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Biologically valuable substances in garlic (*Allium sativum* L.) – A review

Biologicky hodnotné látky v cesnaku (*Allium sativum* L.) – Prehľad

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Abstract

Garlic (*Allium sativum* L.) is one of the most valuable plants in the world because it contains important substances with protective and healing effects on human health. Its health-promoting effects have been already known in ancient Egypt, China, Greece and also the Romans used it. Many studies have shown that garlic can help from colds, coughs, flu, pulmonary diseases, clean blood vessels, lowers blood pressure and cholesterol and has antibacterial, antiviral, anti-carcinogenic, anti-mutagenic and antioxidant properties. Garlic contains antioxidant that support the body´s defence mechanism against oxidative damage. The physiological effect of garlic can be affected by sulphur – containing compounds as well as other biologically active compounds such as polyphenols (mainly flavonoids), minerals (Ca, Fe, I, K, Mg, Na, Zn) and vitamins (A, B_1, B_2, B_6, C). The main sulphur compound in garlic is alliin, converted to allicin by the enzyme alliinase, which results in a characteristic garlic aroma and taste.

Keywords: antioxidants, garlic (*Allium sativum* L.), phenolic compounds, sulphur compounds

Abstrakt

Cesnak (*Allium sativum* L.) je jednou z najcennejších rastlín na svete, pretože obsahuje látky s ochranným a liečebným účinkom na ľudské zdravie. Zdraviu prospešné účinky cesnaku boli známe už v starovekom Egypte, Číne, Grécku a Ríme. Niekoľko štúdií potvrdilo, že cesnak môže pomôcť pri prechladnutí, kašli, chrípke, pľúcnymi ochoreniami, krvnom tlaku, cholesterole a má antibakteriálne, antivírusové, antikarcinogénne, antimutagénne a antioxidačné vlastnosti. Cesnak obsahuje antioxidanty, ktoré podporujú obranný mechanizmus tela proti oxidačnému poškodeniu. Fyziologický účinok cesnaku je ovplyvnený zlúčeninami obsahujúcimi síru, ako aj ďalšími biologicky aktívnymi zlúčeninami, ako sú polyfenoly (najmä flavonoidy), minerály (Ca, Fe, I, K, Mg, Na, Zn) a vitamíny (A, B_1, B_2, B_6, C). Hlavnou zlúčeninou síry v cesnaku je alíín, konvertovaný na allicín enzýmom alíinázou, čo má za následok charakteristickú cesnakovú arómu a chuť.

Kľúčové slová: antioxidanty, cesnak (*Allium sativum* L.), fenolové zlúčeniny, zlúčeniny síry

Introduction

Allium is the largest and most significant representative genus in the family *Alliaceae* and is widespread in the northern hemisphere. The genus *Allium* includes 450 species including garlic (*Allium sativum* L.), onion (*Allium cepa* L.), leek (*Allium porrum* L.), scallion (*Allium fistulosum* L.), shallot (*Allium ascalonicum* Hort.), wild garlic (*Allium ursinum* L.), elephant garlic (*Allium ampeloprasum* L. var. *ampeloprasum*), chive (*Allium schoenoprasum* L.), Chinese chive (*Allium tuberosum* L.) (Benkeblia and Lanzotti, 2007; Lanzotti, 2016).

Garlic (*Allium sativum* L.) is native to Asia and is also known in Europe, America and Africa. Due to aroma and flavour of bulb, it is an important agricultural crop. The main agricultural area of garlic cultivation is Asia, which represents 75% of its total production. China is a major producer of garlic in the world. The total cultivation area in the world is 1 437 690 ha and an annual consumption of garlic is 24 255 303 tons of dry bulbs (Marchese et al., 2016; Martins et al., 2016; Tocmo et al., 2016; El-Sayed et al., 2017; Pinilla et al., 2017).

Garlic was used by the ancient Egyptians as a medicine for the treatment of various diseases. It has been consumed by athletes at the first Olympic Games in history, for better performance. Garlic is currently starting to be more and more interesting, although it has been used for thousands of years. In Chinese medicine, garlic is used more than 3000 years because it contains biologically active substances with demonstrated positive effects on human health. Garlic contains a greater amount of biologically active substances and the chemical composition is rich. It contains water (65%), fiber, sulfur compounds, adenosine, pectin, fructan, carbohydrates, fatty acids, essential amino acids, nicotinic acid, phospholipids, prostaglandins, lectins, enzymes, vitamins (C, E, B_1, B_2, B_6) and minerals (P, Zn, Se, K, Fe, Mg, Ca, Na) (Marchese et al., 2016; Martins et al., 2016; Sahebkar et al., 2016; Tocmo et al., 2016; El-Sayed et al., 2017; Pinilla et al., 2017).

The genus *Allium* is a rich source of sulphur compounds. Garlic contains about 33 sulphur compounds. The major biological active compound in garlic is allicin or diallyl thiosulphate. The recent attention has been focused on polar compounds that are more stable to cooking and to the storage such as sapogenins, saponins and flavonoids (Lanzotti, 2016). It is also important to note, that garlic compounds are associated with potential anti-lipidemic, anti-thrombotic, anti-hypertensive, anti-atherogenic and anti-glycemic modes of action (Schwingshackl et al., 2016).

Phenolic compounds in garlic

Natural polyphenols are products of plants. Thanks to experimental studies more than 8,000 polyphenols were identified. Natural polyphenols are antioxidant molecules containing aromatic rings with one or more hydroxy (- OH) groups. Polyphenol compounds (polyphenols) are distributed in plants from roots to the plant seeds. In nature, polyphenol compounds occures in simple structure with one aromatic ring to very complex polymeric substances - tannins and lignins (Yagi et al., 2013; Ngoungoure et al., 2015). Polyphenol compounds are naturally presented in foods of plant origin such as fruit, vegetable, chocolate, cereals and beverages (coffee, tea, cocoa, wine). Polyphenols are characterized by their chemical structure because the hydroxy groups that are connected to two or three aromatic rings have an impact to the properties of polyphenols (Weichselbaum and Buttriss, 2010). Phenolic compounds are considered as the most important and ubiquitous groups of chemicals in the plant kingdom. These chemicals are synthesized in natural development of plants and the reactions of plants taking place in changing environment - stress, UV radiation. Phenolic compounds are classified according to solubility in water. The first group is a water-soluble, phenolic compounds (phenolic acids, flavonoids and quinones), and the other is a water-insoluble phenolic compounds (condensed tannins, lignin) (Naczk and Shahidi, 2004; Haminiuk et al., 2012).

Fratianni et al*.* (2016) reported that gallic acid was one of the most abundant metabolites detected in the endemic varieties that were analysed. Gallic acid content it ranged from 81.41 mg*kg^{-1} to 96.48 mg*kg^{-1} in the dry matter of the analyzed varieties of garlic. Bystrická et al*.* (2013) published that the content of polyphenols is influenced by various factors such as temperature, light, availability of water and nutriens. Lenková et al. (2017) published that the content of polyphenols in fresh garlic was in the range 621.13 mg*kg^{-1} to 763.28 mg*kg^{-1}. According to Chekki et al. (2014) was content of total polyphenols 436 mg*kg^{-1}. Kavalcova et. al. (2014) published that the content of polyphenols in fresh garlic was in the range 260.62 mg*kg^{-1} to 279.74 mg*kg^{-1}.

Phenolic acids in garlic

Phenolic acids are plant secondary metabolites that occure in vegetables, fruits, medicinal plants, and are part of the human diet. Phenolic acids make up one third of phenolic compounds in plant foods. The structure of phenolic acids is formed by a benzene ring, a carboxyl group and one or more hydroxy or methoxy groups (Liu et al., 2015).

Phenolic acids are classified into two main groups. The first group is a cinnamic acid derivatives and the other group is benzoic acid derivatives (Ondrejovič et al., 2009). Several studies showed that content of phenolic acids in garlic such as caffeic acid, *p*-coumaric acid, ferulic acid, and sinapic acid was two times higher as in the onion (Brewer, 2011). Drozd et al. (2011) deals with the content of selected phenolic acids in garlic. The content of pyrocatech acid was 1.7 ± 0.1 mg*kg^{-1}; coffee acid 0.06 ± 0.01 mg*kg^{-1}; *p*-hydroxybenzoic acid 0.05 ± 0.01 mg*kg $^{-1}$; of *p*-coumaric acid 2.1 ± 0.1 mg*kg $^{-1}$; ferulic acid 4.3 ± 0.2 mg*kg^{-1}.

Phenolic acids are among the important antioxidants that protect the human organism against the negative effects of free radicals (Piazzon et al., 2012). A summary of the phenolic acid constituents in fresh garlic is given in Table 1.

Table 1. The phenolic acid constituents in fresh garlic (Kim et al., 2013)

Acid derivatives	Selected acids	Content of acids ($mg*kg^{-1}$)
Hydroxybenzoic acid derivatives	*p*-Hydroxybenzoic acid	-
	Gallic acid	2.06 ± 0.09
	Vanillic acid	-
Hydroxycinnamic acid derivatives	Chlorogenic acid	-
	Caffeic acid	7.48 ± 0.23
	p-Coumaric acid	1.25 ± 0.03
	Ferulic acid	1.57 ± 0.02
	m-Coumaric acid	4.84 ± 0.04
	o-Coumaric acid	0.66 ± 0.03
	Total hydroxybenzoic acid derivatives	2.06 ± 0.09
Total hydroxycinnamic acid derivatives		15.80 ± 0.08
Total phenolic acids		17.86 ± 0.07

Flavonoids in garlic

Flavonoids are a group of polyphenolic substances. These are secondary metabolites of plants produced from aromatic amino acids, phenylalanine and tyrosine. Experimental studies were discovered more than 6500 different of flavonoids in different plant species (Xu et al., 2013). Basic structure of flavonoids (C6 – C3 – C6) consists of three circles. The flavonoids include two benzene rings which are joined through the third ring - pyran heterocyclic ring containing oxygen (Kamboh et al., 2015). However, according to recent studies, flavonoids of garlic such as nobiletin, tangeretin, rutin could also significantly contribute to pharmacological activity (Berginc et al., 2010). Chemical structures of Flavonoid skeletons are shown in Figure 1.

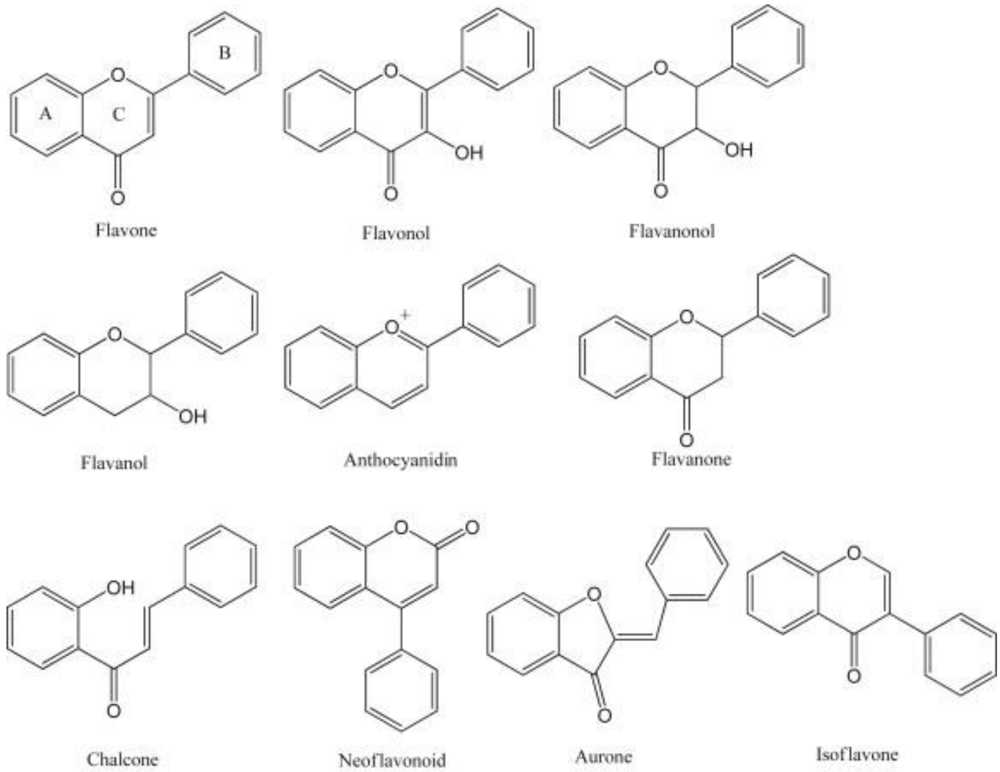

Figure 1. Chemical structures of Flavonoid skeletons (Yang et al., 2015)

Chekki et al. (2014) published that the content of flavonoids in garlic was 132 mg*kg^{-1}. Fratianni et al. (2016) published that identified of flavonoids in garlic such as epicatechin (1.178 mg*kg^{-1}), rutin (43.43 mg*kg^{-1}), luteolin (0.15 – 22.92 mg*kg^{-1}), hyperoside (0.37 – 20.24 mg*kg^{-1}), quercetin (6.55 – 10.17 mg*kg^{-1}), apigenin (3.24 mg*kg^{-1}) and naringenin (11.75 – 56.71 mg*kg^{-1}) (Figure 2).

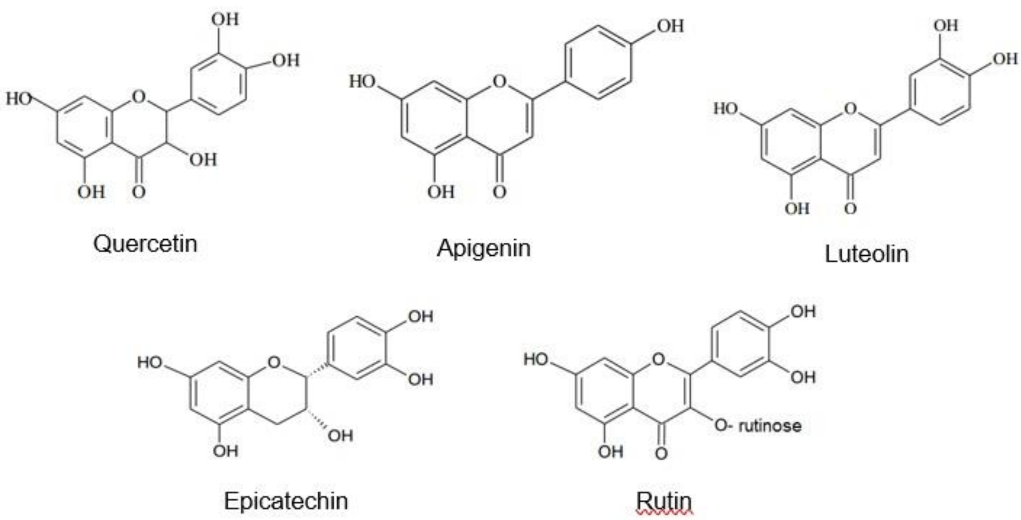

Figure 2. Chemical structures of Flavonoid skeletons in garlic (Dubber and Kanfer, 2004; Mahmood et al., 2010; Brunetti et al., 2013)

Thiosulfinates and other sulphur compounds in garlic

Thiosulfinates are the best studied compounds arising from *Allium* species and these molecules originate from S-alk(en)yl-l-cysteine-S-oxide located in the cytoplasm (Lanzotti, 2016).

Fresh garlic (*Allium sativum* L.) contains at least thirty-three sulfur compounds and seventeen amino acids. The main bioactive constituents of garlic (*Allium sativum* L.) are organosulfur compounds (diallyl, allyl methyl and dimethyl mono- to hexasulfides) which are responsible for health benefits. The main allyl cysteine sulfoxides of garlic are methiin (S-methyl-l-cysteine sulfoxide), alliin (S-2-propenyl-l-cysteine sulfoxide) and isoalliin (S-trans-1-propenyl-l-cysteine sulfoxide). The main γ- glutamyl peptides of garlic are γ-glutamyl-S-trans-1-propenyl-cysteine and γ-glutamyl-S-methyl cysteine (Jabbes et al., 2012; Lu et al., 2013; Jangam and Badole, 2014).

Alliin (S-allyl-l-cysteine sulfoxide) is the major sulfur-containing amino acid in garlic (*Allium sativum* L.) and the content of alliin in fresh garlic is about 1.29%. However, content of alliin in garlic is affected by weather and soil. Alliin is susceptible to degradation. This process occurs primarily at elevated temperature. Alliin´s tendency towards degradation is caused by unstable sulfoxide linkages (Chen et al., 2016).

Mechanisms and the structure-activity relationships of organosulfur compounds are still not clear. It is also important to note that organosulfur compounds have a positive impact on human health. Garlic (*Allium sativum* L.) contains at least 100 volatile and non-volatile sulphur-containing bioactive compounds. During processing (cutting, crush) and digestion, organosulfides of garlic undergo the complex of chemical reactions. The rupture of cell structure caused by cutting and crushing of garlic initiates the reaction between the enzyme alliinase and the substrate alliin (S-allyl-L-cysteine-sulfoxides) leading to the formation of allicin (allyl 2-propenethiosulfinate) (Tocmo et al., 2016).

Wang et al. (2011) published that Under normal circumstances, in the intact cells of the garlic bulbs, the two molecules are physically separated: the enzyme alliinase is compartmentalized in the vacuoles while the alliin is localized in the cell cytoplasm. Upon rupturing or wounding of the cells, the enzyme located in the vacuoles and the alkyl cysteine sulfoxides located in the cytoplasm can react and produce allicin. Alliinase is present in garlic at high levels, representing up to 6% of the soluble proteins in the bulb.

Alliin is the most important amino acid of garlic. Alliin is a thermally stable compound and therefore its biological activity is preserved when drying garlic. Its content in fresh garlic is 0.2 – 2%. Allicin is not found in garlic, it is produced by the enzyme allinase from alliin. After processing, such as cutting, crushing, chewing or dehydration, the alline is converted to allicin by allinase treatment. Allicin is disproportionated in an aqueous (polar) medium to form diallythiosilicone (pseudoallicin) and diallyldisulfide, which furthermore provides diallylsulfide and diallyl trisulfide. In a non-polar environment (e.g. when fried in oil), allicin forms a so-called ajoenes and vinyldithiins (Lenková et al., 2016). Enzymatic reaction of alliin are shown in Figure 3.

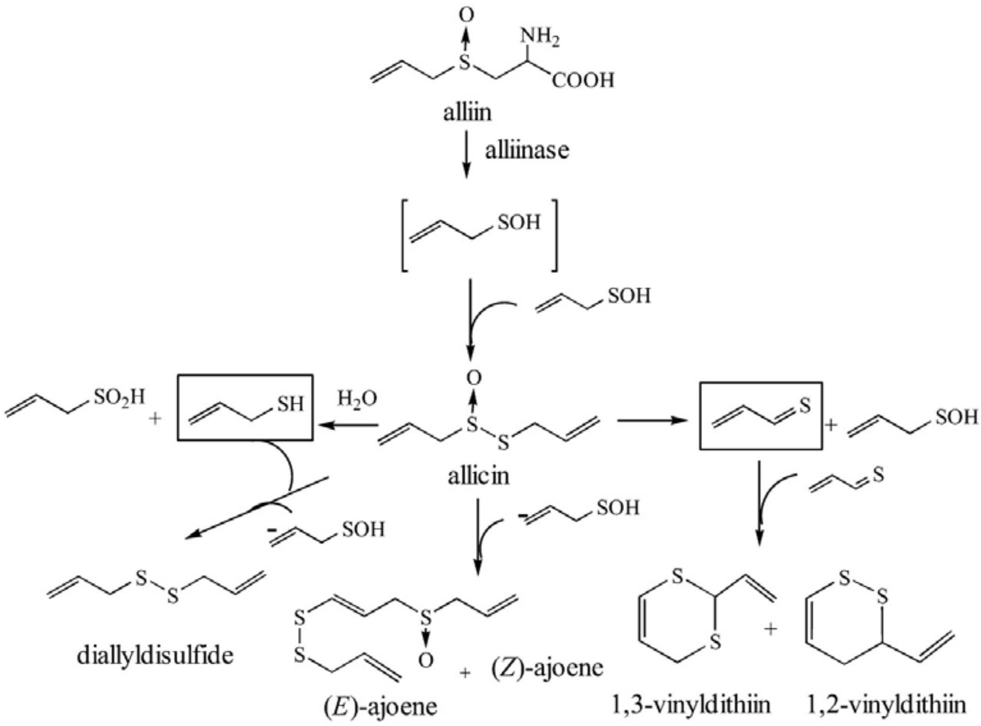

Figure 3. Enzymatic reaction of alliin (Amagase, 2006)

The chemical compound allicin is active compound which are labelled thiosulfinates most plentiful in freshly crushed garlic. The chemical structure of allicin was identified in 1944. Allicin has been reported to possess various biological activities, antifungal, antiviral, antiparasitic, including antibacterial and anticancer activities, in addition to the capacity to inhibit platelet aggregation and decrease serum lipid levels (Miron et al., 2002; Arnault and Auger, 2006; Jabbes et al., 2012; Lu et al., 2013; Jangam and Badole, 2014; Chen et al., 2016). It is also important to note that allicin is very unstable chemical compound and is rapidly degraded into diallyl disulfide, 2-vinyl-(4H)-1,3-dithiin, 3-vinyl-(4H)-1,3-dithiin and ajoene. Recent experimental studies proved that diallyl disulfide is oxidized back into chemical compound allicin, which react non-enzymatically to form glutathione and allylglutathione sulphide (Arnault and Auger, 2006).

Antioxidants and healing properties of garlic

In the human body there is a constant formation of free radicals as a part of normal cellular function. It is also important to note, that exceed production of free radical production originating from endogenous or exogenous sources, might play a role in many diseases. The free radicals are the reactive oxygen species, hydrogen peroxide, singlet oxygen, nitric oxide and nitrite proxy server (Rahimi-Madiseh et al., 2016). An antioxidants can be defined as to any compound that, when present at a lower concentration compared to that of an oxidizable substrate, is able to either delay or prevent the oxidation of the substrate (Young et al., 2001; Pisoschi and Pop, 2015).

Trought the decades, garlic has been considered as a precious folk medicine with available influences on numerous pathological processes (Ezer et al., 2016). Garlic together with shallots have antioxidant and free radical-scavenging characteristics and identifiable odors at low concentrations. However, garlic and shallots comprises two main group of antioxidants. The first group of antioxidants are the flavonoids such as flavones and quercetins, and the second group of antioxidants are sulfur-containing compounds such as allyl-cysteine, diallyl sulfide, and allyl trisulfide. Several studies showed that a combination of the alkyl group ($-CH_2\ CH=CH_2$) and the −S(O)S− group is important for the antioxidant action of sulfur compounds in extract of garlic (Brewer, 2011).

Organosulfur compounds are major antioxidants in garlic (*Allium sativum* L.). Aged garlic extract is rich in antioxidants such as fresh garlic and helps improve cellular antioxidants, which in turn helps in maintaining a healthy immune system (Santhosha et al., 2013). Lenková et al. (2017) reported that the value of antioxidant activity in garlic was in interval from 13.61% to 20.22%. Kavalcová et al. (2014) published that the value of antioxidant activity in garlic was in interval from 4.05% to 5.07%. Fratianni et al. (2016) indicate that the value of antioxidant activity in onion was in interval from 20.05% to 25.82%. Garlic is often used, and is important in the production of meat products, bakery products and various dishes (El-Hamidi and El-Shami, 2015).

Kwiecień (2008) published that garlic has the ability to accumulate the selenium from soil and the major selenium compound in both Se-enriched and unenriched garlic was identified as γ-glutamyl-Se-methyl selenocysteine along with lesser amounts of Se-methyl selenocysteine, selenocysteine, selenomethionine among other compounds.

The pure Se-compounds have proved to be superior anticancer agents than their corresponding S-analogues. The two major Se-compounds possessing anticancer activity in onion and garlic are γ-glutamyl-Se-methyl selenocysteine and Se-methyl selenocysteine, being Se-methyl selenocysteine and Se-allyl selenocysteine the most chemopreventive Se-compounds (Corzo-Martínez et al., 2007).

Rahman and Lowe (2006) published that garlic is also reported to inhibit the pathogenesis of cardiovascular disease and to prevent cancer and other chronic diseases associated with aging. Over the last one-quarter century the role of garlic in treating cardiovascular disease has received much attention.

Conclusions

Garlic is the crop of the genus *Allium* and constitute a potential source of antioxidants, minerals, polyphenols, fiber and organosulfur compounds. In the last ten years, numerous properties of garlic have been discovered for the application in the production of different kinds of functional food due to the content of polyphenols, organosulfur compounds and vitamins. Garlic (*Allium sativum* L.) is valued for its bulbs having characteristic odour, flavor and pungency. Garlic positively affect the physiological condition of the human body, especially of those suffering from diabetes, hypertension, obesity and cardiovascular diseases. Hence a brief review was presented to clarify content of bioactive compounds in garlic (*Allium sativum* L.).

It is also important to note that the content of bioactive compounds may be affected also by variety, agrochemical composition of the soil for example content of humus, climatic condition and nutrients.

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