horticulturae

Review

Allium Species in the Balkan Region—Major Metabolites, Antioxidant and Antimicrobial Properties

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Abstract: Ever since ancient times, *Allium* species have played a significant role in the human diet, in traditional medicine for the treatment of many ailments, and in officinal medicine as a supplemental ingredient. The major metabolites of alliums, as well as their antioxidant and antimicrobial properties, with an emphasis on the species most represented in the Balkan region, are discussed in this review. Due to its richness in endemic species, the Balkan region is considered the genocenter of alliums. There are 56 recorded *Allium* species in the Balkans, and 17 of them are endemic. The most common and well-studied Allium species in the Balkans are *A. cepa (onion)*, *A. sativum* (garlic), *A. ampeloprasum* (leek), *A. schoenoprasum* (chives), *A. fistulosum* (Welsh onion), and *A. ursinum* (wild garlic or bear's garlic), which are known for their pungent taste and smell, especially noticeable in garlic and onion, and attributed to various organosulfur compounds. These plants are valued for their macronutrients and are used as desirable vegetables and spices. Additionally, phytochemicals such as organosulfur compounds, phenolics, fatty acids, and saponins are associated with the antioxidant and antimicrobial properties of these species, among many other bioactivities. All parts of the plant including the bulb, peel, clove, leaf, pseudostem, root, flower, and seed exhibit antioxidant properties in different *in vitro* assays. The characteristic phytocompounds that contribute to the antimicrobial activity of alliums include allicin, ajoene, allyl alcohol, and some diallyl sulfides. Nanoparticles synthesized using *Allium* species are also recognized for their notable antimicrobial properties.

Keywords: *Allium cepa* L.; *Allium sativum* L.; metabolites; organosulfur compounds; phenolics; phytosterols; terpenoids; fatty acids; antimicrobial activity

Citation: Vuković, S.; Popović-Djordjević, J.B.; Kostić, A.Ž.; Pantelić, N.D.; Srećković, N.; Akram, M.; Laila, U.; Katanić Stanković, J.S. *Allium* Species in the Balkan Region—Major Metabolites, Antioxidant and Antimicrobial Properties. *Horticulturae* **2023**, *9*, 408. https://doi.org/10.3390/horticulturae9030408

Academic Editor: Xiuxiu Sun

Received: 21 February 2023
Revised: 14 March 2023
Accepted: 17 March 2023
Published: 22 March 2023

1. Introduction

Allium species are considered to be the oldest cultivated plants, as evidenced by illustrations that are over 5000 years old, found in Egypt. Namely, the illustrations show models of onion and garlic bulbs, which are assumed to be the first domesticated species of this genus [1,2]. That their use in human nutrition has persisted to this day is evidenced by the size of the areas in which these species are grown, as well as the number of scientific papers in which these plants have been described and tested. In addition to orchids, *Allium* is one of the largest plant genera of monocotyledonous plants. According to accessible scientific sources, the genus *Allium* includes more than 700 species, divided into 15 subgenera and 72 sections. It is estimated that around 650 species have several names—synonyms.

The taxonomic classification of this genus is complex. Earlier classifications, based on inflorescence morphology, traditionally placed *Allium* in the family Liliaceae, then in the family Amarilidaceae, while recent knowledge which relies on molecular techniques, puts this genus in the following taxonomic position: class Monocotiledones, order Asparagales, family Amarilidaceae [3–6].

Species of this genus are distributed across the northern hemisphere. They grow in preferably arid climates and thrive well on open, dry, and sunny terrains. They are rarely found in dense vegetation and are recognized as weak competitors to weeds. The area richest in *Allium* species spreads from the Mediterranean basin to Central Asia and Pakistan. The western part of North America is listed as the second most diverse area of these species. Only one species (*A. dregeanum*) has been identified in the southern hemisphere (South Africa) [2,7]. According to FAOStat, in 2021, the top producers of *Allium* species were China (23,659,708 tons of onion and 20,712,087 tons of garlic) and India (26,738,000 tons of onion and 2,907,000 tons of garlic) [8].

The genus *Allium* holds significant economic importance as many of its species are edible and valued for their use as vegetable crops, spices, or medicinal plants. Among these species, *Allium cepa* is the most widely consumed due to its widespread use as a basic condiment in a variety of dishes. Other important species in terms of nutrition and economics include *A. sativum*, *A. ampeloprasum*, *A. fistulosum*, *A. tuberosum*, and *A. schoenoprasum* (Figure 1). The edible parts of these species are rich sources of carbohydrates, including fructose and glucose. The outer scale of the bulb onion contains significant amounts of arabinose and galactose. Some essential amino acids such as glutamic acid and arginine are important reserves of nitrogen that contribute to the nutritional value of the onion species. Other complex bioactive compounds include saponins, vitamins (A, C, B6, and B9), and essential elements such as phosphorus, potassium, calcium, magnesium, zinc, manganese, sodium, iron, selenium, and copper [9,10]. It is well known that bioactive substances such as phenolic compounds, phytosterols, and fatty acids are an integral part of many plants and they have attracted great attention from researchers due to their benefits for human health. Many studies have shown the pharmacological properties of *Allium* species including antimicrobial, anti-inflammatory, antitumor, antiviral, and antioxidant activities that are linked to the mentioned phytochemical compounds [11–15].

Figure 1. The most important *Allium* species: (**a**) *A. cepa*; (**b**) *A. sativum*; (**c**) *A. ampeloprasum*; (**d**) *A. fistulosum*; (**e**) *A. tuberosum*; and (**f**) *A. schoenoprasum* (photos by S. Vuković).

This study aims to review the morphological, chemical, antioxidant, and antimicrobial properties of *Allium* species that are characteristic of the Balkan region, based on the most relevant and up-to-date scientific literature in the field.

2. Morphological Characteristics of *Allium* Species

Alliums have the following morphological characteristics: underground parts (true stem, bulb structure, pseudostem), leaf, flower stalk, flower, inflorescence, fruit, and seed (Figure 2). While *Allium* species share many similar characteristics, each species also has its own unique morphological features.

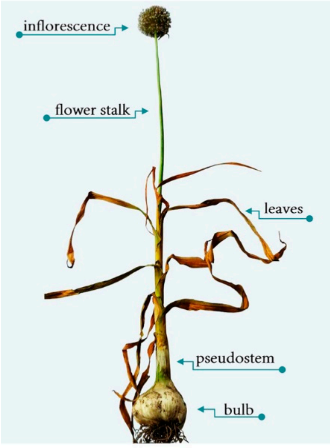


Figure 2. Morphological description of the *Allium* plant (photo by S. Vuković).

These are biennial or perennial plants with rhizomes, tunicate bulbs, or swollen roots as storage organs. The bulb consists of a true stem, known as the basal plate, fresh thickened leaves, dry coated leaves, and buds from which a flower stalk develops. The bulbs appear solitary (true bulb—onion or pseudobulb—leek) or clustered (the bulb contains several densely packed cloves arranged on a basal plate—garlic). Some species form little bulbs, known as daughter bulbs, as propagation material, around the old bulbs. Leaves are of different shapes (tubular in onion/flat in garlic). The base part of the leaves forms a pseudostem. The inflorescences are umbellate or head-like and located at the top of the leafless flower stalk. Young inflorescences are enclosed with leaves, known as spathe. The flowers contain six free or almost free tepals arranged in two whorls; there are six stamens, also arranged in two whorls, sometimes basally connected; the ovary is trilocular, superior. Some species can form bulbils instead of all or some of the flowers in the inflorescences, which can be used as propagating material. The fruits are capsules; the seeds are black, with rhomboidal or spheroidal shape [2,4,7]. The described, specific morphological parts of the *Allium* plants are presented in Figure 3.

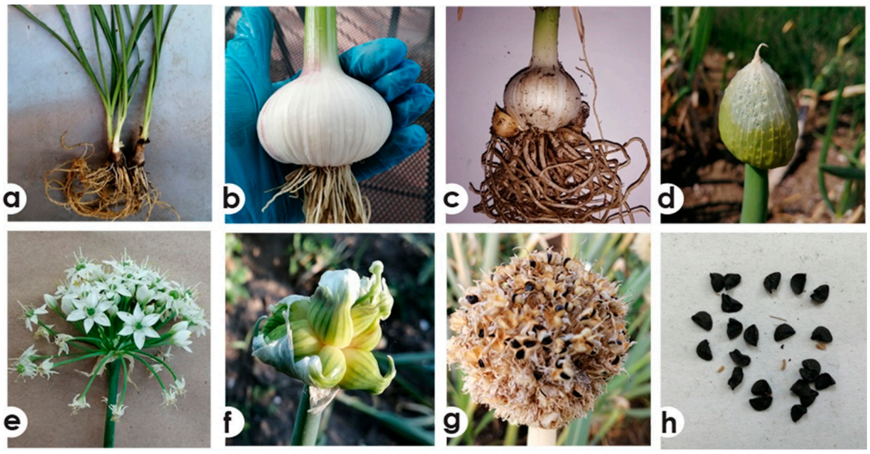


Figure 3. Morphological parts of *Allium* plants: (**a**) rhizomes; (**b**) tunicate bulb; (**c**) little bulbs, as propagating material; (**d**) spathe; (**e**) flowers in the inflorescence; (**f**) bulbils in the inflorescence; (**g**) fruits (capsules); (**h**) seeds (photos by S. Vuković).

3. Usage of *Allium* Species

The characteristic smell and taste of alliums are responsible for their wide use: in the culinary arts, where they are very popular ingredients and usually used as vegetables or as spices; in officinal medicine as ingredients of supplements; and in folk medicine for the prevention and treatment of many ailments. In general, all plant parts of alliums are edible and may be consumed by humans, but which part will be consumed depends on the species. According to some authors, the consumption of seeds is questionable. However, in modern kitchens, the seeds are sprouted, and then the young plants are used in the diet, as microgreens [16]. Furthermore, the edible parts can be used raw, cooked, frozen, pickled, canned, dehydrated, or processed in various products. They play an important role in the daily diet of almost all cultural areas. Shallots, green onions, or spring onions are very popular as a fresh salad during spring months and are often grown in home gardens. Dry bulbs, commonly of onions and garlic, are an indispensable condiment, omnipresent in green markets throughout the year [17,18]. The study conducted by Alimardanova et al. [19], described the use of dry *A. odorum* in cheese production technology, in order to improve the organoleptic properties of cheese and its nutritional properties. Onion rings, dry onions, garlic powder, etc. are market favorites in the form of processed products. Moreover, numerous wild species are used as food or remedy, mostly as common alliums [20].

The use of alliums in officinal and traditional medicine is closely related to their rich nutritional composition. They are characterized as plants with a high content of phytochemicals with great therapeutic potential. Many studies indicate the effectiveness of alliums against various illnesses: *A. cepa* is used to treat high blood pressure, bronchitis, migraine, coronary heart disease, hypercholesterolemia, cataract, hypertension, and diabetes; *A. sativum* is used as a carminative, a stimulant, an antiseptic, to alleviate stomach discomfort, respiratory infections, and it also exhibits heart disease-preventing and anti-asthmatic effects; *A. fistulosum* is a common remedy for headaches, diarrhea, abdominal pain, heart disease, and the common cold; *A. ampeloprasum* is traditionally used for relieving symptoms associated with various inflammatory ailments, and as a digestive stimulant in hypertension; *A. schoenoprasum* is employed for hypertension, to treat the common cold, and to increase appetite and digestion. Wild species, such as *A. ursinum*, *A. vinale*, and *A. scorodoprasum* also show a wide range of medical properties that can be identified with the medicinal effects of common alliums. In general, the antioxidative activity of *Allium* species is well described in many scientific sources, which indicates that these species can be used as a remedy against diseases whose main core is considered to be reactive oxygen species (ROS) [20–23].

In officinal medicine, alliums are very much appreciated, especially garlic. Dietary supplements that contain garlic are intended to strengthen the immune system, lower serum lipids, and prevent atherosclerosis. They are sold in several types of preparation, such as garlic oil, garlic oil macerate, garlic powder, and aged garlic extract (AGE) [24]. The main benefit of these products is reflected in the absence of the smell characteristic of garlic. Onion has found its application in the cosmetic industry; it is used as an ingredient in skin and hair care products [25,26]. The beneficial effects of alliums can be attributed mainly to their chemical composition, especially to sulfurous compounds, which are the most abundant constituents of *Allium* species.

4. *Allium* Species in the Balkan Region

The common Allium species, including edible, ornamental, and weed species, are presented in Table 1. The diversity of *Allium* species widespread in the Balkans, as well as in the region of Aegean Greece and the Aegean islands, including Crete, is similar to the diversity of alliums distributed in North Africa. Moreover, the Balkan region is mentioned as the genocenter of alliums, because of its richness in endemic species [27–29]. Data published by Anačkov [27] indicate that 56 *Allium* species have been recorded in the Balkans, 17 of which are endemic. In general, in the Balkan region, the following species are common and well-studied: onion (*A. cepa*), garlic (*A. sativum*), Welsh onion (*A. fistulosum*), chives (*A. schoenoprasum*), leek (*A. ampeloprasum*), and ramson, wild garlic, or bear's garlic (*A. ursinum*) (Table 1). The most popular species are onion and garlic (cultivated species), as well as bear's garlic (wild species). Bulbs and leaves are the most frequently consumed parts of the plant [20,30]. Figure 4 depicts the average annual yields in tons per hectare (t per ha) of onion and garlic in the countries of the Balkans during 2021 [8].

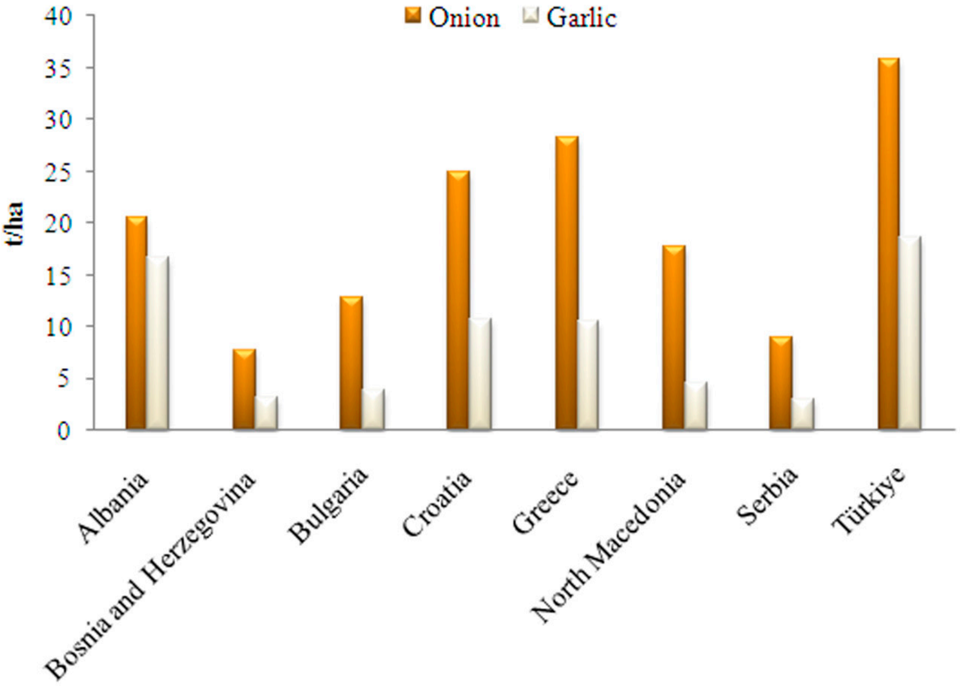


Figure 4. Average annual yield (tons per hectare) of onion and garlic in the Balkan region countries (according to FAOStat 2021 [8]).

4.1. *A. cepa*—Onion

Onion is economically the most important Allium species, which is grown and consumed all over the world. It is native to Central Asia, or more precisely, Iran and Pakistan. Today, it is produced in more than 175 countries around the world [31]. India and China are ranked as the biggest producers in terms of the total area under onion cultivation. However, according to FAOStat (2021), the highest productivity was achieved in the Republic of Korea and the USA, with about 60 t per ha, while the world average yield was about 19 t per ha. Furthermore, in the Balkan region, onion production and export are economically important. Namely, it is estimated that 1% of onions produced in the countries of the Balkan region, especially in North Macedonia and Serbia, are sold on the European Union (EU) market [8]. Other alliums characteristic of the Balkan region are also produced, although statistical data are scarce. On the other hand, the Lebanese take the first place in terms of the amount of onion consumed per capita (30 kg), followed by Americans (16 kg) [1,32].

Onion has been suggested for many purposes: for cooking (bulbs, leaves, or whole plants used raw, fried, roasted, or pickled) to enhance the flavor of different foods; and in medicine (in treating a broad range of disorders). In addition, pharmacological activities, such as antioxidant, antibacterial, antiviral, anticancer, etc., are well explained in many studies. The main compounds responsible for the aroma, pungency, and multiple health effects of this species are organosulfur and phenolic compounds [33]. In human nutrition, the recommended daily dosage is 50 g of fresh or 20 g of dry onion [34].

Table 1. Most common *Allium* species, and species characteristic for the Balkan region.

Food Species		**Ornamental Species**		**Weed Species**		**Species in the Balkan Region**	**Reference**
A. cepa [1]	Onion, shallot [2]	*A. cernuum* [1]	Lady's leek [2]	*A. vinale* [1]	Crow garlic [2]	*A. cepa* [1]	[2,3]
A. sativum	Garlic	*A. longifolium*		*A. carinatum*	Keeled garlic or witch's garlic	*A. sativum*	[2,3]
A. fistulosum	Welsh onion or Japanese bunching onion	*A. moly*	Lily leek			*A. fistulosum*	[2,3]
A. schoenoprasum	Chives	*A. bisculum*				*A. schoenoprasum*	[2,3]
A. ampeloprasum	Leek, kurrat, great-headed garlic, or pearl onions	*A. neapolitanum*	Naples garlic			*A. ampeloprasum*	[2,3]
A. tuberosum	Chinese chives	*A. hollandicum*	Dutch allium			*A. ursinum*	[2,3]
A. nutans	/	*A. giganteum*	Giant allium				[2,3]
A. odorum	Chinese chive or Chinese leek	*A. cyaneum*					[2,3]
A. chinense	Rakkyo	*A. rosenbachianum*					[2,3]
A. rotundum	/	*A. ramosum*	Garlic fragrant				[2,3]
A. ursinum	Ramson, Bear‘s garlic, or Wild garlic	*A. cristophii*	Star of Persia				[2,3]
A. oschaninii	French grey shallot	*A. flavum*	Yellow-flowered garlic				[2,3]
A. tricoccum	Ramp						[2,3]
A. victorialis	Long-rooted onion or long-rooted garlic						[2,3]

[1]—Species; [2]—English name.

4.2. *A. sativum*—Garlic

Garlic is, next to onion (*A. cepa*), the most important, and the most studied species from the genus *Allium*. Today, it is widely cultivated throughout the world, especially on the Asian continent. China is listed as the largest consumer and producer with around 20 million tons per year [35].

Garlic is widely used in many cultures of the world and in many ways—as a vegetable, a spice, and a medicinal agent in officinal and folk medicine. The main edible and economic organ of garlic is the bulb, composed of many cloves. It is propagated entirely vegetatively, by cloves. Moreover, the whole plant is consumed as a spring vegetable, alone or in combination with other vegetables [36]. Due to its complex chemical composition, garlic exhibits many biological activities—antioxidant, anti-bacterial, anti-viral, and anti-fungal [37]. As a preventive measure against many diseases that cause oxidative stress, daily use of 2–4 g of garlic (about 1–2 cloves) is recommended [38]. Furthermore, some medical studies have examined the effect of garlic in the prevention of COVID-19 [39]. The negative side of using garlic in raw form is the breath odor. Therefore, there are various odorless garlic supplements, which have proven to be as useful as fresh garlic.

4.3. *A. fistulosum*—Welsh Onion or Japanese Bunching Onion

Welsh onion is a perennial species, morphologically close to onion, but less known than traditional onion. Unlike onion, Welsh onion does not form a true bulb. The entire plant, i.e., false bulb, pseudostem, and leaves, is edible and usually eaten raw in salads mixed with other vegetables, boiled as pottage, or cooked in various dishes. It is cultivated in a wide range of climatic conditions—from temperate to tropical and arid regions. The species is popular in Asian countries and the leading producers are China (about 500,000 ha), Japan, and South Korea (about 25,000 ha). In folk Chinese medicine, all plant parts, including roots, pseudostems, leaves, flowers, and seeds are used for medicinal purposes. Available research indicates a similar pharmacological activity of Welsh onion and traditional onion [40,41].

4.4. *A. schoenoprasum*—Chives

Allium schoenoprasum is a perennial plant with multiple applications: an edible product, a healing herb, and an ornamental plant. It originates from northern Europe and North America. Fresh leaves smell and taste like onion and they are most often used in nutrition. The leaves can be harvested several times during the growing season. Dry leaves are also used in food processing and cooking, and as a spice, but do not have an intense flavor. Purple, ball-shaped flowers classify this species as an attractive ornamental plant [42]. Considering their healing effect, many studies have indicated that chives exhibit antioxidant activity [43]. Research by Eisazadeh et al. has shown that chives are suitable for phytoremediation, especially for reducing the concentration of cadmium in contaminated soil [44].

4.5. *A. ampeloprasum*—Leek

This species includes several different types, known as wild leek, European leek cultivars, Egyptian kurrat, and great-headed garlic. This species complex is distributed throughout the countries of the Mediterranean basin. In general, the mentioned types are robust herbaceous biennial plants with flat leaves. The taste is milder than that of onion and garlic. The main difference between these types is in the bulb. Actually, leek cultivars do not form bulbs, while great-headed garlic forms bulbs with several oversized cloves. In the case of leek cultivars, the leaves and the long, white pseudostems are edible, and used as raw or cooked vegetables, in place of onions. On the other hand, the young whole plants or cloves of great-headed garlic are used as garlic substitutes, usually as a flavoring agent. *A. ampeloprasum* is considered a health-promoting vegetable due to its chemical composition, which is similar to garlic and onion, and whose pharmacological properties are well-studied [45,46].

4.6. *A. ursinum*—Ramson, Wild Garlic, Bear's Garlic

Ramson is the most popular wild *Allium* species. It is a perennial herbaceous plant, native to a wide area of Europe and Asia. It prefers soils well-supplied with nutrients and well-drained soils in addition to full-shade and semi-shade localities. The plants form elongated bulbs and 2–3 elliptic-lanceolate, flat leaves. The edible parts are collected in the wild; the harvesting of leaves is carried out during early spring (April–May), before the appearance of flowers, while the bulbs are collected in autumn (September–October). Although the bulb is edible, the leaves are the main edible organs, which are eaten either raw or cooked. The plant smells and tastes like garlic. Ramson is characterized by a high content of biologically active compounds. It is valued as a natural remedy in traditional medicine, usually used for the treatment and prevention of gastrointestinal, cardiovascular, and respiratory diseases [47,48].

5. Major Metabolites of Common *Allium* Species

The phytochemical composition of *Allium* species is complex, which contributes to their biological activities. Organic sulfur compounds are an important and commonly present group in alliums. These compounds possess different characteristics, such as flavor and odor. Other groups of biologically active compounds found in alliums include polyphenols, flavonoids, phenolic acids, anthocyanins (which are responsible for the color characteristics of onion bulbs), phytosterols, fatty acids, and terpenoids [9,10].

Metabolomics is a comprehensive approach used to explore the chemical context of a plant genus/species by determining the qualitative and quantitative profiles of some of the nutrients/phytochemicals. This modern method is made possible by the development of highly sophisticated analytical tools, and it is important because it allows us to understand the complexity of biological systems such as plants [49]. With around 900 species [50], the *Allium* genus is recognized as an excellent source of different bioactive compounds with antioxidant, antimicrobial, and anti-cancer properties [16,51–56]. However, among them, some stand out as excellent examples of singular metabolites with pronounced benefits for human health.

5.1. Organosulfur Compounds

The organosulfur compounds commonly present in alliums are depicted in Figure 5, whereas the most important ones are described in this section.

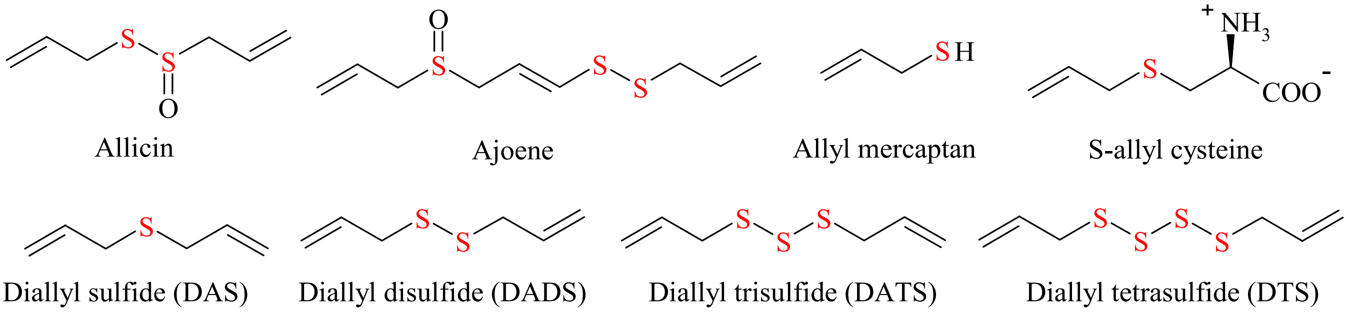


Figure 5. Leading organosulfur compounds of *Allium* spp.

Allicin (*S*-(prop-2-en-1-yl)prop-2-ene-1-sulfinothioate; allyl 2-propenethiosulfinate, diallyl thiosulfinate, *S*-allyl cysteine sulfoxide; $C_6H_{10}OS_2$) presents the basic odor component in garlic (*A. sativum* L.) and several other *Allium* species, including the well-known smell when a garlic clove is crushed [57]. This is probably the most common organosulfur compound isolated from *Allium* species with highly expressed bioactivity. It is biosynthesized from alliin, a non-protein *S*-containing amino acid [58], through the activation of the alliinase enzyme when plant material is pressured or damaged [57]. Actually, non-protein amino acids are an important group of secondary metabolites among *Allium* species comprising about 1–5% of the dry-weight mass of intact plants [51]. Allicin is a colorless, highly reactive oil with stability strongly influenced by environmental factors such as temperature, applied solvent system, and pH [57,59]. A lower temperature (4 °C) is recommended for allicin preservation in plant material as the shelf life of allicin rapidly decreases when the temperature rises [59]. Furthermore, higher temperature inactivates the alliinase enzyme preventing alliin conversion to allicin. Consequently, alliin dominates at high temperatures compared to allicin [60]. The extraction procedure with 20% alcohol as the solvent is the best choice since the presence of hydroxyl groups from alcohol apparently stabilizes the chemical structure of allicin. On the other hand, in aqueous extracts allicin is less stable, while the application of some non-polar solvents, such as hexane or vegetable oils, is strongly inadvisable since its stability is very limited (half-life time is 2 h only) and it starts to transform into a metabolite compound known as ajoene [59]. In addition, the stability of allicin is inversely related to pH value [57].

Allicin has been recognized as a "double player" since it can act both as an antioxidant and a prooxidant. As an antioxidant, this compound exhibits a good ability to quench free radicals, both DPPH and hydroxyl, and a positive correlation has been observed between allicin concentration and increased antioxidant properties [57]. Furthermore, allicin can inhibit the generation of nitric oxide (NO) originating from cytokine-induced nitric oxide synthase activity in rats [61], as well as lipopolysaccharides-induced NO production in macrophages [62]. Interestingly, although allicin generates elevated production of reactive oxygen species (ROS) as a prooxidant, this property can be used in selective cancer treatment since increased ROS levels can become cytotoxic for cancer cells and cause their extinction [63].

Allicin can be used in cancer treatment because its thiol (-SH) group can oxidize several important sulfuric compounds such as different proteins, peptides, and *S*-containing amino acids, leading to a change in redox potential in cancer cells that disrupts/decreases their proliferation process [57]. Although significant anti-cancer activity has been shown in different in vivo studies conducted on experimental animals, there is still a lack of human trials to support/refute the obtained data. Two important reasons for this are the chemical instability of allicin and limited data about its pharmacokinetic and pharmacodynamic metabolic transformations and possible toxicity [57]. In addition, allicin is the primary active metabolite that has made garlic a useful plant food for those suffering from some cardiovascular disorders for several thousand years. According to the working hypothesis, this *S*-containing molecule has the ability to form hydrogen sulfide and to improve the phosphorylation process in endothelial cells by enhancing NO synthase enzyme activity. Consequently, it improves the bioavailability of nitric oxide and protects the cardiovascular system [57]. Still, there are not enough studies that compare the activity of allicin with currently used drugs against cardiovascular diseases.

Ajoene ((*E*)-1(prop-2-enyldisulfanyl)-3-prop-2-enylsulfinylprop-1-ene; $C_9H_{14}OS_3$) is one of the unsaturated sulfuric compounds regularly found in garlic and onions. The compound is named after the Spanish word for garlic, "ajo". In nature, a mixture of *E*- and *Z*-isomers is present in a 1:2 ratio. Ajoene is slightly soluble in water (0.3 g/L) and is almost neutral, with a high pKa value (14.9) and low acidity. Ajoene has been reported to have several beneficial effects on humans, making it an important bioactive metabolite from *Allium* species. For instance, it has been shown that ajoene can inhibit platelet (thrombocyte) aggregation in the blood, preventing the formation of potential thrombi. It can also influence the cholesterol levels in the blood [52] by suppressing cholesterol biosynthesis through the inhibition of several cholesterolgenic enzymes in our body. Ajoene is considered a better antiviral agent compared to allicin, which is more effective against bacteria and fungi. Additionally, ajoene exhibits promising antiparasitic activity [53] against *Spironucleus vortens* (a parasite in freshwater angelfish) and *Trypanosoma cruzi*, a parasite that causes Chagas disease in humans as well as dourine and surra diseases in horses. Ajoene possesses good antiproliferative properties and can inhibit the growth of different human cancer cells [52].

***S*-allyl cysteine** (SAC; (*R*)-2-Amino-3-prop-2-enylsulfanylpropanoic acid; $C_6H_{11}NO_2S$) is a solid substance (melting point is around 220 °C) soluble in water as well as in 10% NaCl and 0.1 M NaOH solutions. However, it can be considered practically insoluble in several organic solvents including ethanol, acetonitrile, and ethyl acetate [64]. It can be easily obtained from mature garlic extract [65] since it is built from a precursor compound, γ-glutamyl-*S*-allyl cysteine, present in fresh garlic [64]. In aged garlic extracts, SAC is stable for 2 years [64]. It has been demonstrated that this amino acid is rapidly absorbed from consumed garlic [64], with excellent bioavailability of more than 90% [65]. The compound exhibits good antioxidant properties, especially in the case of the central nervous system (CNS) as an important neuroprotective metabolite against ROS species in the brain during research on experimental models [65]. In addition, SAC can be helpful in so-called nitrosative stress i.e., it can act as a scavenger of reactive nitrogen species (RNS) developed in the body, such as peroxynitrite ion, nitrogen dioxide, and dinitrogen trioxide free radicals. Together with reactive oxygen species, RNS are responsible for different types of cell damage. There is some evidence that SAC can protect cells from an expression of mitochondrial dysfunction, especially in the CNS and heart. This disorder is provoked by several factors such as oxidative stress caused by ROS or RNS, different inflammations, the presence of toxic substances, etc. [65]. After pretreatment with *S*-allyl cysteine sulfoxide, a higher content of mitochondrial phospholipids was observed as well as a decreased amount of cholesterol, free fatty acids, Ca^{2+} ions, and triglycerides in the blood of experimental rats [66]. The observed changes lead to improved myocardial function. In addition, SAC exhibited protective roles in endoplasmic reticulum stress in the CNS as well as anti-apoptotic activity [65]. This compound showed very low acute and sub-acute toxicity for mice and rats with LD_{50} values above 54.7 mM/kg of body weight [64], making it a safe and promising garlic metabolite for further pharmacological examination.

Allyl mercaptan (prop-2-ene-1-thiol; C_3H_6S), also known as allyl mercaptan (AM), or 2-propenyl mercaptan or 3-mercaptopropene, belongs to allyl sulfur compounds with an allyl sulfur functional group. It is slightly soluble in water and behaves as a weak acid (predicted pKa is 9.83). The compound is found in the cell cytoplasm, present in human saliva, while it can be ingested by consuming different *Allium* species, including the most important ones i.e., onion and garlic. Interestingly, green körmen (*A. scorodoprasum* L. spp. *rotondum*), a plant traditionally used in Turkey, is an even better source of this compound (4.9% of total volatile compounds) compared to garlic (0.08–0.11% of total volatile compounds) [67]. There is evidence in the literature that this metabolite is useful as an inhibitor of cholesterol biosynthesis and its secretion in Hep-G2 cells. The authors observed that it can be effective at a very low concentration range, from 5 to 25 µg/mL [68,69]. In addition, research has proved that allyl mercaptan is the most effective garlic metabolite as an inhibitor of histone deacetylase (HDAC) which can slow down the development of some cancer cells [70]. Among the volatile sulfur compounds of *Allium* species, AM is recognized as one of the most important antidiabetic garlic compounds [71].

Diallyl trisulfide (DATS; $C_6H_{10}S_3$) also known as allitridin, is one of the most important metabolites obtained from the hydrolysis of allicin with a yield of between 900 and 1100 µg/g of DATS [72]. It belongs to the group of trisulfides. It is insoluble in water and neutral without any acidic or basic properties. In cells, DATS is mostly located in cell membranes, where it can interact with non-polar parts of lipid bilayers causing a modification of membrane fluidity [73]. In this way, it can influence cancer cell development. Experimental data have shown that DATS can induce tumor cells to respond to cell death signals such as oxidative stress, cell disruption, and DNA damage [72].

5.2. Phenolic Compounds

In addition to sulfur-containing substances, alliums are a good source of phenolic compounds, which are believed to have a beneficial effect on human health. Several studies have demonstrated the presence of a considerable amount of flavonoids, especially derivatives of quercetin, kaempferol, and isorhamnetin (Figure 6) in different onion varieties [74–78]. Price and Rhodes have reported that 80–85% of total flavonoids in onion species belong to quercetin glucosides (quercetin-3,4′-*O*-diglucoside (QDC) and quercetin-4′-*O*-monoglucoside (QMG)) [78]. Furthermore, 3-β-D-glucosides of quercetin, kaempferol, and isorhamnetin were found in the green leaves of *A. schoenoprasum* [79]. On the other hand, by examining the content of flavonoids (by HPLC) in 70% ethanol extracts of *A. fistulosum* and *A. ursinum*, the presence of kaempferol in the non-hydrolyzed and hydrolyzed extracts of *A. fistulosum* and only in hydrolyzed samples of *A. ursinum* flowers and leaves was determined. Moreover, isoquercetin and quercetin were detected only in *A. fistulosum* [80]. In comparison to other vegetables and fruits, *A. cepa* contains 5- to 10-fold higher amounts of quercetin than blueberries, broccoli, and apples [81]. Analysis of *A. cepa* and *A. sativum* via UPLC/MS has demonstrated that onion contains significantly higher amounts of flavonoids in comparison to the garlic extract [82]. Among flavonols, myricetin and apigenin are found in *A. sativum* [83]. It is considered that flavonoids play an important role in the total antioxidant activity of dietary plants [84]. They are associated with reducing the risk of neurodegenerative disorders, osteoporosis, ulcer development, and the formation of cancer cells [85]. Some studies demonstrate that quercetin expresses anti-HIV properties and protects low-density lipoprotein (LDL) cholesterol from oxidation, and therefore decreases the risk of cardiovascular diseases [82,83].

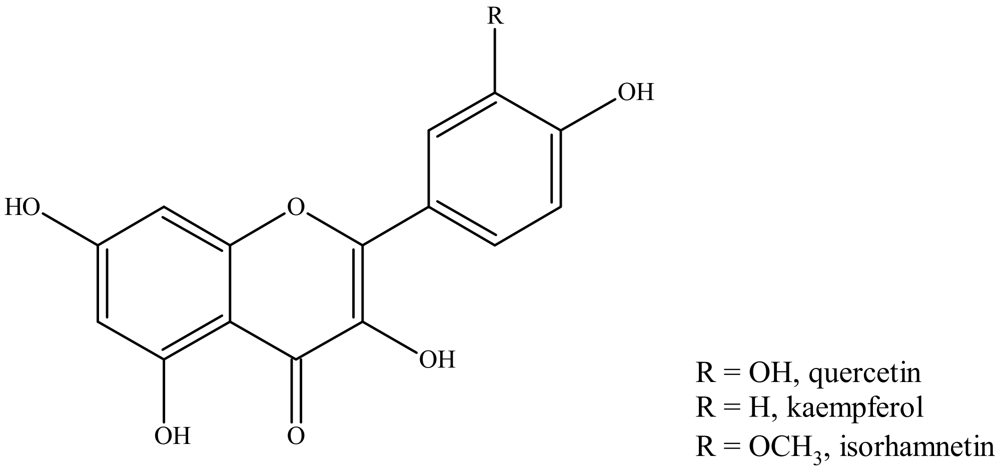


Figure 6. Structures of the most represented flavonoids in *Allium* spp.

Quercetin is one of the most abundant flavonoids in the plant kingdom. The pure compound is a yellow powder with a bitter taste, hydrated with water at room temperature. It becomes anhydrous at 95–99 °C. It is soluble in methanol, ethanol, and acetic acid, but poorly soluble in water (60 mg/L) at room temperature. Among vegetables, red and common onions contain 3.9 and 2.0 mg of quercetin per gram of fresh weight, respectively. Although the daily intake of quercetin is high in the Western diet (15 mg per day), it is poorly bioavailable and usually transformed into several different metabolites during digestion [86]. In order to improve its solubility and availability in plants, quercetin, as an aglycone, is linked to different sugars' moieties forming some glycosides. Among them, the most common are quercetin-3-*O*-glucoside, quercetin-3-*O*-galactoside, quercetin-3-*O*-rhamnoside, and rutin (quercetin-3-*O*-rutinoside) [87]. Amongst different *Allium* species, besides quercetin aglycone (131.9 mg/g), a significant amount of quercetin-4′-*O*-β-D-glucopyranoside (74.8 mg/g) was also obtained [88]. Quercetin exhibited good antioxidant properties measured by applying two usual assays—DPPH and FRAP. Compared to its glycoside derivatives, it possessed a higher ability to quench DPPH radicals due to a greater number of free OH groups. In addition, it was reported that Fe-chelation capacity decreased among quercetin derivatives, especially in the case of glycosides made through the substitution of the OH group in the C-3 position. This flavonoid is also recognized as a good anti-inflammatory agent. However, in the case of the anti-inflammatory activity of quercetin, its derivative tamarixetin (*O*-methylated quercetin in B ring, position C-4′)

is a compound with an excellent ability to inhibit in vitro production of cyclooxygenase (COX-1) and lipoxygenase (12-LOX), significantly higher compared to quercetin itself [86]. It should be pointed out that quercetin has been recognized as an important compound with the ability to inhibit the development of Parkinson's disease symptoms [89].

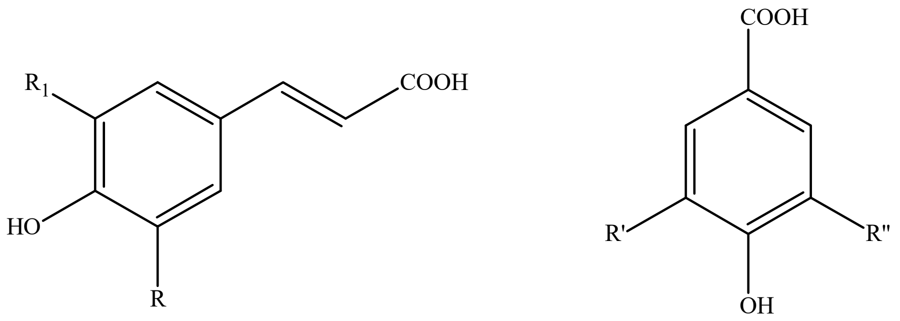
Anthocyanins such as cyanidin-3-glucoside, cyanidin-3-malonylglucoside, cyanidin-3-arabinoside as well as cyanidin-3-malonylarabinoside are major pigments detected in Spanish red onion [90,91]. Furthermore, cyanidin-3-glucoside, cyanidin-3-laminaribose, cyanidin-3-(6″-malonylglucoside), and cyanidin-3-(6″-malonyllaminaribioside) were found as major anthocyanins in red onion grown in Canada and the USA, while cyanidin-3″-malonylglucoside, peonidin-3-glucoside, peonidin-3-malonylglucoside, and cyanidin-3-dimalonyllaminaribioside were detected in slight concentrations [92]. Additionally, Fossen et al. found that the flowers and the stem of *A. schoenoprasum* contain four major anthocyanins: 3-(3, 6-dimalonylglucoside), 3-(6-malonylglucoside), 3-(3-malonyl-glucoside), and 3-glucoside of cyanidin [93].

Several phenolic acids, such as caffeic acid, ferulic acid, phthalic acid, and caffeic acid dimethyl ether, were identified in the methanol extract of *A. sativum* with the aid of UPLC-MS analysis [82]. Interestingly, the mentioned acids were not found in the sample of *A. cepa*. However, in the study conducted by Prakash et al. on four varieties of *A. cepa* (red, violet, white, and green) ferulic acid (13.5 -116 μg/g), gallic acid (9.3–354 μg/g), and protocatechuic acid (3.1–138 μg/g) were quantified by HPLC technique [94]. The amounts of gallic acid and protocatechuic acid were reduced in all tested samples from the outer dry to the inner fleshy parts of plants. On the other hand, the concentration of ferulic acid increased from the outer to inner layers in the red, violet, and white onion, whereas it decreased in the green variety [94]. *p*-Coumaric acid, ferulic acid, sinapic acid, and gallic acid were successfully identified by Kucekova et al. in a 90% methanol extract of *A. schoenoprasum* using the HPLC method [13]. It was found that the most abundant phenolic component was ferulic acid with approximately 887 μg per g of dry-weight sample. It is proven that ferulic acid has many biological properties, such as an anti-inflammatory effect, elimination of free radicals, and inhibition of cellular proliferation [95,96]. Additionally, Vlase et al. confirmed by HPLC-UV-MS analysis that ferulic acid is the most dominant component in *A. schoenoprasum* [97]. Moreover, ferulic acid and *p*-coumaric acid were detected in both non-hydrolyzed and hydrolyzed ethanol extracts, while sinapic acid was identified only in the non-hydrolyzed sample. It has been established that the amount of phenolic acids depends on the extraction agent used as well as on the part of the plant used for extraction. The studies conducted on the identification of phenolic acids in methanol extracts of fresh bulbs and leaves of *A. ursinum* have shown the differences between free and bound compounds in the investigated samples. Ferulic acid was found in free and bound forms in both bulbs and leaves. On the other hand, vanillic acid was detected in free form in leaves and bulbs, while the same acid was not found in bound form in bulbs. In addition, *p*-coumaric acid was quantified as a bound form in leaves and bulbs [98]. Furthermore, Condrat et al. have shown that 96% methanol is the best choice of solvent in the quantification of gallic acid in *A. ursinum* leaves, followed by 80% methanol and 96% ethanol, respectively [99]. It is believed that gallic acid has a protective effect on plants against bacterial infections, and it is also used in treating gastritis, urinary tract infections, and bloating [100–102]. The structures of the most abundant phenolic acids in *Allium* species are presented in Figure 7.

5.3. Steroids

Phytosterols represent a large family of naturally occurring lipophilic compounds found in the cell membranes of plants and they have an important role in the regulation of many cellular functions [103,104]. It has been reported that the phytosterols, such as β-sitosterol, stigmasterol, and lanosterol (Figure 8), were identified in the tissue of *A. cepa* [105]. Furthermore, Vlase et al. investigated phytosterols in fresh *A. fistulosum* herba, *A. ursinum* leaves, and *A. ursinum* flowers using 70% ethanol as an extraction agent [80].

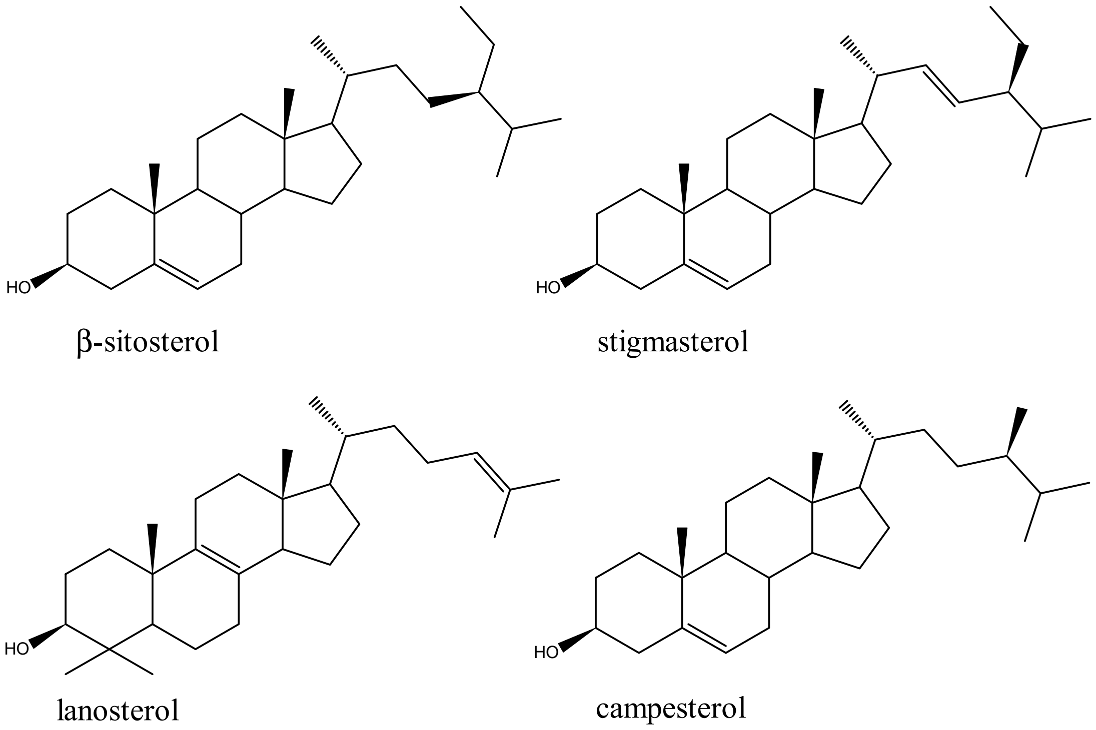
The results showed the presence of β-sitosterol and campesterol in *A. fistulosum* and *A. ursinum* flowers, while stigmasterol was revealed only in *A. fistulosum*. In addition, using ESI-MS and 1/2-dimensional ^{1}H and ^{13}C NMR spectroscopic techniques, Sabha et al. quantified β-sitosterol 3-*O*-β-D-glucopyranoside in an ethanolic extract from fresh leaves of *A. ursinum* [106]. It is proven that phytosterols reduce the risk of atherosclerosis and cardiovascular diseases as well as colon, prostate, and breast cancers [107–109].



$R = H, R_1 = H$; *p*-coumaric acid
$R = OCH_3, R_1 = H$; feluric acid
$R = H, R_1 = OH$; caffeic acid
$R = OCH_3, R_1 = OCH_3$; sinapic acid

R' = OH, R" = OH; gallic acid
R' = H, R" = OH; protocatechuic acid
R' = H, R" = OCH_3; vanillic acid

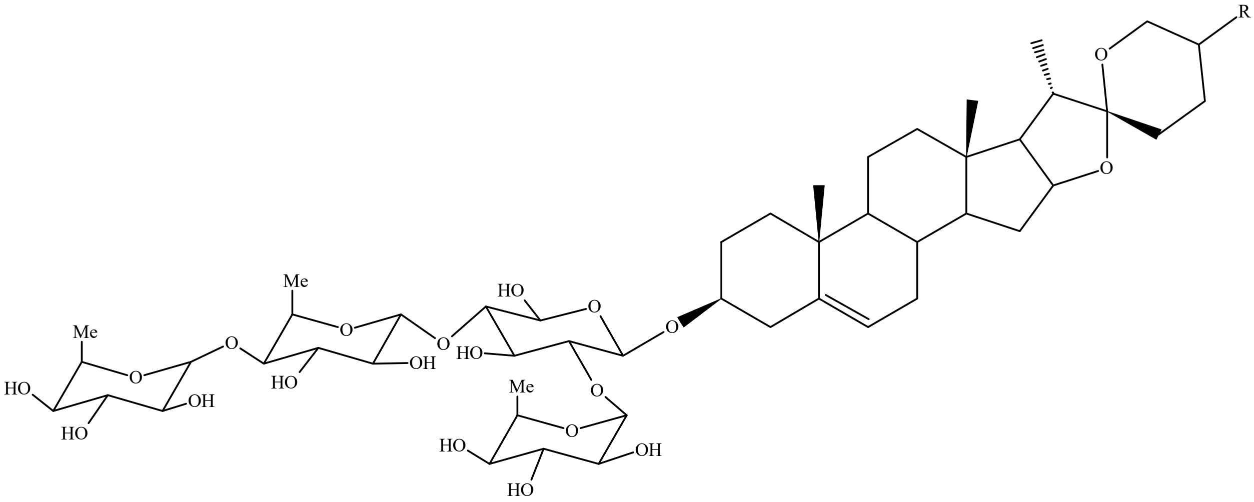
Figure 7. Structures of phenolic acids in *Allium* spp.



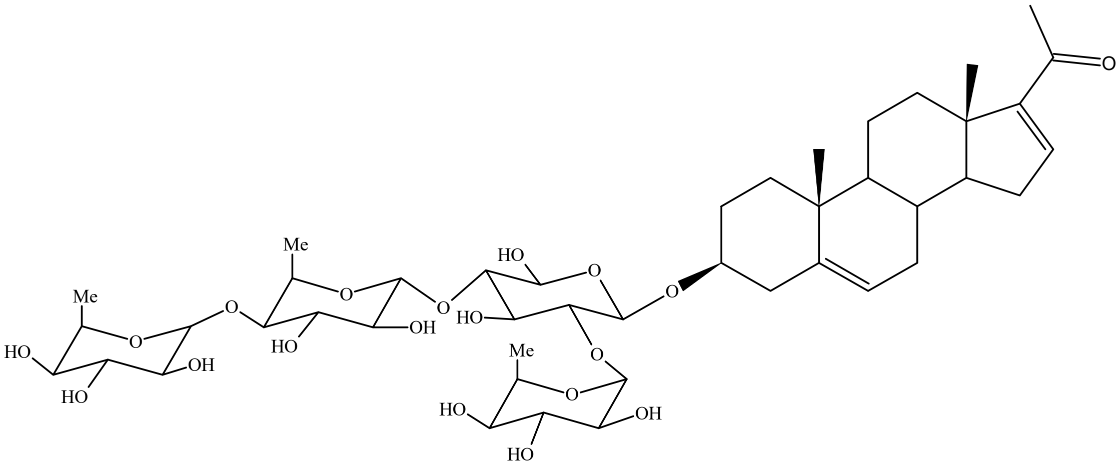
β-sitosterol
stigmasterol
lanosterol
campesterol

Figure 8. The structures of sterols identified in *A. cepa*.

Sobolewska et al. [110] isolated two spirostanol saponosides from wild garlic (*A. ursinum*), (25R)-spirost-5,25(27)-dien-3β-ol 3-*O*-α-L-rhamnopyranosyl- (1→4)-α-L-rhamnopyranosyl-(1→4)-[α-L-rhamnopyranosyl-(1→2)]-D-glucopyranoside and (25R)-spirost-5-en-3β-ol 3-*O*-α-L-rhamnopyranosyl-(1→4) -α-L-rhamnopyranosyl- (1→4)-[α-L-rhamnopyranosyl-(1→2)]-D-glucopyranoside (Figure 9) which show activity toward murine melanoma B16 and sarcoma XC. Additionally, a pregrane glycoside 3-hydroxy-pregna-5,16-dien- 20-on-3-*O*-α-L-rhamnopyranosyl-(1→4)- α-L- rhamnopyranosyl-(1→4)-[α-L-rhamnopyranosyl-(1→2)]-β-D-glucopyranoside (Figure 9) was found in the bulbs of *A. ursinum* [110].



R = CH2; (25*R*)-spirost-5,25(27)-dien-3*β*-ol 3-*O*-*α*-rhamnopyranosyl-(1→4)-
α-rhamnopyranosyl-(1→4)-[*α*-rhamnopyranosyl-(1→2)]-glucopyranoside
R = CH3; (25*R*)-spirost-5-en-3*β*-ol 3-*O*-*α*-rhamnopyranosyl-(1→4)-
α-rhamnopyranosyl-(1→4)-[*α*-rhamnopyranosyl-(1→2)]-glucopyranoside



3-hydroxy-pregna-5,16-dien-20-on 3-*O*-*α*-rhamnopyranosyl-(1→4)-
α-rhamnopyranosyl-(1→4)-[*α*-rhamnopyranosyl-(1→2)]-glucopyranoside

Figure 9. The structures of steroidal glycosides isolated from *A. ursinum*.

5.4. Fatty Acids

Fatty acids (FAs) are an integral part of triglycerides. As one of the major components of every living organism, FAs play an important role in the human diet [111]. Dietary FAs, by themselves or through their metabolites, have the ability to affect human health [112]. Multiple studies have shown that some polyunsaturated FAs are positively associated with serum high-density lipoprotein (HDL) as well as with low-density lipoprotein (LDL) [112,113]. Additionally, they can reduce blood pressure, and have beneficial effects on some neurodegenerative and neurological disorders [114,115]. Furthermore, the essential FAs are able to protect the human body from oxidative stress by acting as antioxidants [116]. Using ultra-performance liquid chromatography coupled with high-resolution MS (UPLC/MS) on *A. sativum* and *A. cepa* methanol extracts, Farag et al. detected linoleic acid, as well as a novel hydroxylated FA identified as 9,12,13-trihydroxy-octadeca-7-enoic acid [82]. It has been found that hydroxyl FAs exhibit antimicrobial, anti-inflammatory, and antiproliferative properties [82,117]. In addition, Waiater et al. revealed myristic, palmitic, stearic, oleic, linoleic, and α-linolenic acids in hexane extracts from the bulbs of *A. ursinum* (Figure 10) [118]. Moreover, the examination of *A. schoenoprasum* leaves by GC analysis revealed noticeable quantities of unsaturated FAs, linoleic and linolenic, with 32.3 and 38.7% of the total amount, respectively, while the most dominant saturated FA was palmitic with 25.9% of the total amount [119].

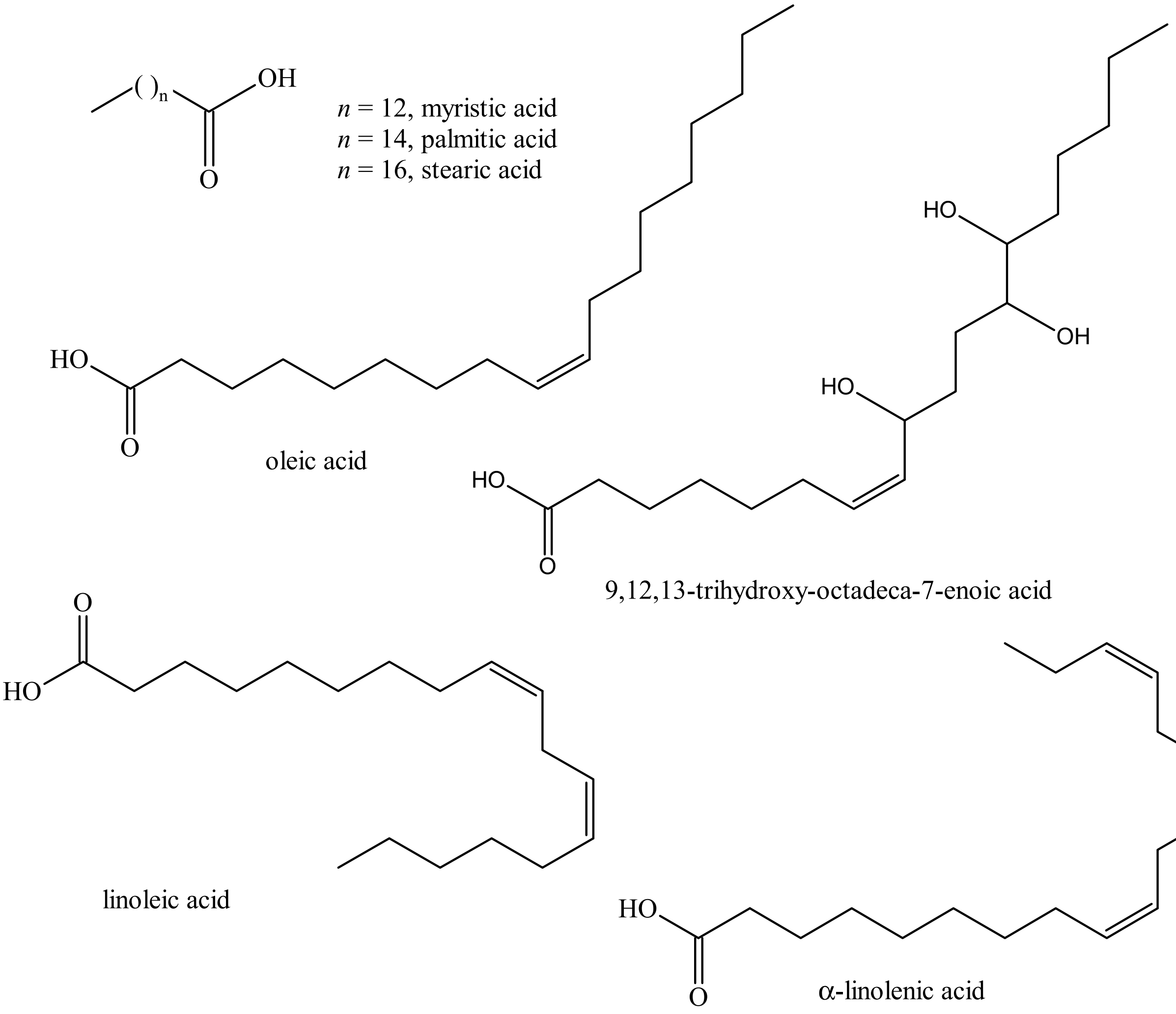


Figure 10. Structures of most common fatty acids in *Allium* spp.

5.5. Terpenoids

Many studies have demonstrated that natural terpenoids show numerous health benefits and it is also well-known that their intensive aromas protect plants from predators [120–122]. Ajayi et al. investigated the aqueous extract of *A. fistulosum* by GS-MS analysis and found that the D-limonene (Figure 11) was the most dominant monoterpenoid in the tested samples [123]. Moreover, it has been reported that D-limonene exhibits antioxidant, anticancer, anti-inflammatory, and cardio-protective properties [124–128]. Additionally, it is believed that the found monoterpenoid relieves symptoms of bronchitis and helps with treating heartburn and gastroesophageal reflux [129,130]. Further, Lachowicz et al. have determined the carotenoids in wild garlic using the UPLC-PDA-MS/MS method [131]. The study identified five dominant carotenoids: *trans*-β-carotene, 9-*cis*-β-carotene, all-*trans*-lutein, α-cryptoxanthin, and β-cryptoxanthin (Figure 11). The obtained results indicated that the average total carotenoid content was significantly higher in the leaves than in the stems, flowers, and bulbs [131]. It should be mentioned that carotenoids, as natural substances, are responsible for assigning colors to plants and animals [132]. More importantly, carotenoids show many biological functions, including absorption of light energy, oxygen transport, antioxidant, and antiproliferative activities which are directly connected to their molecular structure [133–135].

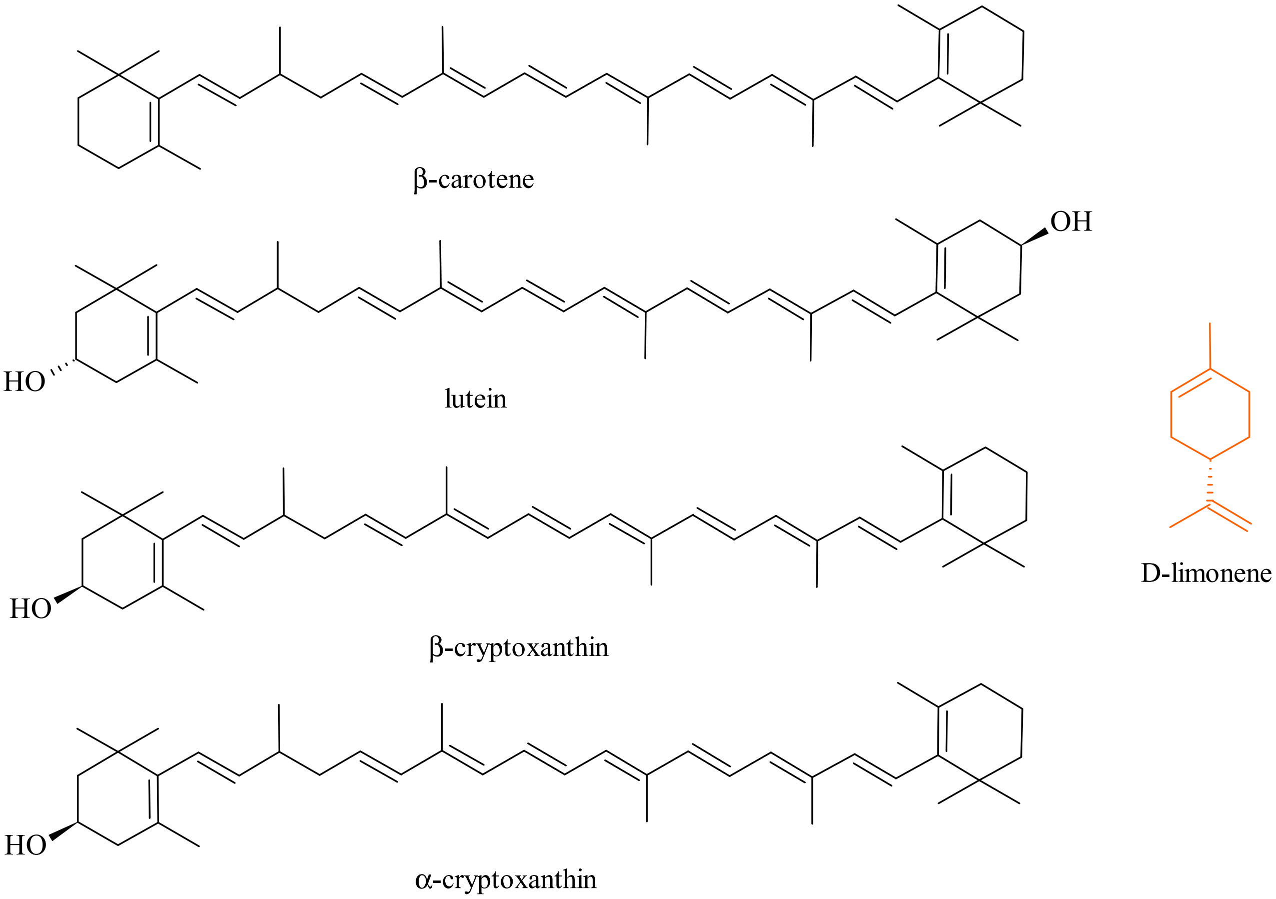


Figure 11. Structures of terpenoids identified in *A. ursinum*.

6. Overview of Antioxidant Activity of Alliums Common in the Balkans

The antioxidant properties of *Allium* species that are common in the Balkan region based on different assays are summarized in Table 2. The high antioxidant activity of alliums could be attributed to their rich chemical composition and a high content of organosulfur compounds [57,64,65,72,136], phenols (especially flavonoids) [74–78,90,91], and carotenoids [131,133–135]. In general, all parts of the plant including the bulb, peel, clove, leaf, pseudostem, root, flower, and seed exhibit antioxidant properties to varying degrees. However, it should be noted that antioxidant potential is strongly influenced by the extraction method as well as the applied solvent [14,137–152]. DPPH$^{\cdot}$ assay has most frequently been used to study the free radical scavenging activity of *Allium* species, followed by FRAP and ABTS$^{\cdot+}$ (Table 2). The results of the DPPH$^{\cdot}$ assay showed a high inhibition percentage for *A. cepa* bulb peel (72.25%) [143], *A. schoenoprasum* leaves (78.37%) [149], *A. fistulosum* pseudostem (59.45%) [146], and *A. ursinum* bulb (32.06–66.61%) [150] as well as fair inhibition percentages for *A. cepa* bulb (24.79%) [141], *A. schoenoprasum* root (24.33%) [147], and *A. ursinum* leaves (27.69%, respectively) [150,152]. Moreover, *A. ursinum* bulbs showed high antioxidant activity in the FRAP assay (42.11 mM TE/g) [148].

Table 2. Antioxidant activity of *Allium* species recorded in different assays.

Species/Plant Parts	Solvent	Assays	Results [1]	Reference
A. sativum				
Garlic peel	70 % methanol	* DPPH$^{\cdot}$(IC$_{50}$, mg/mL)	0.24 ± 0.00	[137]
		ABTS$^{\cdot+}$ (IC$_{50}$, mg/mL)	0.51 ± 0.01	
	70% ethanol	DPPH$^{\cdot}$ (IC$_{50}$, mg/mL)	0.20 ± 0.00	[137]
		ABTS$^{\cdot+}$ (IC$_{50}$, mg/mL)	0.44 ± 0.01	
Clove	70 % methanol	TEAC (μmol Trolox/g FW)	57.86 ± 1.43	[138]
		FRAP (μmol Trolox/g FW)	8.94 ± 0.31	
		DPPH$^{\cdot}$ (μmol Trolox/g FW)	7.60 ± 0.39	
	deionized water	DPPH$^{\cdot}$ (inhibition %)	4.65	[139]
		ABTS$^{\cdot+}$(mmol/L Trolox/g FW)	92.43	
Whole bulb	50% ethanol	ABTS$^{\cdot+}$(mmol/L Trolox/kg FW)	16.03 ± 0.41	[140]
A. cepa				
Bulb	distilled water	DPPH$^{\cdot}$ (Inhibition %)	24.79–25.61	[141]
	80% methanol	FRAP (mg AAE/g FW)	5.37 ± 1.185	[142]
		TAC (mg AAE/g FW)	12.94 ± 1.944	
		DPPH$^{\cdot}$ (IC$_{50}$, mg/mL)	0.24 ± 0.017	
Leaves	distilled water	DPPH$^{\cdot}$ (Inhibition %)	14.76–15.86	[141]
Bulb peel	80% methanol	FRAP (mg AAE/g FW)	8.59 ± 2.220	[142]
		TAC (mg AAE/g FW)	63.91 ± 1.312	
		DPPH$^{\cdot}$ (IC$_{50}$, mg/mL)	0.19 ± 0.047	
	70% ethanol	DPPH$^{\cdot}$ (Inhibition %)	72.25 ± 2.74	[143]
	hot water (80 °C)	DPPH$^{\cdot}$ (Inhibition %)	49.68±1.55	[143]
A. ampeloprasum				
Clove	70 % methanol	TEAC (μmol Trolox/g FW)	47.50 ± 1.52	[138]
		FRAP (μmol Trolox/g FW)	7.62 ± 0.64	
		DPPH$^{\cdot}$ (μmol Trolox/g FW)	6.95 ± 0.14	
Seed oil	hexane	ABTS$^{\cdot+}$ (μM TEAC/g oil)	136.30 ± 2.40	[138]
		DPPH$^{\cdot}$ (mM TEAC/g DW)	4.16 ± 0.12	
Pseudostem	70% ethanol	DPPH$^{\cdot}$ (μmol TE/g DW)	2–11	[144]
		FRAP (μmol FeSO$_4$/g DW)	3–18	
Leaves	70% ethanol	DPPH$^{\cdot}$ (μmol TE/g DW)	5–14	[144]
		FRAP (μmol FeSO$_4$/g DW)	14–37	
A. fistulosum				
Whole plant	80% methanol	FRAP (mg AAE/g FW)	3.38 ± 0.227	[142]
		TAC (mg AAE/g FW)	6.35 ± 1.698	
		DPPH$^{\cdot}$ (IC$_{50}$, mg/mL)	0.58 ± 0.002	
Pseudostem	rice wine (34% alcohol)	DPPH$^{\cdot}$ (IC$_{50}$, mg/mL)	15.2 ± 0.2	[145]
		TEAC (mmol TE/g extract)	15.1 ± 2.5	
	70% ethanol	ABTS$^{\cdot+}$ (Inhibition %)	57.44 ± 0.45	[146]
		DPPH$^{\cdot}$ (Inhibition %)	59.45 ± 0.24	
A. schoenoprasum				
Root	0.1 mol/L phosphate buffer (pH 7)	DPPH$^{\cdot}$ (Inhibition %)	24.33 ± 0.46	[147]
		FRAP (FRAP unit)	82.00 ± 7.00	
Leaves	0.1 mol/L phosphate buffer (pH 7)	DPPH$^{\cdot}$ (Inhibition %)	13.714 ± 0.378	[147]
		FRAP (FRAP unit)	52.66 ± 6.34	
	distilled water	DPPH$^{\cdot}$ (Inhibition %)	11.25 ± 0.50	[148]
		FRAP (mM TE/g DW)	5.40 ± 1.93	
	70% ethanol	DPPH$^{\cdot}$ (EC$_{50}$, g/mg)	6.72 ± 0.44	[14]
		TEAC (μg TE/g)	132.8 ± 23	
	ethanol	DPPH$^{\cdot}$ (Inhibition %)	61.08	[149]
	ethyl acetate	DPPH$^{\cdot}$ (Inhibition %)	78.37	[149]
	hexane	DPPH$^{\cdot}$ (Inhibition %)	49.46	[149]
Flower stalk	0.1 mol/L phosphate buffer (pH 7)	DPPH$^{\cdot}$ (Inhibition %)	10.428 ± 0.330	[147]
		FRAP (FRAP unit)	25.66 ± 4.41	

Table 2. *Cont.*

Species/Plant Parts	Solvent	Assays	Results [1]	Reference
A. ursinum				
Bulb	distilled water	DPPH$^{\cdot}$ (Inhibition %)	32.06–66.61	[150]
Leaves	distilled water	DPPH$^{\cdot}$ (Inhibition %)	10.10 ± 0.10	[148]
		FRAP (mM TE/g DW)	42.11 ± 0.50	
	0.85% saline	DPPH$^{\cdot}$ (μm TE/mL)	0.45 ± 0.05	[151]
	80% acetone	CUPRAC (mg AAE/g FW)	2.75 ± 0.11	[152]
		TAC (mg GAE/g FW)	3.27 ± 0.19	
		DPPH$^{\cdot}$ (Inhibition %)	27.69 ± 0.27	
		FRP (mg AAE/g FW)	0.87 ± 0.00	
Leaves and flowers	85% ethanol	DPPH$^{\cdot}$ (μM TE/g FW)	0.25 ± 0.01	[153]
		ABTS$^{\cdot+}$ (μM TE/g FW)	2.65 ± 0.04	
		FRAP (μM TE/g FW)	2.02 ± 0.01	

[1] Results are presented as mean ± SD (standard deviation) or as mean; * DPPH$^{\cdot}$—2,2-Diphenyl-1-picrylhydrazyl radical; ABTS$^{\cdot+}$—2,2′-Azino-bis (3-ethylbenzothiazoline-6-sulfonic acid diammonium salt; CUPRAC—cupric ion reducing antioxidant capacity; TAC—total antioxidant capacity; TEAC—trolox equivalent antioxidant capacity; FRP—ferric reducing power; FRAP—ferric reducing antioxidant power; AAE—ascorbic acid equivalents; GAE—gallic acid equivalents; TE—trolox equivalents; FRAP unit—100 μmol/dm^3 Fe^{2+}; FW—fresh weight; DW—dry weight.

7. Exploration of *Allium* Metabolites for Antimicrobial Activity

The antimicrobial potential of plants of the genus *Allium* has been known since ancient times. For decades, plants of the genus *Allium* have been the subject of various studies with the primary goal of finding the species or compounds with potentially high antimicrobial activity. These investigations led to the identification of many compounds with remarkable antimicrobial activity. Exceptional antimicrobial activity has been confirmed in various types of extracts and essential oils of these plants, as can be seen in the studies reported in this section.

Garlic (*A. sativum*) has shown its high antimicrobial properties against a wide spectrum of microbes. It is a rich source of essential amino acids, vitamins A and C, and elements such as zinc, selenium, and potassium, as well as sulfur and phosphorus compounds [154]. The polyphenolic and organosulfur composition as well as the antimicrobial activity of plants of the genus *Allium* largely depends on the growing conditions and the cultivation location. There is also a difference in antimicrobial activity between different garlic tissues, with cloves having a stronger antimicrobial activity than garlic peel. In addition, higher antimicrobial activity was observed in methanolic extracts compared to aqueous extracts against most of the tested microorganisms [155]. According to Chen et al., aqueous extracts of garlic had the largest inhibitory zone against plant pathogenic bacteria (*Erwinia carotovora*, *Pseudomonas syringae,* and *Xanthomonas campestris* pv. *malvacearum*) and fungi (*Fusarium proliferatum*, *Alternaria brassicicola,* and *Magnaporthe grisea*), followed by methanolic and ethanolic extracts [156]. Interestingly, the extracts obtained using acidified deionized water had significantly higher antimicrobial activity than the extracts prepared in a slightly basic medium. Another study showed that lyophilized black garlic (a processed sample of garlic) exhibited higher antimicrobial activity, with a minimal inhibitory concentration (MIC) of 3.125 mg/mL compared to regular garlic samples (which had an MIC of around or above 100 mg/mL), particularly against methicillin-resistant *Staphylococcus aureus* [157].

Considering that onion (*A. cepa*) is one of the oldest cultivated plants and has a long history of use in cooking, its antibacterial potential is still intensively studied. According to the findings of Ye et al., onion essential oil has potential antibacterial properties against the investigated microorganisms (*Escherichia coli*, *Bacillus subtilis*, *Staphylococcus aureus*, *Rhodotorula glutinis*, *Saccharomyces cerevisiae*, *Candida tropicalis*, *Aspergillus niger*, *Monascus purpureus*, and *Aspergillus terreus*) with MIC values ranging from 0.18 to 1.80 mg/mL and minimal bactericidal concentrations (MBCs) ranging from 0.54 to 3.6 mg/mL. On the other hand, *B. subtilis* was the most sensitive of the other examined bacterial species [158]. Sharma et al. examined the phenolic profile as well as the antioxidant and antimicrobial potential of methanolic extracts of different types of onions to assess the biological activity of fresh and aged onions [159]. Based on the obtained results, red onion extract showed potential antimicrobial and antibiofilm activity, yellow onion extract showed moderate activity, while the white one showed negligible effects. Moreover, it was noticed that onions aged 3 months showed better results than the fresh ones and those aged 6 months [159]. Another study that examined the antimicrobial activity of fifteen extracts generated by ultrasonic extraction from various varieties of onion skin found that pink skin was substantially more effective than red and dark red skin. Two extracts of pink skin showed the highest range of inhibition against *S. aureus*, *K. pneumonia*, *B. cereus*, and *S. typhimurium*. On the other hand, white skin extracts did not show any effect on bacterial growth, except cv. 'BhimaShubhra' and 'Udaipur Local', which inhibited the growth of *P. aeruginosa* up to 4.0 mm [160].

A. ursinum is a variety of European garlic known as wild garlic, ramson, and bear's garlic. The name of the plant comes from the Latin word "ursinum" derived from "ursus", which means bear, and is associated with the popular belief that when a bear wakes up from hibernation, it first consumes this plant to expel toxins from the body and regain strength [47]. It was used in folk medicine for diseases caused by microorganisms, digestive, and cardiovascular diseases as well as a preventative measure against respiratory illnesses [161]. However, the research that has been conducted on its composition and pharmacological efficacy is limited. Recently, many investigations have confirmed the antioxidant, antimicrobial, antiparasitic, anti-inflammatory, antiviral, antiproliferative, anticancer, and hypolipidemic effects of wild garlic [151,161–163]. Like in other *Allium* species, the unique odor of wild garlic is thought to be caused by sulfur-containing secondary metabolites [164]. Based on the available literature, it was observed that the antimicrobial activity of *Allium* species largely depended on the type of extract and the pathogenic type of microorganism [153]. The antimicrobial activity of wild garlic was tested against a wide range of bacterial and fungal species. Synowiec et al. examined the antimicrobial activity of aqueous and methanolic *A. ursinum* extracts in different concentrations, and the results showed that the methanolic extract was more active against all tested microorganisms, with average MIC values of 35 mg/mL for bacteria strains [165]. The methanol extracts showed the highest antibacterial potential against *S. aureus* (MIC 17.7 mg/mL), while the highest antifungal activity was reported against *C. lipolytica* (MIC 8.9 mg/mL) [165]. According to Mihaylova et al. [153], the water-ethanolic extracts of *A. ursinum* leaves and flowers did not exhibit any appreciable antimicrobial activity against the examined microorganisms. Only the bacteria *Staphylococcus aureus*, with an inhibition zone of 12 mm, and the fungus *Aspergillus niger*, with an inhibition zone of 6 mm, exhibited some level of sensitivity against tested extracts [153]. The food packaging industry is currently one of the fastest-expanding industries. Recently, new trends have emerged based on the use of environmentally friendly packaging systems that will further contribute to preserving the freshness and safety of food. Radusin et al. successfully synthesized a new active biofilm containing polylactide and ethanol extract of *A. ursinum* (10%) using electrospinning technology. Among many other benefits, this biofilm has shown significant antimicrobial activity against *S. aureus* and *E. coli* [166].

Most research studies have focused on examining the antimicrobial activity of well-known *Allium* species such as garlic (*A. sativum*), onion (*A. cepa*), and wild garlic (*A. ursinum*). These discoveries provided a solid basis for identifying the individual bioactive chemicals responsible for the reported antimicrobial action. In addition to the fact that sulfur compounds are the main constituents of plants of this genus, they are carriers of pharmacological activity. Interestingly, the antimicrobial compounds of *Allium* plants are classified depending on the processing of the plants. Garlic juice obtained by crushing garlic has quite different organosulfur components from those found in intact garlic cloves. For instance, different thiosulfinates are present in the crushed plant, different dialkyl(en)yl sulfides are released when the plant is crushed and stored, ajoene is present when the plant is macerated in oil, and heterocyclic sulfur compounds, 3-(allyltrisulfanyl)-2-aminopropanoic acid, and allyl alcohol are present when the plant is heated to 121 °C. When plants are treated with steam to obtain essential oil, different sulfides characteristic for each species are extracted [53].

The most abundant organosulfur compound in plants of the genus *Allium* is allicin, which has exceptional antimicrobial properties against both Gram-positive (G+) and Gram-negative (G-) bacteria, including multidrug-resistant bacteria [167]. Several studies have confirmed the in vitro activity of pure allicin or garlic extracts against specific kinds of bacteria, such as *Staphylococcus aureus*, *Pseudomonas aeruginosa*, *Escherichia coli*, *Candida albicans*, *Helicobacter pylori* as well as some fungi such as *Trichopyton rubrum*. In addition, in vivo studies proved the powerful antimicrobial activity of allicin against *Staphylococcus epidermidis*, *Leishmania promastigotes*, *H. pylori,* and *C. albicans* [57]. Allicin is an unstable compound synthesized by an allinase-based enzymatic reaction [168]. Until recently, the mechanism of action of allicin has been unknown, and it is supposed that allicin is involved in the oxidation of cysteine in glutathione and proteins. Reiter et al. successfully identified DNA gyrase as an allicin target in bacterial proteomes (*Pseudomonas aeruginosa*) using the differential isotope labeling method (OxICAT) [169]. In untreated bacteria, Cys 433 in DNA gyrase subunit A (GyrA) was oxidized by about 6%. After allicin treatment, the percentage of oxidation in allicin-sensitive *P. fluorescens* (Pf0-1) increased to 55%, but only 10% in tolerant *P. fluorescens* (PfAR-1) [169]. There are several ways by which allicin expresses antimicrobial activity, which include the influence on the biosynthesis of microbes' ribonucleic acids and lipids [57]. In addition, it is believed that the thiosulfinate group (R-SO-S) makes interactions with -SH groups from proteins, creating mixed disulfides [53].

When evaluated in laboratory media, allicin and other allicin-derived compounds exhibit substantial inhibitory effects against all microorganisms, including bacteria, fungi, viruses, and parasites. Due to the fact that allicin and thiosulfinates, in general, react with amino acids and other amino compounds in garlic and meals, allicin is substantially less stable in homogenized garlic and complex food systems than in its pure condition, in water. The reactivity of thiosulfinates with food components may limit the use of alliums as natural food preservatives [53]. Ajoene, on the other hand, is a molecule that is both biologically active and highly stable. It has potent antibacterial properties, particularly in harmful bacteria such as *P. aeruginosa*, where it inhibits quorum sensing [170]. A study conducted by Naganawa et al. showed that ajoene possessed high antibacterial inhibition potential against most Gram-positive (MIC 5–20 µg/mL) and Gram-negative bacteria (MIC between 100 and 160 µg/mL). Moreover, ajoene successfully inhibited yeast growth, with an MIC below 20 µg/mL [171].

According to Casella et al., the main compounds of garlic essential oil are diallyl monosulfide (DAS), diallyl disulfide (DADS), diallyl trisulfide, and diallyl tetrasulfide (DTS), while dipropyl disulfide (DPDS), dipropyl trisulfide, and dipropyl tetrasulfide are the most abundant compounds in leek (*A. porrum*) essential oil [172]. Comparing the antimicrobial activity of diallyl disulfide and dipropyl disulfide against *S. aureus*, *P. aeruginosa,* and *E. coli* showed that the presence of the allyl group was particularly significant for the antimicrobial activity of sulfide derivatives [172].

Not long after the discovery of the first antibiotics, allicin was also discovered, and then it was quickly patented due to its antimicrobial properties *in vitro*. Later, however, it was shown that the compound was not active in in vivo conditions because its stability was hindered by stomach acid. Moreover, its presence in the blood was not detected after use [55]. Allicin has lower antimicrobial activity in comparison to other antibiotics, such as penicillin. This is probably due to the higher affinity of allicin toward all free cysteine residues (-SH groups) in protein molecules while stronger antibiotics bind selectively to the -SH residues of higher importance for cell vitality. On the other hand, the specificity of penicillin is that it binds to cysteine residues in the vicinity of amino groups, which leads to its lessened dispersion on irrelevant targets [173,174].

In addition to the well-known effectiveness of allicin against plant pathogenic fungal species [175], its effectiveness in human fungal infections should not be neglected. The redox impact of allicin appears to be fundamental, but not the only explanation for allicin's fungicidal activity based on its effects on *Saccharomyces cerevisiae*. In comparison with fluconazole (FLU), which has a minimal inhibitory concentration of 1 μg/mL, allicin's MIC for *Cryptococcus neoformans* H99 was 2 μg/mL. Interestingly, even for amphotericin B-insensitive bacteria, allicin showed good antifungal activity against 46 clinical isolates of *C. neoformans*, with MICs ranging from 1 to 8 μg/mL. It is worth mentioning that allicin also had additive or synergistic effects when mixed with FLU and amphotericin B [176]. Aside from the basic interaction mechanism of allicin with the -SH groups of cellular proteins, some studies have indicated that allicin impacts specific target enzymes such as acetyl-CoA synthetase [177].

The -S(O)-S- group, which reacts with the -SH group of cellular proteins and creates mixed disulfides, is responsible for the antimicrobial activity of thiosulfinates, which include allicin. Therefore, from a mechanistic point of view, the antimicrobial activity of allicin is based on its interaction with proteins, and more precisely with the -SH group of cysteine, thereby inhibiting its function. Sulfhydryl compounds such as cysteine nullify the antimicrobial activity of these compounds [174]. It is assumed that all antimicrobial compounds obtained from cysteine sulfoxide in *Allium* plants inhibit the growth of microorganisms by an identical mechanism because their antimicrobial properties are neutralized by cysteine, except for allyl alcohol. Ajoene controls the development of biofilms by inhibiting the QS-induced (quorum signaling) production of virulence factors [178]. The antimicrobial activity of allyl alcohol does not depend on the concentration of cysteine. Allyl alcohol is oxidized intracellularly to acrolein by alcohol dehydrogenase. Acrolein is a very powerful protein-alkylating agent which exhibits exceptional anti-yeast activity [53]. The antifungal activity of *A. sativum* against *C. albicans* is known; however, the activity of allyl alcohol as one of the main constituents of the plant has not been sufficiently investigated. Lemar et al. monitored the change in intracellular responses after exposure of *C. albicans* cells to allyl alcohol and *A. sativum* extract. Changes typical of oxidative stress such as NADH oxidation, glutathione depletion, and an increase in reactive oxygen species were observed using microscopy and flow cytometry. Alcohol dehydrogenases 1 and 2 (in the cytosol) and 3 (in mitochondria) were identified as targets of allyl alcohol, although a more significant reduction in NADPH after the addition of allyl alcohol indicates another mechanism of action [179].

Comparing the antimicrobial activity of 3-(allyltrisulfinyl)-2-aminopropanoic acid with the available antimicrobial compounds of garlic, a similar activity with allyl alcohol against fungi was observed. Based on the obtained MIC values for *S. aureus* (B33), the antibacterial activity of 3-(allyltrisulfinyl)-2-aminopropanoic acid was significantly higher than that of allyl alcohol. As 3-(allyltrisulfinyl)-2-aminopropanoic acid is a water-soluble compound, it exhibits additional antimicrobial activity when the onion extract is heated at 45 °C for 75 min. Since the antimicrobial activity of heated garlic is almost completely neutralized by cysteine or glutathione, as was the case with allicin, garlic oil, and fresh garlic, it is believed that 3-(allyltrisulfinyl)-2-aminopropanoic acid inhibits microorganisms in the same way. The conducted study showed that the number of sulfur atoms in antimicrobial sulfides increased the anti-yeast activity up to 10 times. Dimethyl disulfide was found to be about ten times weaker than diallyl trisulfide [180].

Transcription of most of the quorum-sensing (QS) system genes in *P. aeruginosa*, such as lasR, rhlI/rhlR, and pqsABCDE/pqsR, was inhibited by diallyl disulfide and, as a result, the production of the signal molecules C4-HSL (encoded by rhlI) and PQS (encoded by pqsABCDE) was hindered [181].

Tang et al. exposed *Campylobacter jejuni* to diallyl trisulfide at a concentration of 16 μg/mL (0.5 MIC), and transcriptional analysis revealed 210 differentially expressed genes, the majority of which were connected to the metabolism, bacterial membrane transporter system, and secretion system. The downregulation of 14 ABC transporter-related genes involved in bacterial cell homeostasis and oxidative stress suggests that diallyl trisulfide may reduce the resistance of bacteria to environmental stress [182]. Table 3 summarizes the organosulfur compounds most responsible for the antimicrobial potential of *Allium* species and their mechanisms of action.

Table 3. The most abundant organosulfur compounds in *Allium* species and their mechanism of antimicrobial activity.

Allium Organosulfur Compounds	Mechanism of Action	Reference
Allicin (diallyl-thiosulfinate)	Oxidation of cysteine in glutathione and proteins Inhibition of DNA gyrase in bacterial proteomes Influence on the biosynthesis of microbes' ribonucleic acids and lipids inhibition of acetyl-CoA synthetase	[174] [169] [57] [177]
Ajoene	Controls the development of biofilms by inhibiting the QS-induced (quorum signaling) production of virulence factors	[178]
Allyl alcohol	Oxidized intracellularly to acrolein, which is a very powerful protein-alkylating agent and exhibits exceptional anti-yeast activity. Leads to oxidative stress such as NADH oxidation, glutathione depletion, and increase of reactive oxygen species. Alcohol dehydrogenases were identified as targets of allyl alcohol	[53] [179]
3-(Allyltrisulfinyl)-2-aminopropanoic acid	Similar mechanism as allicin	[180]
Diallyl disulfide	Inhibition of transcription of most of the quorum-sensing (QS) system genes in *P. aeruginosa* (as lasR, rhlI/rhlR, and pqsABCDE/pqsR) which interferes with the production of the signal molecules C4-HSL (encoded by rhlI) and PQS (encoded by pqsABCDE).	[181]
Diallyl Trisulfide	Could destroy the bacterial cell membrane and decrease the activity of the bacterial membrane transporter system.	[182]

Toxicological studies conducted by Lawal et al. [183] showed that the water extract of *A. sativum* did not cause a change in the concentration of serum transaminase, total bilirubin, creatine, erythrocytes, hematocrit, hemoglobin, Na and K ions, as well as granulocytes. There was also no change in the weight of the organs. However, in rats that were given 600 and 1200 mg/kg of the extract, total proteins, serum alanine transaminase activities, Cl^- concentrations, direct bilirubin, and body weight gain were decreased, whereas the concentrations of albumin, urea, white blood cells, mean corpuscular hemoglobin, and mean corpuscular volume count were significantly increased. The dose of 300 mg/kg caused slight changes in the concentration of Cl^- ions, urea, and albumin [184]. The influence of allicin on the autonomic nervous system, as a result of its inhibitory activity on cholinesterase, which acts as an indirectly acting muscarinic agonist, is the second and principal cause of allicin's toxicity. The excess acetylcholine that is not broken down by cholinesterase influences the central nervous system. When cholinergic receptor agonist toxicity is manifested in excess, symptoms such as miosis, sweating, bronchial constriction, nausea, diarrhea, cognitive impairment, convulsions, and coma may occur [183].

Recently, a new discipline that deals with the synthesis of nanoparticles (NPs) of various metals with plant extracts has emerged. One of the many advantages of this synthetic method is that the NPs are enriched with phytocompounds from plants, which further increases the bioactivity and compatibility of such NPs [185]. Considering the increasing resistance of bacteria and fungi to both antibiotics and compounds of plant origin, many researchers have successfully synthesized metal NPs using plant extracts to obtain agents with more pronounced antimicrobial properties. The selection of plant species for their synthesis has mainly been based on plants with already proven biological potentials. Due to their many times confirmed pharmacological properties, several species of the *Allium* genus have been utilized as effective reducing and capping agents for the synthesis of many metal and metal oxide NPs. The research conducted by Velsankar et al. successfully developed the synthesis of CuO NPs using an aqueous extract of *A. sativum* [186]. The synthesized NPs showed strong antimicrobial activity against all tested bacteria and fungi with an inhibition zone of 3 mm at an NP concentration of 50 µg/mL and around 11 mm at an NP concentration of 150 µg/mL. In contrast to standard antimicrobial compounds, which had an inhibition zone of 9 to 10 cm for all microbial strains at a concentration of 30 µg/mL, synthesized CuO NPs failed to inhibit microbe growth at the same concentration. Another study reported the successful synthesis of silver NPs (Ag NPs) using an aqueous onion extract in which compounds from the extract play a role in the reduction of Ag ions and stabilization of the formed Ag NPs [187]. Interestingly, Ag NPs showed pronounced antimicrobial activity with minimal inhibitory concentration (MIC) values ranging from 0.156 to 0.625 mg/mL against all the tested microorganisms except *Klebsiella pneumoniae*, where the MIC value was 2.5 mg/mL. In addition, when compared with onion extract, formed NPs demonstrated much stronger activity. A recent study showed the antibiofilm activity of NPs loaded with garlic extract against multidrug-resistant *Staphylococcus aureus* (MRSA), whereby the active constituents of garlic were released gradually and sustainably from NPs, resulting in significant antibacterial activity [188]. The dried aqueous extract of *A. sativum* was loaded within the fabricated honey, polyvinyl alcohol, and chitosan nanofibers (HPCS/AE) to develop a biocompatible antimicrobial nanofibrous wound dressing. Sarhan et al. reveal that the chitosan nanofiber in combination with the aqueous extract of *A. sativum* allows complete inhibition of *S. aureus* [189]. The same study confirms that HPCS/AE shows similar effects on the wound healing process in comparison with the commercial dressing Aquacel Ag; moreover, HPCS/AE allows an enhanced wound closure rate. Interestingly, the developed nanofibers show full biocompatibility toward cell cultures in relation to commercial Aquacel Ag, which exhibits noticeable cytotoxicity [189]. Table 4 summarizes the antimicrobial activity of different types of metal NPs synthesized using plants of the genus *Allium*.

Table 4. Antimicrobial activity studies of different types of metal nanoparticles synthesized using *Allium* genus plants against different bacteria and fungal species.

Type of Nanoparticles (NPs) [1]	Test Microorganisms	Zone of Inhibition (mm)	MIC [2] (mg/mL)	Reference
Ag NPs synthesized using *A. cepa* extract	*Bacillus subtilis* ATCC 663315	25	0.312	[187]
	Bacillus subtilis NCTC 1040010	27	0.156	
	Bacillus cereus ATCC 1457916	22	0.625	
	Bacillus licheniformis ABRII611	25	0.312	
	Bacillus sp. 2BSG-PDA-1610	19	0.625	
	Bacillus sp. DV2-3711	22	0.312	
	Staphylococcus aureus NCTC 744715	23	0.312	
	Streptococcus mutans ATCC 365415	20	0.312	
	Escherichia coli NCTC 1041811	24	0.312	
	Klebsiella pneumoniae ATCC 10031	11	2.5	
	Salmonella typhimurium NCIMB 933114	20	0.312	
	Pseudomonas aeruginosa ATCC 1014515	29	0.156	
	Proteus vulgaris ATCC 27973	15	0.625	
	Serratia marcescens ATCC 25179	12	0.625	
	Candida albicans	14	0.625	
Ag NPs synthesized using *A. cepa*	*Escherichia coli* MTCC No. 729		0.016	[190]
	Bacillus subtilis MTCC No. 736		0.016	
	Pseudomonas aeruginosa MTCC No. 4637		0.016	
	Fusarium oxysporum MTCC No. 3656		0.032	
Ag NPs synthesized using *A. cepa* and *A. sativa*	Against selected vaginal bacteria *Streptococcus pneumoniae* *Pseudomonas aeruginosa*	Growth inhibition		[191]
Au NPs synthesized using *A. ampeloprasum*	*Staphylococcus aureus* ATCC 29213		0.0612	[192]
	Bacillus subtilis ATCC 11774		0.25	
	Escherichia coli ATCC2 5922		0.5	
	Pseudomonas aeruginosa ATCC 27833		1	
	Candida albicans		0.125	

Table 4. *Cont.*

Type of Nanoparticles (NPs) [1]	Test Microorganisms	Zone of Inhibition (mm)	MIC [2] (mg/mL)	Reference
Cu NPs synthesized using *A. sativum*	*Escherichia coli*	3.9 (50 µg/mL)		[186]
	Staphylococcus. aureus	2.8 (50 µg/mL)		
	Bacillus subtilis	3.35 (50 µg/mL)		
	Streptococcus pyogenes	3.05 (50 µg/mL)		
	Pseudomonas aeruginosa	3.75 (50 µg/mL)		
	Klebsiella pneumonia	3.5 (50 µg/mL)		
	Candida albicans	2.95 (50 µg/mL)		
	Aspergillus flavus	2.35 (50 µg/mL)		
	Aspergillus fumigates	2.70 (50 µg/mL)		
	Aspergillus niger	2.15 (50 µg/mL)		
S NPs synthesized using *A. sativum*	*Candida albicans*	No inhibition effect		[193]

[1] Ag, Au, Cu, and S NPs—silver, gold, copper, and sulfur nanoparticles, respectively; [2] Minimal inhibitory concentration.

By applying some new technologies such as the synthesis of NPs using extracts of different types of *Allium* species, rich in compounds with strong antimicrobial activity, it is possible to improve their activity and increase the range of their application in different forms. Due to the instability of most organosulfur compounds, there is a possibility that binding to the newly formed silver NPs increases their stability.

8. Conclusions

Due to the distinctive aroma derived from various sulfur-containing metabolites and rich nutritional composition, *Allium* spp. are very desirable edible plants widely used in culinary arts. They are also effectively used in ethnomedicine for the prevention of some diseases. Alliums that are commonly used in the Balkans, mainly *A. cepa*, *A. sativum*, *A. ursinum*, and *A. ampeloprasum*, are a rich source of bioactive compounds, which have a major role in the pharmacological properties of plants. The extracts of *A. cepa* bulb peel, *A. schoenoprasum* leaves, *A. fistulosum* pseudostem, and *A. ursinum* bulb expressed notable antioxidant activity in *in vitro* antioxidant assays, such as DPPH, ABTS, TAC, and FRAP. This indicates that extracts of these species can exert antioxidant effects through different mechanisms of action. These plant species are also known for their significant effect on the growth and development of many microorganisms, and thus some of their uses are based on this feature. According to the reviewed literature, the antimicrobial potential of alliums and their application for these purposes can be viewed from several different angles. As the *Allium* extracts and isolated compounds, especially allicin, ajoene, and diallyl sulfides, showed marked antimicrobial effects, the available data on their activity may lead to the conclusion that these plants can be used as whole or that the most effective compounds can be isolated from the plant material and incorporated into the most diverse products in which they could fulfill their antimicrobial potential. On the other hand, new "green" methodologies have emerged, primarily referring to the preparation of nanoparticles using *Allium* species, resulting in the synthesis of nanoscale particles with strong antimicrobial activity that can be used for various applications.

Due to the increasing use of herbal medicine, especially for their lower incidence of side effects, and the extensive research on plants from the genus *Allium* in the Balkans, it can be concluded that alliums growing in this region are valuable plant species that can be used for various purposes. These include their use as potential natural remedies, cooking ingredients, as well as for their antioxidant and antimicrobial potential. In addition, new methods of utilizing these plant species, such as the use of nanoparticles, may be introduced in the future. As a result, these plants will continue to be the subject of interest for numerous research groups due to their vast potential for even more efficient uses.

Author Contributions: Conceptualization, J.B.P.-D. and J.S.K.S.; resources, S.V., A.Ž.K., N.D.P., M.A., U.L., N.S. and J.S.K.S.; writing—original draft preparation, S.V., A.Ž.K., N.D.P., M.A., U.L., N.S. and J.S.K.S.; writing—review and editing, J.B.P.-D. and J.S.K.S.; visualization, J.B.P.-D. and S.V.; supervision, J.B.P.-D. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Ministry of Science, Technological Development, and Innovation of the Republic of Serbia (Grants Nos. 451-03-47/2023-01/200116, 451-03-47/2023-01/200378, and 451-03-47/2023-01/200122). The APC was covered by vouchers provided by J.B. P.-Dj., J.S.K.S., A.Ž.K., and N.Dj.P.

Data Availability Statement: All data are contained within the article.

Acknowledgments: The authors acknowledge Sandra Vuković for providing photos of *Allium* plants, and Daniela Popović-Beogračić for the design of figures and graphical abstract.

Conflicts of Interest: The authors declare no conflict of interest.

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