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NUTRITIONAL VALUE OF CHIVE EDIBLE FLOWERS

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Abstract. Edible flowers have been used in traditional and herbal medicine since ancient times, but its nutritional value have not been studied in depth. The lavender-pink globular flower heads of chive not only beautify the garden or dried bouquets, but they can also be used to prepare chive vinegar, salads or soups. The aim of this work was to determine the nutritional value of flowers of the chive cultivated at the Horticultural Experiment Station in Dołuje (north-western Poland) in the years 2009 and 2010. In the raw plant material, the content of dry matter, total ash, total protein, titratable acidity, vitamin C as L-ascorbic acid, total and reducing sugars, fat, crude fibre, polyphenols, total carotenoids, chlorophylls, pungency, free radical scavenging activity and energy value were measured. The *Allium schoenoprasum* L. dried flowers were extracted by ethanol at 50°C and at room temperature (maceration). The obtained extracts were analyzed by GC-MS method. The analysis revealed that the flowers contained much important fatty acids with palmitic acid (7.94–16.94%), linoleic acid (7.63–13.45%) and stearic acid (3.13–31.16%), the most abundant saturated and unsaturated fatty acids, as well as γ-sitosterol (3.41–6.42%), campesterol (0.34–0.66%), fucosterol (0.29–0.51%) and vitamin E (0.16–0.49%). Moreover, in the dry plant material content of total flavonoids was assessed.

Key words: *Allium schoenoprasum* L., chemical compounds, biological value, antioxidants, GC, MS

INTRODUCTION

Allium schoenoprasum L. is native to the cool regions of Europe and Asia. It has been cultivated by gardeners since the Middle Ages, now can be found at home anywhere.

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This small bulbous member of the onion family (*Alliaceae*), is widely used as a culinary herb to impart mild onion flavour to many foods, including salads, soups, vegetables and sauces [Gardner 1998, Small and Deutsch 2001].

Chive has slim, dark green leaves and pale purple edible flowers. The plant was used in traditional folk medicine to stimulate digestion, treat anemia, enhance the immune system and to cleanse the blood [Roberts 2000]. Recent studies investigated the antioxidant properties of the bulb, leaf and stalk of *Allium schoenoprasum* L. [Stajner et al. 2004].

All the *Allium* species may help to prevent tumor promotion, cardiovascular diseases and aging due to their high concentrations of total flavonoids, carotenoids and chlorophylls, and very low concentrations of toxic oxygen radicals [Stajner et al. 2006]. This vegetable is a good source of vitamins C and E, dietary fibre and essential minerals such as potassium, calcium and folic acid [Vaughan and Geissler 2009].

The chemical composition of chive leaves is well-known, while there is still lack of information about the nutritional value of the *Allium schoenoprasum* flowers.

Biologically active compounds may be obtained from the plant material by organic solvent extraction (maceration, Soxhlet extraction, extraction under reflux, percolation). The choice of solvent is based on its selectivity for the substances to be extracted. A polar organic solvent (ethanol, methanol, or an aqueous alcoholic mixture) is employed in attempt to extract as many compounds as possible. This is based on the ability of alcohol to increase cell wall permeability and extraction of large amounts of polar, medium and low-polarity constituents [Sarker et al. 2006, Raaman 2006].

The aim of the study was to determine biological value of the fresh chive flowers and the components of chive dried flowers (*Allium schoenoprasum* L.) ethanolic extracts.

MATERIAL AND METHODS

The experiment was carried out in 2009–2010 at the Horticultural Experiment Station in Dołuje which belongs to the Department of Horticulture of West Pomeranian University of Technology in Szczecin. The laboratory part of the experiment was conducted in the Laboratory of Storage and Processing (Department of Horticulture) and in the Department of Organic Chemistry of West Pomeranian University of Technology in Szczecin. The research material consisted of fresh and dried flowers of chive (*Allium schoenoprasum* L.), cultivar 'Erfurcki Olbrzymi'. The investigated material was harvested from 2-year-old plants.

Mineral fertilization was quantified according to the results of chemical analysis of the soil. The fertilization was adjusted to the requirements proper for this species ($mg \cdot dm^{-3}$): 70 N, 60 P, 160 K [Sady 2006]. During the growing season the crop management was carried out. It included mainly irrigation, weeding and soil cultivation.

The flower harvest was done at full-bloom stage (in the middle of May). The chemical analyses of raw plant material included determination of the content of dry matter (drying at 105°C to constant weight), total ash (incineration of samples in 500°C), total protein (using factor 6.25 for amount of nitrogen determined by the method of

Kjeldahl), crude fibre [Klepacka 1996], total and reducing sugars (by the method of Luff-Schoorl), fat by Soxhlet's method [Krełowska-Kułas 1993], total chlorophyll, chlorophyll a and b [Lichtenthaler and Wellburn 1983], vitamin C as L-ascorbic acid (by the method of Tillmans), titratable acidity [Krełowska-Kułas 1993], total carotenoids [Lichtenthaler and Wellburn 1983], total polyphenols – by spectrophotometer, using gallic acid as reference, and Follin-Ciocalteu reagent [Singleton and Rossi 1965]. Scavening effect of chive flowers on DPPH-radical was determined according to the method of Yen and Chen [1995]. Raw homogenised material was diluted 200 times in 100% methanol. DPPH percent inhibition was calculated according to Rossi et al. [2003]. The content of pyruvic acid (PA) produced as result of allinase action which indicates the pungency of onion vegetables was assessed by the Schwimmer and Weston [1961] method, modified by Horbowicz [1998]. Energy value of fresh chive flowers was assessed according to formula given by Kunachowicz et al. [1998].

Part of the raw plant material was dried in a through-flow laboratory dryer set at 35°C. In dried and pulverized material, the concentration of flavonoid compounds was determined using the spectrophotometric method [FP VI, 2002].

In both years of the study, each analysis was carried out in triplicates.

Moreover, the chive dried flowers were also used to prepare the ethanolic extracts. Two samples (3 g) of chive flowers were weighted and 100 ml of solvent (96% ethanol) were added. Extraction was performed by: a) heating at 50°C using magnetic stirrer for 3 hours (after filtration, the residue was re-extracted with the same amount of solvent) and b) maceration at room temperature for 14 days. The rotating evaporator was used to eliminate the solvent.

The obtained extracts were filtered and dried under reduced pressure to give 0.39 g; 13% (extraction at 50°C) and 0.31 g; 10.33% (maceration), semi-solid, yellowy-brown residue, respectively.

Qualitative analysis of the samples was performed by GC-MS using a Hewlett-Packard chromatograph 6890 series coupled with 5973 Network Mass Selective Detector. The separation was achieved using an Agilent 19091S-433 HP-5MS fused silica capillary column 30 meters length, 0.25 mm in diameter and with 0.25 μm thick stationary phase film. The GC oven was programmed from 40°C (kept constant for 5 minutes) at a rate of 30°C per minute to 60°C, next to 230°C at a rate of 6°C per minute (kept constant for 10 minutes) and finally at a rate of 30°C per minute to 280°C (kept constant for 30 minutes). The total run time was about 76 minutes. Flow rate of helium was 2.0 ml·min^{-1} at 2.4 psi. The injector temperature was 280°C, the mass detector temperature was 280°C. The injection volume was 4 μl and the solvent delay was 4 minutes. The samples (as solutions in dichloromethane) were introduced using split injection (split ratio, 5.4:1).

The identification of the components was based on the calculation of their retention indices (RI), obtained using n-alkanes (C_6-C_{18}) with those of authentic compounds available in our laboratory (stearic, palmitic and oleic acids). Further identification was made by matching their recorded mass spectra with those stored in the Wiley NBS75K.L and NIST/EPA/NIH Mass Spectral Library (2002 version) of the GC/MS data system. Compounds were identified with a resemblance percentage above 90%.

RESULTS AND DISCUSSION

On the base the study results presented in table 1, it was proved that the flowers of chive are characterized by a very high biological value – higher compared with data given in the case of the leaves of chive [Lisiewska and Kmiecik 1998, Kmiecik and Lisiewska 1999, Stajner et al. 2004, Larsen and Christensen 2005, Viña and Cerimele 2009, Parvu et al. 2010].

Table 1. Content of some chemical compounds in the fresh chive flowers
Tabela 1. Zawartość wybranych składników chemicznych w świeżych kwiatach szczypiorku

Dry matter – Sucha masa, %	20.01
Total ash (% f.w.) – Popiół ogólny (% św.m.)	0.77
Total sugars (% f.w.) – Cukry ogółem (% św.m.)	10.00
Reducing sugars (% f.w.) – Cukry redukujące (% św.m.)	2.13
Total protein (% f.w.) – Białko ogółem (% św.m.)	3.07
Crude fibre (% f.w.) – Błonnik surowy (% św.m.)	1.22
Fat (% f.w.) – Tłuszcz (% św.m.)	0.69
Titratable acidity (% citric acid f.w.) – Kwasowość ogólna (% kw. cytr. św.m.)	0.34
L-ascorbic acid (mg·100 g^{-1} f.w.) – Kwas L-askorbinowy (mg·100 g^{-1} św.m.)	108.48
Total polyphenols (mg·100 g^{-1} f.w.) – Polifenole ogółem (mg·100 g^{-1} św.m.)	375.76
Total flavonoids (% d.w.) – Flawonoidy ogółem (% s.m.)	0.775
Total carotenoids (mg·kg^{-1} f.w.) – Karotenoidy ogółem (mg·kg^{-1} św.m.)	58.24
Total chlorophyll (mg·kg^{-1} f.w.) – Chlorofile ogółem (mg·kg^{-1} św.m.)	166.22
Chlorophyll a (mg·kg^{-1} f.w.) – Chlorofil a (mg·kg^{-1} św.m.)	108.29
Chlorophyll b (mg·kg^{-1} f.w.) – Chlorofil b (mg·kg^{-1} św.m.)	41.91
Antioxidant activity – Aktywność antyoksydacyjna (% DPPH)	14.12
Pungency (μmols PA·g^{-1} f.w.) – Ostrość (μmole KP·g^{-1} św.m.)	16.79
Energy value – Wartość energetyczna (kcal·g^{-1})	0.58

The content of dry matter, total sugars and L-ascorbic acid in the chive flowers was higher in comparison with the results obtained by Lisiewska and Kmiecik [1998] for the chive leaves, respectively by 8.10%, 5.99% f.w. and 9.48 mg·100 g^{-1} f.w. Similar results are presented by Kmiecik and Lisiewska [1999].

Analogically to the above data, Viña and Cerimele [2009] determined lower L-ascorbic acid content in the chive leaves than it was assessed for the flowers in the present study. They also determined a lower content of total polyphenols (84.4 mg·100 g^{-1} f.w.), but almost three times higher content of carotenoids (168 mg·kg^{-1} f.w.).

In opinion of Parvu et al. [2010] the main polyphenolic compounds of chive leaves are p-coumaric acid, frulic acid, isoquercitrin and rutin. While, Yoshida et al. [2009] isolated from *Allium schoenoprasum* flowers malonic diesters of cyanidin 3-glicoside or cyanidin 3-(3-acetylglucoside) and kaempferol 3-sophoroside-7-glucosiduronic acid or kaempferol 3-sophoroside-7-methylglucosiduronic acid.

Table 2. Compounds identified in *Allium schoenoprasum* L. flower ethanolic extracts
Tabela 2. Związki zidentyfikowane w ekstraktach etanolowych z kwiatów *Allium schoenoprasum* L.

No.	Compound Związek	Retention time Czas retencji min	Retention index Indeks retencji	Extraction at 50°C Ekstrakcja w temp. 50°C %	Maceration Maceracja %	Identification method Metoda identyfikacji
1.	acetic acid	3.53	662	1.27	0.48	RI, MS
2.	furfural	7.51	831	0.27	0.08	RI, MS
3.	furfuryl alcohol	8.09	848	0.27	0.24	RI, MS
4.	2,5-dimethyltiophene	9.26	878	0.71	0.23	RI, MS
5.	3,4-dimethyltiophene	9.37	881	0.15	-	RI, MS
6.	methyl n-propyl disulfide	9.95	894	0.32	-	RI, MS
7.	5-methyl-2-furaldehyde	10.79	912	0.73	0.20	RI, MS
8.	dimethyl trisulfide	10.96	916	0.24	0.16	RI, MS
9.	3,5-dihydroxy-6-methyl-2,3-dihydro-4H-pyran-4-one	15.44	993	3.83	1.94	RI, MS
10.	2,3-dihydrobenzofuran	17.16	1066	2.46	1.16	RI, MS
11.	2-methoxy-4-vinylphenol	19.39	1237	1.66	1.39	RI, MS
12.	acetoguaiacon	23.14	1485	-	0.12	RI, MS
13.	lauric acid	24.50	1564	-	0.22	RI, MS
14.	myristic acid	28.21	1761	0.61	0.64	RI, MS
15.	hexadecyl 2-chloropropanoate	29.45	1822	0.25	0.21	RI, MS
16.	pentadecanoic acid	29.94	1845	0.19	0.26	RI, MS
17.	1-octadecene	30.27	1861	0.92	0.18	RI, MS
18..	19-hexadecenoic acid	31.37	1911	-	0.18	RI, MS
19.	**palmitic acid**	**31.77**	**1929**	**7.94**	**16.94**	**S, RI, MS**
20.	palmitic acid ethyl ester	32.13	1944	0.12	1.12	RI, MS
21.	octadecanal	33.18	1989	0.18	0.33	RI, MS
22.	5-eicosene	33.53	2004	0.30	-	RI, MS
23.	oleic acid	33.86	2018	0.36	0.12	S, RI, MS
24.	**linoleic acid**	**34.42**	**2041**	**13.45**	**7.63**	**RI, MS**
25.	9,12,15-octadecatrienal	34.52	2045	-	4.94	RI, MS
26.	linolenic acid methyl ester	34.57	2047	7.29	-	RI, MS
27	9,17-octadecadienal	34.68	2051	1.49	-	RI, MS
28.	**stearic acid**	**34.99**	**2064**	**3.13**	**31.16**	**S, RI, MS**
29.	arachidic acid	38.86	2211	0.45	0.78	RI, MS
30.	(Z)-9-tricosene	42.73	2344	0.54	0.26	RI, MS
31.	behenic acid	44.98	2416	0.27	0.12	RI, MS
32.	octadecylcyclohexane	45.49	2431	0.36	0.15	RI
33.	1-hexacosene	46.37	2458	0.33	0.09	RI, MS
34.	1-eicosanol	46.65	2467	1.55	0.59	MS
35.	13-docosenamide	47.74	2499	0.18	-	RI, MS
36.	9-hexacosene	49.04	2537	0.41	0.24	RI, MS
37.	11-cyclopentylheneicosane	49.43	2548	1.93	0.73	RI
38.	1,3-didecylcyclohexane	52.55	2634	0.57	-	RI
39.	vitamin E	54.00	2672	0.49	0.16	MS
40.	campesterol	56.37	2732	0.66	0.34	RI, MS
41.	γ-sitosterol	59.08	2798	6.42	3.41	RI, MS
42.	fucosterol	59.61	2810	0.51	0.29	RI, MS
43.	9,19-cyclolanost-24-en-3β-ol	61.51	2854	1.08	0.68	RI, MS

RI: retention index
MS: mass spectrum
S: authentic sample

Typical volatile substances of the secondary S-metabolites in bulbiferous plants are alk(en)ylcysteinsulphates. These substances are instable and when the tissue is disturbed they rapidly degrade. The product of degradation is allicin, which produces the typical foul odour [Bloem et al. 2003]. Pungency may also be an indicator of the medicinal quality of onion cultivars because many organosulphur compounds present in fresh onion and other commercially important *Allium* species exhibit cancerpreventive [Block 1994], antibacterial [Yoshida et al. 1999], antiviral properties [Weber et al. 1992].

Jadczak and Wójcik-Stopczyńska [2007] assessed the content of pyruvic acid in the shallot crop. The control plants contained 9.72 and the plants covered with polypropylene non-woven fabric 9.25 μmols of pyruvic acid per 1 g of fresh weight. Horbowicz and Bąkowski [1998] considered cultivars of onion containing 10.2–11.7 μmols PA·g^{-1} to be of medium pungency. Schwimmer and Weston [1961] divided onion cultivars into three categories of pungency: low-pungent (2–4 μmols PA), medium pungent (8–10 μmols PA), and pungent (15–20 μmol PA). The pungency determined in our experiment, for the chive flowers, was high and amounted on average 16.79 μmols PA·g^{-1} f.w.

Determined in the experiment energy value of chive flowers (0.58 kcal per gram) was lower according to USDA [2010] data for fresh chive leaves (0.90 kcal per gram).

The chemical analysis of components of chive flowers revealed the presence of 48 compounds in the extract obtained by heating at 50°C and 43 compounds in the ethanolic extract obtained by maceration (tab. 2). The aliphatic hydrocarbons: docosane (0.75–1.36%), eicosane (1.00–1.54%), heneicosane (0.31–0.50%), heptacosane (0.16–2.46%), hexacosane (1.46–3.38%), nonacosane (2.78–4.09%), octadecane (0.24% – extraction at 50°C), tetracosane (0.25–0.35%) and triacontane (0.75% – extraction at 50°C) are not presented in the table, because they are of dietary interest.

The major components of *Allium schoenoprasum* L. flowers ethanolic extracts were saturated fatty acids (palmitic, stearic, arachidic, myristic, lauric and behenic) and its esters, unsaturated fatty acids (linoleic and oleic, omega-6 and omega-9, respectively), and phytosterols (γ-sitosterol, campesterol, fucosterol, 9,19-cyclolanost-24-en-3β-ol).

The concentration of identified fatty acids and phytosterols depend on the extraction technique. The highest concentration of saturated fatty acids (49.86%) and lowest concentration of unsaturated fatty acids (7.75%) and sterols (4.72%) were noticed in the extract obtained at room temperature. The better results in the extraction of unsaturated fatty acids (13.81%) and sterols (8.67%) were obtained when the higher temperature (50°C) was applied (fig. 1).

Tsiaganis et al. [2006] determined the fatty acids composition of the main edible *Allium* species (onion, garlic and leek) by gas chromatography. They found that four fatty acids: linoleic (46–53%), palmitic (20–23%), oleic (4–13%) and α-linolenic (3–7%), characterize the genus of *Allium* at a percentage above 80%.

Kowalski and Rodkiewicz [2009] assessed the content of fatty acids in the oil from *Allium* seeds. Polyunsaturated and monounsaturated fatty acids dominated in all tested fats (up to 51.4% and 19.6%, respectively). The highest fat content was found in *A. cepa* (25.3–30.2%), while the seeds of *A. schoenoprasum* contained about 16% of fat. Linoleic acid (44.3%) was the most abundant fatty acid found in the fat of chive.

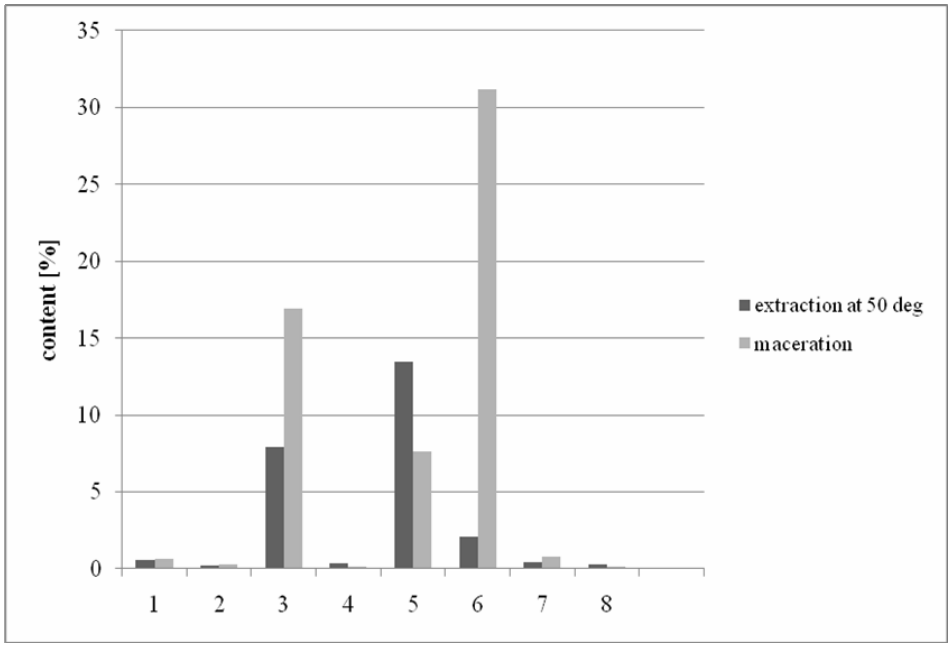

Fig. 1 Content of fatty acids in chive flower ethanolic extracts according to the temperature of extraction: 1 – myristic acid; 2 – pentadecanoic acid; 3 – palmitic acid; 4 – oleic acid; 5 – linoleic acid; 6 – stearic acid; 7 – arachidic acid; 8 – behenic acid

Rys. 1. Zawartość kwasów tłuszczowych w ekstraktach etanolowych z kwiatów szczypiorku w zależności od temperatury ekstrakcji: 1 – kwas mirystynowy; 2 – kwas pentadecanowy; 3 – kwas palmitynowy; 4 – kwas oleinowy; 5 – kwas linolowy; 6 – kwas stearynowy; 7 – kwas arachidowy; 8 – kwas behenowy

The content of linoleic (7.63–13.45%), palmitic (7.94–16.94%) and oleic (0.12–0.36%) acids found in chive flower extracts were lower compared to literature cited above.

Recent studies indicate that fatty acids and plant sterols are important for human health and nutrition. Fatty acids form complexes with protein and are transported to various tissues in the body where are metabolized into other compounds, or serve as source of energy [Kamel and Kakuda 2008]. Phytosterols are known as cholesterol-lowering agents. Same evidence suggests that plant sterols may have anti-inflammatory, possible antioxidant and anticancer activity [Awad and Fink 2000, Bouic 2001, Wang et al. 2002].

The other important components identified in the chive flowers were sulfur-containing compounds: 2,4-dimethylthiophene, 3,4-dimethylthiophene, methyl n-propyl disulfide and dimethyl trisulfide – which are responsible for the chive aroma and onion [Bernhard 1969, Leino 1992] as well as 3,5-dihydroxy-6-methyl-2,3-dihydro-4H-pyran-4-one, which may play important role in the prevention of colon cancer in human cells [Ban et al. 2007].

Organosulphur compounds are known for anticancer, anti-HIV and antifungal properties, so diet rich in plants from family *Alliaceae* have beneficial health effects [Haq and Ali 2003].

CONCLUSIONS

1. Flowers of chive are characterized by a very high biological value (L-ascorbic acid – 108.48 mg·100 g^{-1} f.w., total polyphenols – 375.76 mg·100 g^{-1} f.w.) and a high pungency level (16.79 μmols PA·g^{-1} f.w.).

2. *Allium schoenoprasum* L. flowers are good source of saturated (12.4–49.86%) and unsaturated (7.75–13.81%) fatty acids, sterols (4.72–8.67%), vitamin E (0.16–0.49%) and sulfur-containing compounds (0.39–0.81%). Concentration of these compounds in the extracts obtained strictly depends on the extraction technique.

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WARTOŚĆ ODŻYWCZA JADALNYCH KWIATÓW SZCZYPIORKU

Streszczenie. Kwiaty jadalne stosowano w medycynie tradycyjnej i ziołolecznictwie już w czasach starożytnych, wciąż jednak brak jest dokładnych danych dotyczących ich wartości odżywczej. Lawendowo-różowe, kuliste kwiaty szczypiorku nie tylko upiększają ogrody czy suche bukiety, mogą być również używane do przyrządzenia aromatycznego octu, sałatek czy zup. Celem niniejszej pracy było określenie wartości odżywczej kwiatów szczypiorku uprawianego w latach 2009 i 2010 w Ogrodniczej Stacji Doświadczalnej w Dołujach (północno-zachodnia Polska). W świeżym materiale roślinnym oznaczono zawartość suchej masy, popiołu ogólnego, białka ogółem, kwasowość ogólną, zawartość kwasu L-askorbinowego, cukrów ogółem i redukujących, tłuszczu, błonnika surowego, polifenoli ogółem, karotenoidów ogółem, chlorofili, ostrość, aktywność antyoksydacyjną i wartość energetyczną. Kwiaty *Allium schoenoprasum* L. (wysuszony materiał roślinny) ekstrahowano etanolem w temperaturze 50°C i w temperaturze otoczenia (maceracja). Otrzymane ekstrakty analizowano metodą GC-MS. Analiza wykazała, że kwiaty szczypiorku zawierają ważne kwasy tłuszczowe, nasycone i nienasycone, w tym kwas palmitynowy (7.94–16.94%), kwas linolowy (7.63–13.45%) i stearynowy (3.13–31.16%), jak również γ-sitosterol (3.41–6.42%), kampesterol (0.34–0.66%), fukosterol (0.29–0.51%) i witaminę E (0.16–0.49%). W suchym materiale roślinnym określono również zawartość flawonoidów ogółem.

Słowa kluczowe: *Allium schoenoprasum* L., związki chemiczne, wartość biologiczna, antyoksydanty, GC, MS

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