

Review

Bioactive Compounds in Dietary Spices and Medicinal Plants

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Abstract: Aim of this review is to show the most important bioactive compounds in hot spices such as black pepper (*Piper nigrum* L.), chilli pepper (*Capsicum annuum* L.) and medicinal plant such AS garlic (*Allium sativum* L.), and its modes of action. Piperine is an alkaloid responsible for the pungency of black pepper, along with chavicine (C₁₇H₁₉NO₃) which is an alkaloid found in black pepper and other species of the genus Piper. It is one of the four geometric isomers of piperine. The active compound in black pepper is piperine (Bioperine; N-[(E,E)-Piperoyl]piperidine; Piperine (aliphatic); 1-[(2E,4E)-5-(1,3-benzodioxol-5-yl)penta-2,4-dienoyl]piperidine and etc.) which is responsible for bio enhancing effect. It has been found that piperine bioavailability enhancing property may be attributed to increased absorption, which may be due to alteration in membrane lipid dynamics and change in the conformation of enzymes in the intestines. Capsinoids is a family of compounds that are analogues of capsaicin, which is the pungent component in chilli peppers. Capsinoids are widely present at low levels in chilli pepper fruit which include capsiate, dihydrocapsiate, and nordihydrocapsiate. Capsaicin (C₁₈H₂₇NO₃ or 8-Methyl-N-vanillyl-trans-6-nonenamide) is the active substance responsible for the irritating and pungent effects of various species of hot peppers. Allicin (C₆H₁₀S₂O; allyl 2-propenethiosulfinate or diallyl thiosulfinate) is an organosulfur compound obtained from garlic, a species in the family Alliaceae. It was first isolated and studied in year 1944 and it is thought to be the principal bioactive compound present in aqueous garlic extract or raw garlic homogenate. When garlic is chopped or crushed, alliinase enzyme, present in garlic, is activated and acts on alliin (C₆H₁₁NO₃S) to produce allicin. Other important sulfur containing compounds present in garlic are allyl methyl thiosulfonate, 1-propenyl allyl thiosulfonate, and γ -l glutamyl-S-alkyl-l-cysteine. These compounds provide garlic its characteristic odour and flavour. Small amounts of nonvolatile water-soluble sulfur compounds such as S-allyl cysteine are found in garlic as well. These biological responses of all this bioactive compounds have been largely attributed to reduction of risk factors for cardiovascular diseases and cancer, stimulation of immune function, enhanced detoxification of foreign compound, antihepatotoxicity, cholesterol content reduction, antimicrobial effect, antifungal effect, antiinflammatory effect and antioxidant effect when consumed by animals or humans.

Keywords: black pepper; piperine; chilli pepper; capsaicin; garlic; allicin.

1. Introduction

Medicinal plants, aromatic herbs and spices, which are important part of the human diet, have been used for thousands of years in traditional medicine and to enhance the flavour, colour and aroma of foods [1]. In addition to boosting flavour, herbs and spices are also known for their preservative, antioxidative, and antimicrobial roles. Medicinal and aromatic plants have also been

used therapeutically to improve the health and wellbeing of animals, most were given for prophylactic purposes and to improve growth rate and feed conversion ratio efficiency [2]. In many countries as well in Serbia consumer pressure is pushing the poultry industry to rear animals without antibiotics as growth promoters. Removal of antibiotics as growth promoter has led to animal performance problems, feed conversion ratio increases, and to a rise in the incidence of certain animal diseases [3,4]. The alternatives to antibiotics as growth stimulators from the group of prebiotics, probiotics, organic acids, essential oils, medicinal plants or parts of plants such as thyme, basil, oregano, pepper and plenty of others are numerous [5]. Black pepper (*Piper nigrum* L.) is a flowering vine of Piperaceae family and has been a prized spice in many cultures all over the world. This herb is a known spice which improves digestibility [6,7]. It is a common medicinal herb used in human diet. The volatile oil of pepper has been shown to have antimicrobial activity. Black pepper has many medicinal properties for treatment of vertigo, asthma, indigestion, congestion, fever, diarrhoea. When it is used in broiler chicken nutrition it is found that very small addition of black pepper in the diet, about 0.5 to 1.0% significantly reduces cholesterol levels in meat [8]. Chilli pepper (*Capsicum annum* L.) is one of the most important spices widely used in human nutrition. Beside the pungent effect, in poultry nutrition is added in small amount between 0.25 and 1.0% because of the important role in decreasing deposition of cholesterol and fat in the body which contributes to decrease levels of triglycerides and support the vascular system in the body [9]. Hot red pepper is also rich in vitamin C which has a considerable impact in improving production through the reduction of heat stress on a fact that poultry consumption of hot red pepper induces a considerable change in energy balance [10]. Garlic is one of the most traditionally used plants as a spice, herb and medicinal plant. Garlic has been used for a variety of reasons where the most of them has been approved scientifically. Garlic preparations and extracts have been shown to exhibit: antiatherosclerotic, antimicrobial, hypolipidemic, antithrombotic, antihypertensive, antidiabetic effects and more [11]. There are a lot of active components in garlic like ajoene, s-allyl cysteine, diallyl sulphide and the most active one allicine [12]. Allicine reduces LDL, triglyceride and cholesterol in serum and tissues, and it has been used for cardiovascular diseases. Garlic has been found to decrease serum and liver cholesterol levels, inhibit bacterial growth, inhibit platelet growth and reduce oxidative stress [13]. In broilers, it was reported that garlic, as a natural feed additive improves broiler growth and feed conversion ratio and decreases mortality rate. Improvement of broilers performance and carcass traits can be achieved by supplementation of diets with garlic powder [14].

Aim of this paper is to show the most important bioactive compounds in hot spices such as black pepper (*Piper nigrum* L.) and chilli pepper (*Capsicum annum* L.) as well as medicinal plant garlic (*Allium sativum* L.), and their modes of action.

2. Piperine and Piperic Acid of Black Pepper (*Piper nigrum* L.) and Their Mode of Action

Black pepper is one of the most popular hot spice products in oriental countries (mostly in Southeast Asia). Black pepper is a plant of the Piperaceae family, largely used as a flavoring agent in foods. Its characteristic aromatic odour is due to the volatile oils in the cells of the pericarp. It has been traditionally used for the treatment of malaria in India and the epilepsy in China [15]. Moreover, black pepper has an antiinflammatory activity manifested by stimulating the production of an antiinflammatory cytokine like (IL-10) [16]. On the other hand, black pepper inhibits the expansion of genes encoding the nitric oxide synthase (iNOS) and the cyclooxygenase-2 (COX-2). The iNOS and COX-2 stimulate the production of many inflammatory cytokine mediators such as (Interleukin-4 (IL-4), Interleukin-10 (IL-10), Interleukin-13 (IL-13), interferon-alpha (α -IFN)), and the transformation growth factor b-TGF. Piperine (Bioperine; N-[(E,E)-Piperoyl]piperidine; Piperine (aliphatic); 1-[(2E,4E)-5-(1,3-benzodioxol-5-yl)penta-2,4-dienoyl]piperidine and etc.), which belongs to the alkaloid family, represents the major component in the dry fruit of *Piper nigrum*. Piperine has been reported to have several pharmacological effects such as antidiarrheal and antihepatotoxicity.

Some studies have shown that piperine possesses an antiinflammatory and an analgesic effect [17,18]. In addition, it has a high antioxidant activity and is used for the treatment of Alzheimer diseases. The chemical modification in the structure of piperine to piperic acid was confirmed by the appearance of the carboxyl group during the hydrolysis. Piperic acid has a high antihyperlipidemic activity. Recently, piperine and its derivatives have been evaluated for their inhibitory effects against epimastigote and amastigote [19]. Table 1 gives a preview of some important roles of black pepper fruits and piperine.

Table 1. Selected roles of black pepper and piperine.

Effects	References
Protection against oxidative stress	[20]
Decreased mitochondrial lipid peroxidation	[21]
Stimulation of digestive enzymes	[22]
Increase gastric acid secretion	[23]
Growth stimulatory activity	[24]
Balancing chicken blood cholesterol levels	[25]
Digestibility of fat in broiler nutrition	[26]

3. Alkaloid Compounds of Chilli Peppers (*Capsicum annuum* L.) and Their Mode of Action

Chilli pepper or know as capsicum is a genus of plant under the family of Solanaceae, or nightshades, are an economically important family of flowering plants. The family ranges from annual and perennial herbs to vines, lianas, epiphytes, shrubs, and trees, and includes a number of important agricultural crops, medicinal plants, spices, weeds, and ornamentals [9]. Capsicum has varieties of names according to their location and type. The most familiar peppers names are chilli, bell, red, green or just called as pepper. Chilli (*Capsicum annum* L.) is fruit vegetable commonly found in human daily nutrition. They are extremely popular for the huge content of vitamin C and total soluble phenolic which is higher than other vegetables commonly recognized as a source of this substance [14]. There are many properties that make chilli pepper different from other fruit vegetables, such as their shape, size, colour, flavour and heat, or they can be hot, sweet, fruity, earthy, smoky and floral. Varieties and stages of maturity also have great influence on chillies quantity. Scientific research has proven that, *capsicum annum*, is the only crop that produces alkaloid compound capsaicinoids (Capsaicin $C_{18}H_{27}NO_3$), which is responsible for the hot taste [27]. Capsaicin is alkaloid that is important in the pharmaceutical industry for its neurological effectiveness [28]. Pepper that is fresh is known as the very good source of vitamin C and E as well as vitamin A and carotenoids, and it's also known for antioxidant properties. Vitamin C, including ascorbic acid and its oxidation product dehydroascorbic acid ($C_6H_6O_6$), has many biological activities in the human body due to its antioxidant properties [29]. In human consumption, peppers and bell peppers are an important source of nutrient such as in providing carotenoids, phenols, vitamin C, foliates. In peppers, there is phytochemical property that has many biochemical and pharmacological properties which includes antioxidants, antiinflammatory, antiallergenic and anticarcinogenic activities [30]. It also has been proven that, ripe red peppers can reduce the risk of cancer. In addition, peppers also express antimicrobial properties. Table 2 gives the content review of some selected compounds of chilli peppers.

Table 2. Average content of selected compounds of chilli peppers [31–34].

Compounds	Amount
Capsaicin	309.30 µg/g
Dihydrocapsaicin	238.20 µg/g
Vitamin C	120.25 mg
Carotenoids	1060.24 µg/g
Total phenols	2150.25 µg/g
Total flavonoids	1.60 µmol/g
Antioxidant capacity	150.25 µmol/g

4. Bioactive Constitutes of Garlic (*Allium sativum* L.) and Their Mode of Action

Garlic (*Allium sativum*) has long been used both for flavouring and for the potential benefits of preventing and curing illness in many cultures [12]. Epidemiological, clinical, and preclinical studies have shown the close relation between dietary habits, including garlic intake, and the occurrence of disease. Garlic has been investigated extensively for health benefits and it is considered one of the best disease preventive foods, based on its potent and varied effects. The chemistry of the *Allium* species has been dominated by many sulfur containing compounds that give them a characteristic flavour [26]. However, a variety of components, including nonsulfur compounds, work synergistically to provide various health benefits. Because of the complex chemistry in *Allium* plants, variations in processing are present. Garlic exhibits hypolipidemic, decrease platelet aggregation and inhibit thrombus formation, poses procirculatory effects and promotes the circulatory system [13]. It prevents cold and flu symptoms through immune enhancement and exhibits anticancer and chemoprevention activities. The major sulfur containing compounds in intact garlic are γ -glutamyl-S-allyl-L-cysteines and S-allyl-L-cysteine sulfoxides (alliin) [11]. Both are abundant as sulfur compounds, and alliin is the primary odourless, sulfur containing amino acid, a precursor of allicin, methiin ($C_4H_9NO_3S$), (+)-S-(trans-1-propenyl)-L-cysteine sulfoxide, and cycloalliin ($C_6H_{11}NO_3S$). These sulfoxides, except cycloalliin, are converted into thiosulfinates such as allicin, which is a functional group consisting of the linkage R-S(O)-S-R through enzyme reactions when raw garlic is cut or crushed. Thus, no thiosulfinates are found in intact garlic. Thiolsulfinates are also named as alkanethiosulfinic (or arenethiosulfinic) acid esters. They are the first member of a family of compounds containing an oxidized disulfide bond [35]. Gamma-Glutamyl-(S)-Allyl-L-Cysteine is converted into S-Allyl cysteine ($C_6H_{11}NO_2S$) through an enzymatic transformation with γ -glutamyltransferase when garlic is extracted with an aqueous solution. S-Allyl cysteine a major transformed product from Gamma-Glutamyl-(S)-Allyl-L-Cysteine, is a sulfur amino acid detected in the blood that is verified as both biologically active and bioavailable [36]. The disruption of garlic bulbs causes the formation of thiosulfinates such as allicin through the enzymatic reaction of sulfur substituted cysteine sulfoxides, compartmentalized in the cytoplasmic with alliinase in the vacuole, via sulfur substituted sulfenic acids as a highly reactive intermediate where in Table 3 is showed chemical compounds and their amount found in bulb.

Allicin easily reacts with amino acids and proteins, creating an SH group. Allicin binds to protein and fatty acids in the plasma membrane, are thus trapped before absorption, and cannot circulate in the blood [37]. Typical volatiles that have been identified in crushed garlic and garlic essential oil include DAS, DADS, diallyl trisulfide, methylallyl disulfide, methylallyl trisulfide, 2-vinyl-4H-1, 3-dithiin, 3-vinyl-4H-1, 2-dithiin, and (E,Z)-ajoenes.

Table 3. Chemical compounds found in garlic bulb [38,39].

Compound	ppm	Compound	ppm	Compound	ppm
1,2-Dimercaptocyclopentane	2.4	Ascorbic acid	444.0	Protoeruboside-B	100.0
1,3-Dithiane	1.5	Aspartic acid	8313.0	Quercetin	200.0
2-Vinyl-4H-1,3-dithiin	15.5	Beta-carotene	0.2	Riboflavin	1.8
3,5-Diethyl-1,2,4-trithiolane	21.6	Biotin	22.0	S-(2-carboxy-propyl)-glutathione	92.5
3-Vinyl-4H-1,2-dithiin	5.5	Caffeic acid	20.0	S-allo-mercapto-cysteine	2.0
Alanine	16244.0	Cystine	1105.0	S-allyl-cysteine	10.0
Allicin	14650.0	Diallyl-disulfide	314.0	Sativoside-B-1	30.0
Alliin	7500.0	Diallyl-sulfide	50.5	Scordinine	250.0
Allyl-propyl-disulfide	126.0	Diallyl-trisulfide	535.0	Scordinine-A	39.0
Aniline	10.0	Dimethyl-difuran	17.5	Scordinine-B	800.0

Over 20 sulfides have been identified in steam distilled garlic oil and oil soluble extract of garlic, and many of them, especially sulfides having an allyl group, are responsible for the characteristic smell and taste after ingesting garlic. The major sulfides in garlic oil include DAS (57%), allylmethyl (37%), and dimethyl (6%) mono to hexasulfides, in some cases, together with a small amount of allyl 1-propenyl and methyl 1-propenyl di-, tri-, and tetrasulfides. Diallyl trisulfide is the most abundant in fresh garlic oil, but commercially available garlic oil products have an increased amount of DADS [40].

5. Conclusions

Having in mind the aforementioned fact is that natural products such as the hot spices and medical plants poses chemical compounds found that usually has a pharmacological or biological activity for use in pharmaceutical drug or as original natural products or synthetic products based on natural product models. Many secondary metabolites have been isolated and characterized from a variety of natural sources, such as bacteria, fungi, and in the last three decades most important of them plants. They are of high interest and importance because they often exhibit a wide spectrum of biological activities. The medicinal plants may not be as useful as claimed or they may have more therapeutic properties than are known traditionally by people, but exact mode of action of hot spices and medicinal plants is not scientifically proven and further research in this specific field is still necessary.

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