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Nutraceutical and multi-element profiles of elephant garlic (*Allium ampeloprasum* L.) and common garlic (*Allium sativus* L.) from Slovenia

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Abstract

Bulbous *Allium* spp. such as "big-headed" elephant garlic (*Allium ampeloprasum* L.) and common garlic (*Allium sativus* L.) contain a wide range of bioactive compounds with health-promoting properties and are most commonly used as food seasonings. The objective of the present study is to verify if there is a difference in selected nutraceuticals (dry matter, TPC, and allicin) and elemental profiles (macro- and micro-elements) of the two *Allium* species produced in two growing seasons in Jablje, Slovenia (a sub-Alpine region). The total phenolic content (TPC) was determined spectrophotometrically, the organosulfur compound allicin was determined by the HPLC analysis and the multi-element profiles by an inductively coupled plasma-mass spectrometry (ICP-MS). The results show that elephant garlic bulbs had slightly lower TPC and about six times less allicin, a major organosulfur compound. The content of macro- (Mg, P, S, K, and Ca) and micro-elements (Cr, Mn, Fe, Co, Cu, Zn, and Mo) varied considerably among the *Allium* samples studied. The greatest differences between bulbs of elephant garlic and common garlic were observed for P, Ca, S, and Fe. Our results confirm different nutritional characteristics of the bulbs and cloves of the two *Allium* species.

Key words: allicin, *Allium* spp., ICP-MS, macro-elements, total phenolic content.

Introduction

The bulbous *Allium* species contain a variety of phytochemicals with antioxidant and oxidative properties (Lu et al., 2011). Elephant garlic (*Allium ampeloprasum* L.), also known as big-headed garlic which resembles leeks, is a lesser known species with much larger cloves than common garlic (*Allium sativus* L.) (Ceccanti et al., 2021). Garlic is a well-known spice and an economically important bulb species traditionally used as food and medicine (Shang et al., 2019).

Both species contain a variety of bioactive components such as organosulfur compounds, the most active of which are diallyl thiosulfonate (allicin) and S-allylcysteine sulfoxide (alliin) (Marsic et al., 2019; Shang et al., 2019). Allicin is produced by an enzymatic reaction when raw cloves are peeled, sliced, crushed, or chopped. However, the preservation of allicin is complicated by its unstable and reactive nature. Once formed, it readily transforms into other compounds such as allysulfides, vinyldithines, and ajoenes (Liang et al., 2013). Many studies indicate that allicin is responsible for the characteristic pungent odour, taste, and most of its biological properties (Yusuf et al., 2018; Divya et al., 2017). The key characteristic of elephant garlic is its lower content of sulphur-containing compounds, which favours this species over garlic with a similar but more delicate flavour (Loppi et al., 2021).

Another very large group of bioactive compounds in cloves of both species that are of great importance for human nutrition includes sulphur-free polyphenolic compounds such as anthocyanins, flavonols, tannins, flavonoids, phenolic acids, phytosterols, carotenoids, and saponins (Najda et al., 2016). Furthermore, they contain a variety of vitamins and essential and non-essential elements such as phosphorus, calcium, and iron (Raab et al., 2016). The present study investigates whether there are differences in the nutraceutical and multi-element profiles of elephant garlic and common garlic grown in Slovenia in two consecutive production seasons.

Material and Methods

The *Allium* plant samples used in this study were commercially available elephant garlic (*Allium ampeloprasum* L.) and the Slovenian common garlic variety ‘Jesenski Anka’ (*Allium sativus* L.), which was registered in the national catalogue in 2011 (MAFFSI, 2021). Both species were grown in the experimental field of the Infrastructure Centre Jablje, Agricultural Institute of Slovenia, Slovenia (304 m above the sea level; 46.151°N 14.562°E; sub-Alpine climate). Production took place over two growing seasons (I. – between November 2015 and June 2016; II. – between November 2016 and June 2017) in unheated, protected tunnels following the established cultivation technique for garlic growing. Air temperatures at the experimental site during both seasons are shown in Fig. 1. Harvested bulbs were air dried and stored in dry and dark conditions until analysed. In addition, an edible garlic sample from China was purchased from Slovenian food retail market and used as a comparative sample.

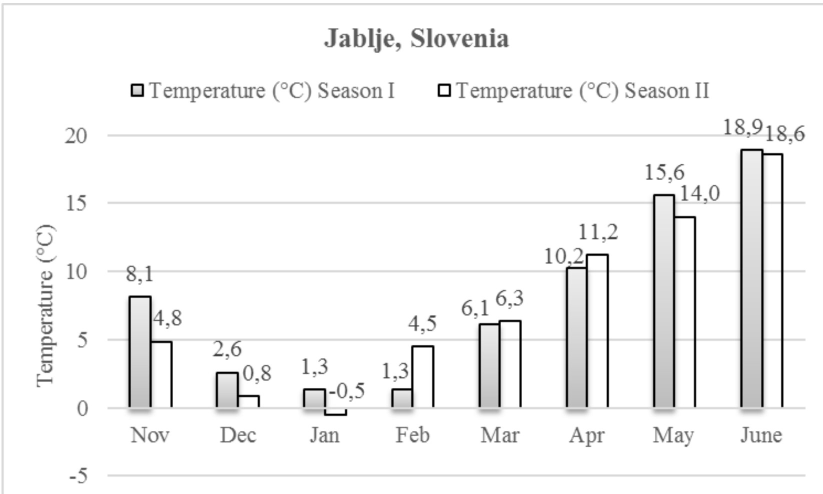

Fig. 1. Air temperatures at the experimental site during growing seasons (I., II.) as obtained from the national meteorological data service centres.

The bulbs of elephant garlic and common garlic samples (Fig. 2) were analysed for their nutraceutical properties and multi-element profile. Allicin content was determined according to the method described by Liang et al. (2013). Peeled or dehusked fresh cloves from ten bulbs were coarsely ground in a laboratory blender. Five grams of the material was mixed with 25 mL of double distilled water and homogenized with an Ultra-Turrax (IKA, Germany) for 1 minute at 11,000 rpm. After the extraction in a shaker at room temperature for 30 minutes, the samples were centrifuged and filtered. The extracts were lyophilized, redissolved, and analysed by HPLC (Agilent 1260 Infinity) using a C18 and analytical guard column. UV-Vis absorption spectra of allicin were recorded at 220 nm. The extracts were diluted in a mobile phase solution and analysed in triplicate. The allicin standard was obtained from LGC (Middlesex, UK).

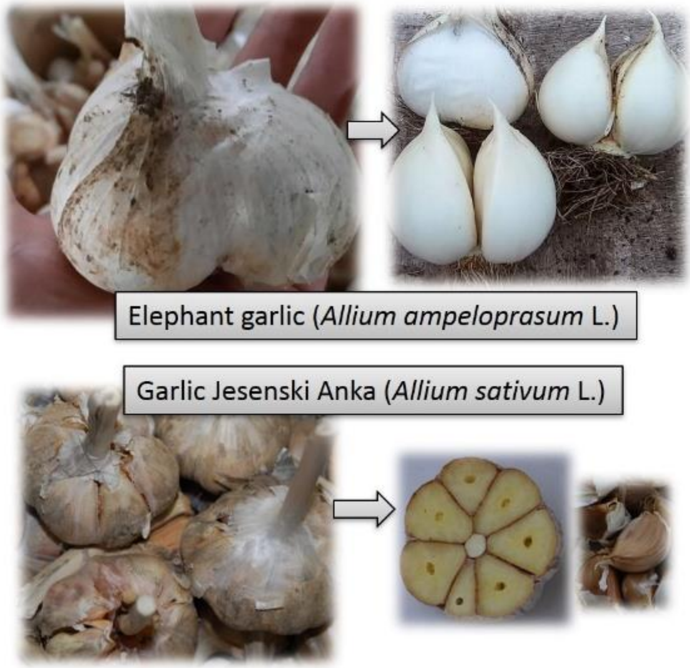

Fig. 2. Bulbs and cloves of elephant garlic (top) and common garlic (bottom)

To determine the dry matter, total phenolic content (TPC), and elemental analysis, the peeled cloves were frozen with liquid nitrogen, freeze-dried, and homogenised with a ball mill. Moisture content (%) was calculated from the dry matter (%), which was determined as the difference between the masses before and after freeze-drying. Total phenolic content (TPC) was determined by the Folin-Ciocalteu method as described by Singleton and Rossi (1965). Absorbance was measured spectrophotometrically at 765 nm and gallic acid was used as a calibration standard curve. The TPC of the samples was determined in triplicate and expressed as mg/g gallic acid equivalent (GAE). A multi-element analysis was performed using inductively coupled plasma mass spectrometry (ICP-MS). Microwave digestion and dilution were performed prior to the sample analysis on the Agilent 7900 ICP-MS. The accuracy of the results and analytical procedures were checked using certified reference material NIST SRM 1573a tomato leaves.

Results and Discussion

The results of nutraceutical and multi-elemental composition of elephant garlic and common garlic bulbs grown in Slovenia and the comparative sample from China are shown in Table 1. Only minor differences were found in the dry matter content of the two studied *Allium* species (39.71% elephant garlic vs. 41.83% common garlic), which is consistent with previous studies (Loppi et al., 2021). Higher TPC content was found in the bulbs of common garlic grown in Slovenia (2.74 mg GAE/g DW) than in elephant garlic (2.30 mg GAE/g DW), while the comparative sample had the highest TPC content (3.50 mg GAE/g DW). These results are in agreement with the findings of Lu et al. (2011) and are in contrast to some reports that found lower TPC content for the common garlic (Ceccanti et al., 2021). In addition, Hirata et al. (2016) reported large differences in phenolic content of garlic clones among geographic regions.

Tab. 1. Nutraceutical and multi-elemental composition of elephant garlic and common garlic cloves from two cultivation seasons.

Species		Elephant garlic			Common garlic			Comparative sample
Cultivation season		I	II	*Mean*	I	II	*Mean*	
Nutraceutical parameters	Moisture content (%)	59.98	60.59	60.29	56.19	60.16	58.89	58.69
	Dry matter (%)	40.02	39.41	39.71	43.81	39.84	41.83	41.31
	TPC (mg GAE/g DW)	2.39	2.22	2.30	2.67	2.81	2.74	3.50
	Allicin (mg/g DW)	0.31	0.68	0.49	2.40	3.86	3.13	1.54
Macro-element	K (g/kg DW)	10.12	12.77	11.45	14.28	14.02	14.15	15.27
	S (g/kg DW)	4.60	6.06	5.33	7.37	8.44	7.90	7.41
	P (g/kg DW)	2.21	2.52	2.37	4.81	4.84	4.83	3.66
	Mg (g/kg DW)	0.98	0.95	0.97	0.65	0.74	0.69	0.72
	Ca (g/kg DW)	0.27	0.24	0.25	0.40	0.44	0.42	0.39
Micro-element	Fe (mg/kg DW)	19.84	18.47	19.15	25.02	36.76	30.89	25.15
	Zn (mg/kg DW)	14.00	8.90	11.45	14.08	17.49	15.78	15.97
	Mn (mg/kg DW)	8.92	4.04	6.48	5.84	8.79	7.32	8.80
	Cu (mg/kg DW)	2.08	1.83	1.96	2.59	2.99	2.79	3.69
	Mo (mg/kg DW)	0.23	1.31	0.77	1.85	1.85	1.85	0.42
	Cr (mg/kg DW)	0.16	0.15	0.15	0.39	0.05	0.22	0.20
	Co (mg/kg DW)	0.043	0.027	0.035	0.036	0.002	0.019	0.039

TPC, total phenolic content; GAE, gallic acid derivatives; DW, dry weight.

The quality of garlic and garlic-related products is usually related to the allicin content, one of the most important flavour compounds in garlic bulbs. In this study, the allicin content of *Allium* samples was determined in fresh cloves of several bulbs. The mean allicin content was about six times higher in common garlic grown in Slovenia (3.13 mg/g DW) and three times higher in the comparative sample grown in China (1.54 mg/g DW) than in elephant garlic

(0.49 mg/g DW). This trend was confirmed by Kim et. al (2018), reporting higher level of allicin in elephant garlic than in common garlic bulbs. Allicin content depends on several factors such as genotypic characteristics, environmental conditions, fertilization practices, and storage duration (Marsic et al., 2019). Growing season had a minor effect on dry matter and TPC, while greater differences were observed in allicin content between cultivation seasons for both species.

A total of twelve elements were determined by ICP-MS and divided into five macro- (Mg, P, S, K, and Ca) and seven micro-elements (Cr, Mn, Fe, Co, Cu, Zn, and Mo). The results of macro-elements are given in g/kg and those of micro-elements as mg/kg (Table 1). The order of elements in the analysed *Allium* samples by abundance is K>S>P>Mg>Ca for macro-elements and Fe>Zn>Mn>Cu>Mo>Cr>Co for micro-elements. Overall, garlic bulbs had higher levels of macro-elements K (20%), S (50%), P (100%), and Ca (70%) compared to elephant garlic bulbs, while the level of Mg was 30% lower. Among micro-elements, the content of Fe, Zn, Cu, Mo, and Cr was also higher, while the content of Co was lower. Here, the growing season showed the effects on the macro-element S and most micro-elements. The comparative sample had higher contents of K, Mn, Cu, and Co and lower contents of P, Fe, and Mo than the garlic grown in Slovenia, indicating that growing conditions significantly affect the elemental composition of garlic bulbs.

Conclusion

In conclusion, the study represents the first overview of the nutraceutical properties and multi-elemental composition of elephant garlic and common garlic grown in Slovenia. Although these bulbs are similar in shape and aspect, they belong to different *Allium* species. The results have confirmed that there are significant differences reflected in the content of sulphur-containing compounds such as allicin and in the content of some nutritionally important elements such as P, Ca, S, and Fe. The results will be useful for future studies to understand the similarities and differences in biochemical properties of different *Allium* species.

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Нутритивни и елементални хемијски састав лажног бијелог лука (*Allium ampeloprasum* L.) и правог бијелог лука (*Allium sativus* L.) поријеклом из Словеније

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Сажетак

Луковичасте врсте *Allium* као што су лажни бијели лук (*Allium ampeloprasum* L.) и прави бијели лук (*Allium sativus* L.) садрже широк спектар биоактивних компоненти са корисним својствима за здравље, а најчешће се користе као зачини за храну. Циљ овог истраживања био је да се утврди постоји ли разлика између ових врста у нутритивном (сува материја, TPC, алицин) и елементалном хемијском саставу (макро-, микро-елементи). Оглед је изведен током двије године у мјесту Јабље, Словенија (предалпски регион). Укупни садржај фенола (TPC) одређен је спектрофотометријски, алицин коришћењем HPLC анализе, а елементална анализа је урађена са индуктивно спрегнуто плаземско-масно спектрометријом (ICP-MS). Резултати су показали да луковице лажног бијелог лука садрже нешто мање TPC и око шест пута мање алицина, који је главни органо-сумпорни састојак. Садржај макро (Mg, P, S, K, Ca) и микроелемената (Cr, Mn, Fe, Co, Cu, Zn, Mo) значајно је варирао између испитиваних врста. Највеће разлике су потврђене у садржају P, Ca, S i Fe. Наши резултати потврђују да се ове двије врсте разликују на основу испитиваних нутритивних и хемијских својстава.

Кључне ријечи: алицин, *Allium* sp., ICP-MS, макро-елементи, укупни садржај фенола

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