanolic extracts (to determine total phenolic compounds content and the antioxidant activity). For determination of chemical composition AOAC [26] methods were used. Leaves of garlic were freeze dried with Christ Alpha 1-4 freeze-drier (Martin Christ Gefriertrocknungsanlagen GmbH, Germany).

In dried leaves of garlic the total proteins (AOAC method No. 950.36), raw fat (AOAC method No. 935.38), total dietary fibre (AOAC method No. 991.43) and ash (AOAC method No. 930.05) content were determined. The content of total carbohydrates was calculated as a differences between content of dry matter and the sum of protein, fat and ash.

Methanolic extracts preparation

The fresh leaves were homogenized with a homogenizer (CAT type X 120, CAT Scientific, Inc. Paso Robles, CA, USA) and were used to prepare methanol extracts (5 g of raw leaves in 80 ml of 70 % methanol solution). In each case, homogenized samples of plant material were extracted by shaking (Elpan, water bath shaker type 357, Elpin-Plus, Lubawa Poland) at room temperature for 2 hours, and solution was centrifuged (Centrifuge type MPW-340, MPW Medical Instruments, Warsaw, Poland), filtered and then the extracts were stored at T = -22 °C [29].

Total phenolic compounds content

Methanolic extracts were used to measure the total phenolic compounds content, using the Folin-Ciocalteau reagent. This method involved colorimetric determination of colored products which are formed when polyphenolic compounds react with the Folin-Ciocalteau reagent (Sigma, St. Luis, Missouri, USA). The level of total polyphenolic compounds in the garlic's leaves extracts was determined spectrophotometrically (at a wavelength of λ = 760 nm using a RayLeigh UV-1800 spectrophotometer, Beijing Beifen-Ruili Analytical Instrument, Beijing, China) according to the Folin-Ciocalteau method [38]. Results have been expressed as chlorogenic acid equivalents (CGA) in milligrams per kilogram of fresh matter, based on a standard curve.

The antioxidant activity

Methanol extracts were also used to determine antioxidant activity by the sample's ability to scavenge an free radical i.g. $ABTS^{\bullet +}$ (2, 2'-azinobis-(3-ethylbenzothiazoline-6-sulfonic acid) [34]. The absorbance was measured at a wavelength of λ = 734 nm using a RayLeigh UV-1800 spectrophotometer. Values obtained for each sample were compared to the concentration–response curve of the standard Trolox solution and expressed as millimoles of Trolox equivalent per kilogram of fresh weight.

Micro- and macroelements content

The samples for the measurement of minerals were prepared according to the EN 13804 Standard [30]. Mineralization was performed with the dry-ashing method, modified according to AOAC 985.01 method [26]. Modification concerned a lowered temperature and prolonged time of ashing. Applied temperature was lowered from T = 500 °C to 460 °C and ashing time in both steps was three times longer than in original method. Content of Ca, P, Mg, S, Fe and Zn in the solution obtained after mineralization (ash was dissolved in HNO_3) were measured with the inductively coupled plasma atomic emission spectrometer JY 238 Ultratrace (Jobin-Yvon, Longjumeau Cedex, France) following procedures presented in EN-14084 Standard [31].

Statistical analysis

For each sample the chemical analyses were done in three replicates. The standard deviations (SD) were calculated for all mean values. All calculations were made by using Statistica 9.1. package (Stat Soft, Tulsa, Oklahoma, USA). One-way analyses of variance were applied. The significance of differences was estimated with Duncan test at the critical significance level of $p < 0.05$.

Results and discussion

Basic chemical composition

The lowest content of dry matter was determined in leaves of wild garlic as compared to other evaluated leaves. The highest content of this parameter was determined in varieties 'Mega' and 'Jankiel' ($p < 0.05$). The lowest content of protein was found in wild garlic leaves compared to other examined varieties ($p < 0.05$). Leaves of garlic were characterized by low content of fat (range from 1.6 $g \cdot kg^{-1}$ of fresh matter to 5.6 $g \cdot kg^{-1}$ f.m.). The higher content of this compound was found in leaves of wild garlic and the lowest one in 'Huzar' and 'Zawrat' varieties ($p < 0.05$). Total carbohydrates content was lowest in wild garlic leaves compared to rest examined varieties. The highest content of total carbohydrates was determined in 'Mega' variety ($p < 0.05$). Content of the dietary fibre was determined in range 26.9 ÷ 57.0 $g \cdot kg^{-1}$ f.m. The highest content of this compound was determined in the 'Mega' variety . The lowest level of fibre was found in wild garlic variety ($p < 0.05$). The lowest content of ash was found in the leaves of 'Arkus' variety and the highest one in 'Zawrat' ($p < 0.05$) (Tab. 1).

Table 1. Content of nutrient components in different garlic's leaves varieties (in fresh matter) [$g \cdot kg^{-1}$]
Tabela 1. Zawartość składników odżywczych w liściach różnych odmian czosnku (w świeżej masie) [$g \cdot kg^{-1}$]

Variety Odmiana	Dry matter Sucha masa	Protein Białko	Fat Tłuszcz	Total carbohydrates Weglowodany ogółem	Fibre Błonnik	Minerals as ash Związki mineralne jako popiół
'Harnaś'	$118.9^{cd} \pm 4.8$	$22.8^{d} \pm 0.5$	$2.4^{d} \pm 0.0$	$79.6^{d} \pm 5.9$	$43.4^{e} \pm 0.7$	$14.1^{g} \pm 0.0$
'Ornak'	$132.5^{d} \pm 8.2$	$28.0^{g} \pm 0.1$	$2.5^{e} \pm 0.0$	$89.0^{e} \pm 0.3$	$40.2^{c} \pm 0.1$	$13.1^{f} \pm 0.1$
'Mega'	$157.4^{e} \pm 3.1$	$25.9^{e} \pm 0.4$	$2.8^{f} \pm 0.0$	$116.5^{h} \pm 9.7$	$57.0^{h} \pm 0.9$	$12.2^{e} \pm 0.0$
'Arkus'	$100.7^{b} \pm 0.2$	$26.7^{f} \pm 0.2$	$1.8^{b} \pm 0.0$	$61.3^{b} \pm 4.7$	$33.7^{b} \pm 0.3$	$10.9^{c} \pm 0.0$
'Jankiel'	$152.1^{e} \pm 7.2$	$35.7^{h} \pm 0.2$	$1.9^{c} \pm 0.0$	$105.6^{g} \pm 1.1$	$42.9^{d} \pm 1.0$	$8.9^{a} \pm 0.1$
'Huzar'	$113.2^{c} \pm 1.5b$	$22.5^{c} \pm 0.2$	$1.6^{a} \pm 0.0$	$78.0^{c} \pm 6.4$	$47.1^{g} \pm 0.6$	$11.1^{d} \pm 0.0$
'Zawrat'	$134.4^{d} \pm 1.8$	$20.9^{b} \pm 0.1$	$1.6^{a} \pm 0.0$	$102.5^{f} \pm 8.9$	$47.0^{f} \pm 0.6$	$9.4^{b} \pm 0.0$
Wild garlic	$79.0^{a} \pm 4.1$	$13.7^{a} \pm 0.2$	$5.6^{g} \pm 0.0$	$50.8^{a} \pm 3.6$	$26.9^{a} \pm 0.5$	$8.9^{a} \pm 0.1$

Objaśnienia: / Explanatory notes:
Table shows mean values and standard deviation / W tabeli przedstawiono wartości średnie ± odchylenia standardowe; n = 3. Mean values shown in columns and denoted by different letters are statistically significant ($p < 0.05$) / Wartości średnie przedstawione w kolumnach i oznaczone różnymi literami różnią się statystycznie istotnie ($p < 0.05$).

Vitamin C, phenolic compounds content and antioxidant activity

The highest content of vitamin C was determined in leaves of ‘Harnaś’ variety compared to other examined leaves. The lowest level of vitamin C was determined in leaves of wild garlic ($p < 0.05$). The significantly highest content of phenolic compounds was determined in leaves of ‘Arkus’ variety compared to other ones. The significantly lowest level of phenolic compounds was determined in ‘Ornak’ variety compared to other examined varieties ($p < 0.05$). The highest antioxidant activity was determined in the leaves of ‘Zawrat’ variety compared to leaves of the ‘Harnaś’, ‘Ornak’, ‘Mega’ and wild garlic varieties ($p < 0.05$) (Tab. 2).

Table 2. Content of vitamin C, total phenolic components and antioxidant activity of different garlic’s leaves varieties (in fresh matter)

Tabela 2. Zawartość witaminy C, fenoli ogółem i aktywność przeciwutleniająca liści różnych odmian czosnku (w świeżej masie)

Variety Odmiana	Vitamin C Witamina C [mg·kg^{-1}]	Total phenolic components CGA Fenole ogółem jako kwas chlorogenowy [mg·kg^{-1}]	Antioxidant activity Aktywność przeciwutleniająca [mmol TEAC·kg^{-1}]
‘Harnaś’	459.7^{g} ± 26.0	649.5^{d} ± 9.0	27.43^{bc} ± 1.14
‘Ornak’	98.8^{cd} ± 5.1	335.3^{a} ± 01.6	26.96^{b} ± 1.63
‘Mega’	75.4^{ab} ± 5.3	849.3^{e} ± 55.0	28.12^{bc} ± 0.59
‘Arkus’	83.5^{bc} ± 14.2	1895.1^{f} ± 30.7	29.22^{cd} ± 1.33
‘Jankiel’	125.0^{e} ± 0.0	400.4^{b} ± 15.2	28.74^{bcd} ± 0.74
‘Huzar’	148.5^{f} ± 18.7	827.6^{e} ± 62.0	28.66^{bcd} ± 1.48
‘Zawrat’	106.3^{de} ± 5.2	579.1^{c} ± 17.6	30.14^{d} ± 0.72
Wild garlic	56.1^{a} ± 5.3	529.7^{c} ± 23.5	24.98^{a} ± 0.11

Explanatory notes as in Tab. 1. / Objaśnienia jak w tab. 1.

Mineral compounds content

The significantly highest content of calcium was determined in the leaves of ‘Harnaś’ variety compared to other examined varieties ($p < 0.05$). The significantly lowest level of calcium was determined in ‘Jankiel’ variety compared to the other leaves ($p < 0.05$). The significantly highest level of potassium, magnesium, iron and zinc was found in the leaves of wild garlic compared to other varieties ($p < 0.05$). The significantly highest content of sulphur was found in leaves of ‘Ornak’ variety compared to other ones ($p < 0.05$). The lowest content of sulphur was determined in the leaves of 'Huzar' variety compared to the other varieties ($p < 0.05$) (Tab. 3).

Table 3. Content of macro- and microelements in different garlic's leaves varieties (in dry matter)
Tabela 3. Zawartość makro- i mikroelementów w liściach różnych odmian czosnku (w suchej masie)

Variety Odmiana	Calcium / Ca [g·kg^{-1}]	Potassium / K [g·kg^{-1}]	Magnesium / Mg [g·kg^{-1}]	Sulphur / S [g·kg^{-1}]	Iron / Fe [mg·kg^{-1}]	Zinc / Zn [mg·kg^{-1}]
'Harnaś'	$28.96^{e} \pm 0.47$	$23.28^{d} \pm 0.65$	$0.86^{a} \pm 0.03$	$5.39^{d} \pm 0.10$	$58.94^{b} \pm 1.03$	$9.79^{a} \pm 0.04$
'Ornak'	$17.79^{c} \pm 0.39$	$22.38^{d} \pm 0.53$	$1.32^{c} \pm 0.01$	$6.22^{e} \pm 0.12$	$83.61^{c} \pm 1.15$	$13.78^{a} \pm 0.80$
'Mega'	$13.45^{b} \pm 0.01$	$15.92^{a} \pm 1.56$	$1.13^{b} \pm 0.14$	$5.10^{d} \pm 0.11$	$85.71^{c} \pm 0.01$	$12.32^{a} \pm 0.27$
'Arkus'	$25.33^{d} \pm 0.22$	$20.47^{c} \pm 0.18$	$1.06^{b} \pm 0.01$	$4.35^{c} \pm 0.05$	$61.51^{b} \pm 0.01$	$11.71^{a} \pm 0.25$
'Jankiel'	$7.55^{a} \pm 0.08$	$17.94^{b} \pm 0.18$	$0.85^{a} \pm 0.01$	$3.06^{b} \pm 0.01$	$34.38^{a} \pm 0.31$	$10.60^{a} \pm 0.07$
'Huzar'	$18.73^{c} \pm 0.1$	$27.99^{d} \pm 0.35$	$0.86^{a} \pm 0.02$	$2.41^{a} \pm 0.02$	$58.41^{b} \pm 1.00$	$9.32^{a} \pm 0.09$
'Zawrat'	$12.50^{b} \pm 0.38$	$17.35^{ab} \pm 0.47$	$1.13^{b} \pm 0.02$	$3.33^{b} \pm 0.09$	$79.67^{c} \pm 3.95$	$11.32^{a} \pm 0.31$
Wild garlic	$13.44^{b} \pm 0.02$	$34.64^{f} \pm 1.21$	$1.72^{d} \pm 0.03$	$5.08^{d} \pm 0.03$	$230.34^{d} \pm 9.55$	$58.76^{b} \pm 7.14$

Table shows mean values and standard deviation/ W tabeli przedstawiono wartości średnie ± odchylenia standardowe; n = 3. Mean values shown in columns and denoted by different letters are statistically significant ($p < 0.05$) / Wartości średnie przedstawione w kolumnach i oznaczone różnymi literami różnią się statystycznie istotnie ($p < 0.05$).

The content of dry matter in different leaves of the garlic was in the range 79.0 ÷ 157.4 g·kg^{-1}. Results obtained in this study are similar to Dyduch and Najda [11] data. These authors reported that the dry matter in leaves of garlic was in the range 10.7 ÷ 15.8 %. The content of proteins was in the range 13.7 ÷ 35.7 g·kg^{-1} f.m. In comparison to parsley leaves 14.0 g·kg^{-1} the level of the proteins in garlic's leaves is similar. Additionally in comparison to other vegetables for *Allium* family the level of proteins is in similar range, for example leek roots contains 22.0 g·kg^{-1} f.m. and chives – 14.0 g·kg^{-1} f.m.. On the other hand the content of proteins was lower compared to the garlic cloves (64.0 g·kg^{-1} f.m. ÷ 92.6 g·kg^{-1} f.m.) [15, 19, 23].

The content of crude fat in leaves of different varieties of garlic was low (1.6 ÷ 5.6 g·kg^{-1} f.m.). The highest content of crude fat was determined in leaves of wild garlic. Compared to the onion and leek roots (4.0 g·kg^{-1} f.m., 8.0 g·kg^{-1} f.m. respectively), garlic leaves have lower content of this component.

The level of total carbohydrates in leaves of different varieties was in the range 50.8 ÷ 116.5 g·kg^{-1} f.m. Dyduch and Najda [11] reported higher content of total carbohydrates in leaves of autumn garlic cultivated from the air bulbs i.g. 188.2 ÷

215.2 g·kg^{-1} f.m. Garlic leaves have lower content of total carbohydrates compared to garlic cloves (260 ÷ 320 g·kg^{-1} f.m.) [20].

The content of dietary fibre was in the range 26.9 ÷ 57.0 g·kg^{-1} f.m. These results are different form data published by Dyduch and Najda [11] which showed that content of fiber in leaves of garlic was in the range 13.7 ÷ 16.0 g·kg^{-1} f.m. Garlic leaves are also the source of vitamin C and phenolic compounds. The level of vitamin C was in the range 56.1 ÷ 459.7 mg·kg^{-1} f.m. These results are different from data published by Dyduch and Najda [11] which reported that content of vitamin C in leaves of garlic was in the range 71.6 ÷ 85.1 mg·kg^{-1} f.m. As compared to the chives 310 mg·kg^{-1} f.m. the level of vitamin C in leaves of garlic is similar [19]. On the other hand Kmiecik and Lisiewska [18] showed that chive leaves contained about two times less vitamin C of edible parts. The amount of phenolic components depended on the variety of garlic's leaves. The highest level of these compounds was determined in 'Arkus' variety. This result is similar to data published by Mahmutovic et al. [23]. These authors reported that the level of phenolic components in leaves of autumn garlic was 1970 mg·kg^{-1}. They also reported higher content of polyphenols in leaves of spring and wild garlic (1490 mg·kg^{-1}, 1280 mg·kg^{-1} respectively). The content of phenolic components in leaves of different varieties used in our studies was lower that the level of these compounds in cloves. Some authors reported that garlic cloves contained 4000 ÷ 5500 mg·kg^{-1} f.m. polyphenols [22]. According to Oszmiański et al. [28] the kaempferol derivatives were found to be predominant in yellow leaves (2362.96 mg/100 g d.m.), followed by green leaves (1856.31 mg/100 g of d.m.) of *A. ursinum*. These results are different from data published by Błażewicz-Woźniak and Michowska [6]. They reported that dependent upon the ecotype, the sum of all flavonoids and *O*-dihydroxyphenyls varied from 318.5 and 788.2 mg/ 100 g of leaf d.m. of 'Dukla' ecotype to 342.9 and 709.0 mg/100 g of leaf d.m. in 'Roztocze' ecotype, respectively. Nencini et al. [25] reported that polyphenol content in leaves of three *Allium* species growing wild in Italy and two clones of *Allium sativum* L. ranged from 0.41 mg of GAE/g fresh weight to 0.59 mg of GAE/g fresh weight and was generally directly correlated with the antioxidant/antiradical activity. In our study we did not show this correlation. Rice-Evans [35] has explained that differences in activity among and within various classes of polyphenols result from their chemical structure and individual ability to transfer a hydrogen atom to a radical. The Folin-Ciocialteau method is a routine and commonly used to determine polyphenols. According to Prior et al. [33] this method is characterized by great simplicity and usability to a standard biological materials. It seems necessary to add that the disadvantage of this method is the low specificity. Folin-Ciocialteau reagent reacts with many compounds include sugars, ascorbic acid, amino acids and proteins, thereby increasing the result of the analysis of phenolic compounds.

Antioxidant activity of methanolic extracts of garlic was in the range 24.98 ÷ 29.22 mmol TEAC·kg^{-1}. In available literature there is a lack of data concerning antioxidant capacity of garlic leaves extract. Compared to the antioxidant activity of extracts prepared form fresh garlic cloves the antioxidant activity showed as the percentage of scavenged of free radicals was lower (mean for all varieties 48 %). There was no general differences in the antioxidant activity despite the differences between the content of total polyphenols and vitamin C, among the varieties of garlic. Antioxidant capacity is affected by mentioned antioxidants and another ones which were not detected, for example beta-carotene and chlorophyll. Gorinstein et al. [14] reported that the percentage of scavenged of free radicals for fresh cloves was 68.9 %. Nencini et al. [25] reported that leaves of tested clones of *Allium sativum* seem to have higher antioxidant capability than the bulbs, and what is more garlic exhibited very low antioxidant power in comparison with species growing wild.

The level of minerals compounds in leaves of garlic was varied. Albeit the leaves of wild garlic had the highest level of potassium, magnesium, iron and zinc. 'Harnaś' variety had the highest content of calcium. Leaves of 'Ornak' variety had highest level of magnesium, sulphur and zinc compared to the other cultivars (Tab. 3).

Compared to the content of selected minerals in cloves of garlic the leaves are better source of calcium. Haciseferogullari et al. [15] reported that in garlic cloves the content of calcium was 0.36 g·kg^{-1} f.m. The level of potassium and magnesium in our study are comparable with content of these compounds in cloves of garlic reported by Haciseferogullari et al. [15].

The content of sulphur in leaves of garlic was in the range 2.41 d.m. ÷ 6.22 g·kg^{-1} d.m. Muradic et al. [24] reported that the leaves of garlic contained similar level of sulphur. Additionally these authors did not report differences in content of this mineral in leaves and cloves. Arzanlou and Bohloodi [2] reported that green parts of garlic are good source of allicin.

Conclusions

1. Leaves of wild garlic had the significantly lowest amount of dry matter, proteins, total carbohydrates (including dietary fiber), ash, vitamin C, and antioxidant activity, but the highest level of crude fat, potassium, magnesium, iron and zinc as compared to winter and spring varieties.
2. At the same time, in most cases there were no significant differences in the level of basic chemical components, antioxidants, antioxidant activity and in the amount of minerals between winter and spring varieties as well as between winter varieties.

Literatura

[1] Anonim.: Hela Gusto czosnek niedźwiedzi. Gosp. Mięs., 2005, **12**, 46 (in Polish).

[2] Arzanlou M., Bohlooli S.: Introducing of green garlic plant as a new source of allicin. Food Chem., 2010, **120 (1)**, 179-183.

[3] Asdaq SM, Inamdar MN.: Potential of garlic and its active constituent, S-allyl cysteine, as antihypertensive and cardioprotective in presence of captopril. Phytomedicine, 2010, **17**, 1016-1026.

[4] Bat-Chen W., Golan T., Peri I., Ludmer Z., Schwartz B.: Allicin purified from fresh garlic cloves induces apoptosis in colon cancer cells via Nrf2. Nutr. Cancer, 2010, **62 (7)**, 947-57.

[5] Berginc K, Trdan T, Trontelj J, Kristl A.: HIV protease inhibitors: garlic supplements and first-pass intestinal metabolism impact on the therapeutic efficacy. Biopharm. Drug Dispos., 2010, **31**, 495-505.

[6] Błażewicz-Woźniak M., Michowska A.E.: The growth, flowering and chemical composition of leaves of three ecotypes of *Allium ursinum* L. Acta Agrobot., 2011, **64 (4)**, 171-180.

[7] Bordia T., Mohammed N., Thomson M., Ali M.: An evaluation of garlic and onion as antithrombotic agents. Prostaglandins Leukot. Essent. Fatty Acids**,** 1996, **54 (3)**, 183-186.

[8] Condrat D, Mosoarca C, Zamfir AD, Crisan F, Szaba MR, Lupea AX.: Qualitative and quantitative analysis of gallic acid in *Alchemilla vulgaris*, *Allium ursinum, Acorus calamus* and *Solidago virgaaurea* by chip- electrospray ionization mass spectrometry and high performance liquid chromatography. Cent. Eur. J. Chem., 2010, **8 (3)**, 530-535.

[9] Dębski B., Milner JA.: Molecular mechanissms of anticancer properties of garlic; the role of free radicals. Bromat. Chem. Toksykol., 2007, **40 (3)**, 223-228 (in Polish).

[10] Durak I., Kavutcu M., Ayta B.: Effects of garlic extract consumption on blood lipid and oxidant/antioxidant parameters in humans with high blood cholesterol. J. Nutr. Bioch., 2004, **15**, 373-377.

[11] Dyduch J., Najda A.: Estimation of the biological value of winter garlic leaves from early cultivation on bunch crop. Part II. Plants grown from planting air bulbs. EJPAU, 2001, **4 (2***)*, 04.

[12] Elkayam A., Mirelman D., Oleg E.: The effects of allicin on Wright in fructose-induced hyperinsulinemic, hyperlipidemic hypertensive rats. Am. J. Hypertens*.,* 2003, **12**, 1053-1056.

[13] Gonen A., Harats D., Rabinkov A., Miron T., Mirelman D., Wilchek M., Weiner L., Ulman E., Levkovitz H., Ben-Shushan D., Shaish A.: The antiatherogenic effect of allicin: possible mode of action. Pathobiology, 2005, **72 (6)**, 325-34.

[14] Gorinstein S., Drzewiecki J., Leontowicz H., Leontowicz M., Najman K., Jastrzębski Z., Zachwieja Z., Barton H., Shtabsky B., Katrich E., Trakhtenberg S.: Comparison of bioactive compounds and ntioxidant potentials of fresh and cooked Polish, Ukrainian, and Israeli garlic. J. Agric. Food Chem., 2005, **53**, 2726-2732.

[15] Haciseferogullari H., Özcan M., Demir F.: Calısır, S.: Some nutritional and technological properties of garlic (*Allium sativum* L.). J. Food Eng., 2005, **68**, 463-469.

[16] Ivanova A, Mikhova B, Najdenski H, Tsvetkova I, Kostova I.: Chemical composition and antimicrobial activity of wild garlic *Allium ursinum* of Bulgarian origin. Nat. Prod. Commun., 2009, **4 (8)**, 1059-1062.

[17] Janeczko Z., Sobolewska D.: Bear's garlic. A valuable herbal plant. Wiad. Ziel., 1995, **4**, 12-14.

[18] Kmiecik W., Lisiewska Z.: Effect of pretreatment and conditions and period of storage on some quality indices of frozen chive (*Allium schoenoprasum* L.). Food Chem., 1999, **67**, 61-66.

[19] Kunachowicz H., Nadolna I., Iwanow K., Przygoda B.: Tabele składu i wartości odżywczej żywności. Wyd. Lekarskie PZWL, Warszawa 2005.

[20] Kwiecień H.: Skład chemiczny i aktywność biologiczna czosnku (Chemistry and biological activity of garlic (*Allium sativum*). Wiad. Chem., 2008, **62**, 900-942.

[21] Kwiecień M., Winiarska-Mieczan A.: Czosnek jako zioło kształtujące właściwości prozdrowotne. Prob.. Hig. Epidemiol., 2011, **92 (4)**, 810-812 (in Polish).

[22] Leelarungrayub N., Rattanapanone V., Chanarat N., Gebicki J.M.: Quantitative evaluation of the antioxidant properties of garlic and shallot preparations. Nutrition, 2006, **22**, 266-274.

[23] Mahmutovic O., Mujic E., Toromanovic J., Mustovic F., Muradic S., Huseinovic S., Sofic E.: Comparative analysis of total phenols and sulfur content in some plant organs of ramsons and two garlic species. Planta Med., 2009, **75***,* PD43. DOI: 10.1055/s-0029-1234522.

[24] Muradic S., Karacic D., Mahmutovic O., Mutovic F., Sofic E., Kroyer G.: Total sulphur and organosulphur compounds in garlic and ramsons plant organs at the end of vegetative. Planta Med., 2010, **76**, P292. DOI: 10.1055/s-0030-1264590.

[25] Nencini C., Cavallo F., Capasso A., Franchi G.G., Giorgio G., Micheli L.: Evaluation of antioxidative properties of Allium species growing wild in Italy. Phytother. Res., 2007, **21**, 874-878.

[26] Official Methods of Analysis of AOAC International. 18th Ed., Gaintersburg, Association of Official Analytical Chemists International, 2006.

[27] Omar S.H., Al-Wabel N.A.: Organosulfur compounds and possible mechanism of garlic in cancer. Saudi Pharmac. J., 2010, **18**, 51-58.

[28] Oszmiański J., Kolniak-Ostek J., Wojdyło A.: Characterization and content of flavonol derivatives of *Allium ursinum* L. Plant. J. Agric. Food Chem., 2013, **61 (1)**, 176-184.

[29] Swain T., Hillis W. E.: The phenolic constituents of *Prunus domestica* (L.). The quantity of analysis of phenolic constituents. J. Sci. Food Agric., 1959, **10**, 63-68.

[30] Pellegrini N., Serafini M., Colombi B., Del Rio D., Salvatore S., Bianchi M., Brighenti F.: Total antioxidant capacity of plant foods, beverages and oils consumed in Italy assessed by three different in vitro assays. J. Nutr., 2003, **133**, 2812-2819.

[31] PN-EN-13804. Food products. Determination of trace elements. Criteria.

[32] PN-EN-14084:2003. Food products. Determination of trace elements. Determination of Pb, Cd, Zn, Cu, and Fe content by the use of atomic absorbtion spectroscopy (AAS) after microwave mineralization.

[33] Preuss H. G., Clouatre D., Mohamadi A., Jarrell S.T.: Wild garlic has a greater effect than regular garlic on blood pressure and blood chemistries of rats. Int. Urol. Nephrol.**,** 2001, **32 (4)**, 525-30.

[34] Prior R.L., Wu X., Schaich K.*:* Standardized methods for the determination of antioxidant capacity and phenolics in foods and dietary supplements. J. Agric. Food Chem., 2005, 53, 4290-4302.

[35] Re R., Pellegrini N., Proteggente A., Pannala A., Yang M., Rice-Evans C.: Antioxidant activity applying an improved ABTS radical cation decolorization assay. Free Radic. Biol. Med.*,* 1999, **26**, 1231-1237.

[36] Rice-Evans C.: Flavonoid antioxidants. Curr. Med. Chem., 2001, **8 (7)**, 797-807.

[37] Rutkowska U.: Wybrane metody badań składu i wartości odżywczej żywności. PZWL, Warszawa 1981.

[38] Shirazd H., Taji F., Rafieian-Kopaei M.: Correlation between antioxidant activity of garlic extracts and WEHI-164 fibrosarcoma tumor growth in BALB/c mice. J. Med. Food, 2011, **14 (9)**, 969-974.

[39] Tang FY, Chiang EP, Chung JG, Lee HZ, Hsu CY.: S-allylcysteine modulates the expression of E-cadherin and inhibits the malignant progression of human oral cancer. J. Nutr. Biochem., 2009, **20**, 1013-1020

[40] Zhang W., Ha M., Gong Y., Xu Y., Dong N., Yuan Y.: Allicin induces apoptosis in gastric cancer cells through activation of both extrinsic and intrinsic pathways. Oncol. Rep., 2010, **24 (6)**, 1585-1592.

PODSTAWOWY SKŁAD CHEMICZNY, ZAWARTOŚĆ MIKRO- I MAKROELEMENTÓW ORAZ WŁAŚCIWOŚCI PRZECIWUTLENIAJĄCE LIŚCI RÓŻNYCH ODMIAN CZOSNKU POLSKIEGO POCHODZENIA

S u m m a r y

Celem badań było porównanie podstawowego składu chemicznego, zawartości mikro- i makroskładników, aktywności przeciwutleniającej w liściach czosnku odmian ozimych i jarej otrzymanych z firmy POLAN (Kraków, Polska), a także w liściach czosnku niedźwiedziego. Analizowano zawartość: suchej masy, białka, tłuszczu, węglowodanów ogółem, błonnika pokarmowego oraz popiołu standardowymi metodami AOAC, jak również zawartość wybranych składników mineralnych metodą ASA. Oznaczono także zawartość witaminy C (metodą Tillmansa), polifenoli metodą Folina-Ciocaltea'a. Wykonano ponadto oznaczenie zdolności eliminowania wolnego rodnika $ABTS^{\bullet+}$ metodą Re i wsp.

Liście czosnku niedźwiedziego charakteryzowały się istotnie najmniejszą zawartością suchej masy (79,0 $g \cdot kg^{-1}$), białka (13,7 $g \cdot kg^{-1}$), węglowodanów (50,8 $g \cdot kg^{-1}$), błonnika pokarmowego (26,9 $g \cdot kg^{-1}$), popiołu (8,9 $g \cdot kg^{-1}$), witaminy C (956,1 $mg \cdot kg^{-1}$) i najmniejszą aktywnością przeciwutleniającą (25,0 mmol $TEAC \cdot kg^{-1}$), ale największą zawartością tłuszczu surowego (5,6 $g \cdot kg^{-1}$), potasu (34,6 $g \cdot kg^{-1}$), magnezu (1,72 $g \cdot kg^{-1}$), żelaza (230,3 $mg \cdot kg^{-1}$) i cynku (58,8 $mg \cdot kg^{-1}$) w stosunku do czosnku odmian ozimych i odmiany jarej. Równocześnie nie stwierdzono jednoznacznych różnic w składzie podstawowym (białko 20,9 ÷ 35,7 $g \cdot kg^{-1}$, tłuszcz 1,6 ÷ 2,8 $g \cdot kg^{-1}$, węglowodany ogółem 61,3 ÷ 116,5 $g \cdot kg^{-1}$, błonnik 33,7 ÷ 57.0 $g \cdot kg^{-1}$, popiół 8.9 ÷ 14.1 $g \cdot kg^{-1}$), poziomie przeciwutleniaczy (witamina C 75,4 ÷ 459,7 $mg \cdot kg^{-1}$, polifenole 335,3 ÷ 1895,1 $mg \cdot kg^{-1}$), aktywności antyoksydacyjnej (27,0 ÷ 30,1 mmol $TEAC \cdot kg^{-1}$) i poziomie składników mineralnych (wapń: 7,55 ÷ 28,9 $g \cdot kg^{-1}$, potas: 15,9 ÷ 28,0 $g \cdot kg^{-1}$, magnez: 0,85 ÷ 1,32 $g \cdot kg^{-1}$, siarka: 2,41 ÷ 6,22 $g \cdot kg^{-1}$, żelazo: 34,4 ÷ 85,7 $mg \cdot kg^{-1}$, cynk: 9,32 ÷ 13,8 $mg \cdot kg^{-1}$) pomiędzy odmianami ozimymi a odmianą wiosenną, jak również pomiędzy odmianami zimowym.

Key words: liście czosnku, czosnek niedźwiedzi, skład chemiczny, fenole ogółem, witamina C