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Novel Nutritive Garlic Product ''Black Garlic'': A Critical Review of Its Composition, Production and Bioactivity

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Abstract

Garlic has organosulfur compounds and bioactive enzymes in its composition. Garlic has been shown to display anti-bacterial, anti-fungal, anti-atherosclerotic, detoxification, and anti-carcinogenic effects due to its bioactive components. Although garlic has been widely used as one of the popular condiment for foods and traditional medicine against various disease, consumption of garlic is very limited due to its unpleasant odor and taste. In recent years various processing methods were applied to obtain new garlic products to eliminate undesirable odor of garlic without damage its health benefits. Black garlic is a heat treated and fermented garlic product at controlled high temperature (60-90 C°) and controlled high humidity (80-90%) for a period of time without any additives. As a result of this fermentation process white-fresh garlic cloves turns to black and get sweet taste, chewy and jelly-like structure. Garlic lose its pungent taste and irritative odor during the ageing process due to the conversion of allicin into water-soluble antioxidant compounds including S-allylcysteine and S-allylmercaptocysteine moreover many sulfur-containing compounds are formed, which contribute to health benefits. Black garlic has stronger antioxidant activity than fresh garlic, and better efficacy in preventing metabolic diseases. Furthermore, non enzymatic browning reactions are take place like Maillard reaction, the chemical oxidation of phenols and caramelisation during aging process. The results of these reactions color of garlic samples turn to dark brown and some antioxidant compounds formation is occur. Process time, process temperature and applied relative humidity effect the black garlic physical, chemical and sensorial properties thus several studies revealed that effect these parameters on black garlic. All process conditions there was a decrease in moisture content, pH, reducing sugar and increase in browning intensity, antioxidant, SAC content in garlic samples after fermentation. Aim of this study is review the composition, bioactivity, production and applications of black garlic during production process and compare them with fresh garlic at different process conditions.

Keywords: Black garlic, alliin, alicine, S-Allycysteine, fermentation, antioxidant, anti-carcinogen

Öz

Sarımsak, bileşiminde organosülfür bileşikleri ve biyoaktif enzimler içerir ve içeriğindeki bu bileşenleri nedeniyle anti-bakteriyel, anti-fungal, anti-aterosklerotik, hipoglisemi, detoksifikasyon ve anti-kanserojen etki göstermektedir. Sarımsak gıdalarda çeşni olarak kullanılmasının yanı sıra, geleneksel bir ilaç olarak ta birçok hastalığın tedavisinde kullanılmaktadır ancak sarımsak tüketimi, sarımsağın sahip olduğu hoş olmayan kokusu ve tadı nedeniyle sınırlıdır. Son yıllarda sağlığa yararlı etkileri korunmuş ve istenmeyen kokularından izole edilmiş yeni sarımsak ürünleri elde edebilmek için birçok metot uygulanmıştır. Siyah sarımsak, herhangi bir katkı maddesi olmaksızın belirli bir süre yüksek ısıya (60-90 ° C) ve neme (% 80-90) maruz bırakılarak üretilmiş,fermente bir sarımsak ürünüdür. Bu fermentasyon işlemi sonucunda beyaz-taze sarımsağın dişleri siyaha dönüşür ve tatlı bir tada, jöle benzeri bir yapıya kavuşurlar. Bu süreçte sarımsak içerisinde bulunan alisinin suda çözünebilen antioksidan maddeler olan S-Alilsistein , S-alilmerkaptosistein ve birçok sağlığa yararlı, kükürt içeren bileşiğe dönüşerek keskin ve istenmeyen kokusunu kaybeder. Siyah sarımsak, taze sarımsaktan daha güçlü antioksidan etkiye sahiptir ve metabolik hastalıkların önlenmesinde daha etkilidir. Ayrıca, bu olgunlaşma sürecinde Maillard reaksiyonu, fenollerin kimyasal oksidasyonu ve karamelizasyon gibi enzimatik olmayan esmerleşme reaksiyonları gerçekleşir. Bu reaksiyonlar sonucunda da sarımsak örneklerinin rengi kahverengiye dönüşür ve bazı antioksidan bileşikler oluşur. Yapılan çalışmalarda proses süresinin, sıcaklığının ve bağıl neminin üretilen siyah sarımsakların fiziksel, kimyasal ve duyusal özelliklerine etkileri incelenmiştir ve fermentasyon sonrası sarımsak örneklerinin nem, pH, indirgen şeker, antioksidan, SAC içerikleri ve esmerleşme yoğunluklarında bir artış gözlemlenmiştir. Bu çalışmanın amacı, farklı üretim koşullarında üretilmiş siyah sarımsağın kompozisyonunu, biyoaktivitesini özetleyerek bu özelliklerini beyaz sarımsak ile karşılaştırmak, böylelikle üretim koşullarının ürün üzerindeki etkilerini net bir şekilde ortaya koymaktır.

Anahtar kelimeler:*siyah sarımsak ,* alisin, S-Alilsistein,fermentasyon, antioksidan, anti-kanserojen

1. Introduction

Garlic (*Allium sativum L.)* is a species of the onion genus and among the oldest cultivated plants. It has been widely used as a spice and also as a medicinal agent for treatment of multiple human diseases and disorders. Garlic has organosulfur compounds and bioactive enzymes in its composition. Allicin, the major component present in freshly crushed garlic, is one of the most biologically active compounds of garlic [1]. It also contains the sulfur containing compounds alliin, ajoene, diallylsulfide, dithiin, and S-allylcysteine, as well as enzymes, vitamin B, proteins, minerals, saponins, flavonoids, and Maillard reaction products, which are non-sulfur containing compounds [2,3]. Garlic has been shown to display anti-bacterial, anti-fungal, anti-atherosclerotic, hypoglycemia, detoxification, and carcinogenic effects due to its bioactive components [4,5]. Although garlic has been widely used as one of the popular condiment for foods and traditional medicine against various disease, consumption of garlic is very limited due to its unpleasant odor and taste. In recent years various processing methods were applied to obtain new garlic products to eliminate undesirable odor of garlic without damage its health benefits. Black garlic is a heat treated and fermented garlic product at controlled high temperature (60-90 C°) and controlled high humidity (80-90%) for a period of time. As a result of this fermentation process white-fresh garlic cloves turns to black and garlic cloves get sweet taste, chewy and jelly-like structure. Fermentation conditions vary depend on manufacturers, purposes and cultures [6]. This sweet product can be used as food ingredient or eaten as a culinary snack in Asian cuisines, particularly those from Korea, China and Japan. Garlic lose its pungent taste and irritative odor during the ageing process due to the conversion of allicin into water-soluble antioxidant compounds including S-allylcysteine and S-allylmercaptocysteine [7]. moreover many sulfur-containing compounds are formed, which contribute to health benefits. Through the heating process, unstable and unpleasant compounds in raw garlic are converted into stable and tasteless compounds. As a result, black garlic generally has a sweet–sour flavour instead of the offensive odour and taste. [7,8]. It is reported that black garlic has stronger antioxidant activity than fresh garlic, [7, 9, 10]. and better efficacy in preventing metabolic diseases [11,12]. Furthermore, non enzymatic browning reactions are take place like Maillard reaction, the chemical oxidation of phenols and caramelisation during aging process. The results of these reactions color of garlic samples turn to dark brown and some antioxidant compounds formation is occur [13,14]. This review aims to examine the composition, bioactivity, production and application areas of black garlic as well as the proposed improve its possible functions and application.

2. Comparison Fresh and Black Garlic Components

Two classes of organosulfur compounds are found in whole garlic cloves: L-cysteine sulfoxides and γ-glutamyl-L-cysteine peptides. When raw garlic cloves are crushed, chopped, or chewed, an enzyme known as alliinase is released. Alliinase catalyzes the formation of sulfenic acids from L-cysteine sulfoxides. Sulfenic acids spontaneously react with each other to form unstable compounds called thiosulfinates. In the case of alliin, the resulting sulfenic acids react with each other to form a thiosulfinate known as allicin. The formation of thiosulfinates is very rapid and has been found to be complete within 10 to 60 seconds of crushing garlic. [15]. Black garlic does not have the strong odor of fresh garlic because the compound allicin responsible for the unique pungent odor [16,17]. is converted into water-soluble antioxidant compounds including S-allylcysteine and S-allylmercaptocysteine during the ageing process [7]. Crushing garlic does not change its γ-glutamyl-L-cysteine peptide content. γ-Glutamyl-L-cysteine peptides include an array of water-soluble dipeptides, including γ-glutamyl-S-allyl-L-cysteine, γ-glutamylmethylcysteine, and γ-glutamylpropylcysteine. Water-soluble organosulfur compounds, such as S-allylcysteine(SAC) and S-allyl mercaptocysteine (SAMC), are formed from γ-glutamyl-S-allyl-L-cysteine during long-term incubation of crushed garlic in aqueous solutions, as in the manufacture of aged garlic extracts. SAC ($C_6H_{11}NO_2S$) is a colorless, odorless, water-soluble, stable and bioactive organosulfur compound existing in garlic (Allium sativum). It has protective effects against oxidation, free radicals, cancer, cardiovascular diseases and neuronal degeneration diseases [18,19,20,21]. In garlic, SAC is derived from γ-glutamyl-S-allyl-L-cysteines (GSAC, $C_{11}H_{18}N_2O_5S$) through an enzymatic transformation with the catalysis of γ-glutamyltranspeptidase (γ- GTP, EC 2.3.2.2) [19]. So far, aging is considered as a typical process to accumulate SAC in garlic. By aging of fresh garlic bulbs or cloves for 40 days in a thermo-hydrostat chamber controlled at 65–80 °C in temperature and 70%–80% in relative humidity, the SAC content reached 98–194 μg/g, i.e. 4.5–8 times higher than that in fresh garlic [20,22]. The antioxidant activity of food phenolic compounds is of nutritional interest, since it has been associated with the potentiation of the promoting effects of human health through the prevention of several diseases [23].

Several studies have reported that physicochemical characteristics, amino acid contents, water soluble sugars,total polyphenols and flavonoids variations, minerals, color values of garlic during thermal processing (Table 1,2).

3. Black Garlic Processing and Effects of Prosess Conditions on Product Characteristics

Black garlic is a garlic product that has been fermented for a period of time at a control high temperature (60-90°C) under controlled high humidity (80-90%) [26]. Process time, process temperature and applied relative humidity effect the black garlic physical, chemical and sensorial properties thus several studies revealed that effect these parameters on black garlic. But all process conditions there was a decrease in moisture content, pH, reducing sugar and increase in browning intensity, antioxidant, SAC, HMF (hydroxymethylfurfural) content in garlic samples after fermentation.

Generally the black color formation in garlic is associated with a non-enzymatic browning reaction widely depend on heating temperature. [26, 27, 28]. Heated garlic samples browning intensity increased with rising temperature [29] and rate of increase in browning intensity was faster at higher heating temperature. [22] studied browning intensity of garlic samples that processed at 40,55,70 and 85°C during 45 days black garlic production. The browning intensity of garlic sample heated at 85 °C rapidly increased during the first 15 day of process and reached a plateau but browning intensity of other garlic samples were increased continuously during 45 days of production. In the garlic sample heated at 70°C, the browning intensity reached a similar level as that in the garlic sample heated at 85°C in the final stages of heat treatment but garlic samples heated at 40 and 55°C showed lower browning intensity than heated at 70 and 85°C garlic samples. On the contrary browning intensity, SAC content of garlic samples are increase in this 45 days period but high temperature adversely affect SAC contents of garlic samples.

Table 1. Comparison black and fresh garlic components

Components	Components of black garlic compared with fresh garlic	Original concentration
Water-soluble sugar	Increased 1.88-7.91-fold [6]	450 mg/g
Fructan	Decreased 0.15-0.01-fold [6]	580 mg/g
Leucine	Increased 1.36-fold [24]	71.25 mg/100 g
Isoleucine	Increased 1.67-fold [25]	50.04 mg/100 g
Cysteine	Decreased 0.58-fold [25]	81.06 mg/100 g
Phenylalanine	Increased 2.43-fold [25]	55.64 mg/100 g
Tyrosine	Decreased 0.18-fold [25]	449.95 mg/100 g
Valine	Increased 1.31-fold [24]	60.80 mg/100 g
Methionine	Increased 2.25-fold [25]	31.56 mg100/g
Polyphenol	Increased 4.19-fold [25]	13.91 mg GAE/g
Flavonoid	Increased 4.77-fold [25]	3.22 mg RE/g
Amadori & Heyns	Increased 40-100-fold [6]	10 mg/g
Al	Increased 46.98-fold [24]	0.54 mg/100 g
Fe	Increased 1.34-fold [24]	3.30 mg/100 g
Mg	Increased 1.73-fold [24]	15.70 mg/100 g
Zn	Increased 1.03-fold [24]	1.50 mg/100 g
Ca	Increased 1.74-fold [24]	7.48 mg/100 g

Similarly [30] studied at four different temperature in black garlic production (60, 70, 80, 90 °C) with controlled humidity. According to sensory evaluations; at high temperature treated garlic samples brown color formation was shown early than other samples but obtained product more bitter and had a sour flavor. At low temperature the color of black garlic did not reach the desired and homogeneous blackness. Under 70 and 80 °C desired sensory characteristic and homogeneous blackness was acquired. HMF is a common Maillard reaction product; the reaction occurs during heat-processing and the preparation of many types of foods and beverages [31] and it is one of the main antioxidant ingredients in black garlic [30].Black color formation of garlic sample with regarded to the accumulation of HMF [32].Thus increase in HMF content as an indicator of black color formation in garlic. [30] processed garlic to black garlic at 60°C, 70°C, 80°C, 90 °C temperature and observed the HMF content until they reach maturity. When HMF content reach 4 g kg^{-1} garlic samples had basically aged and turn to black. The samples processed 90 °C reached the maturity about 9 days, 80 °C processed samples reached about 21 days, 70°C processed samples reached about 33 days and 60 °C HMF content increased very slowly during the whole process so obtained worse quality garlic product at that temperature. There was a sharp increase in HMF values but there was a decrease in color and flavor of garlic samples at high temperature processes. When black garlic production process was took place at 70 °C, best quality products could be obtained.

[33] revealed that the garlic processing conditions lead to changes in the contents of its bioactive compounds, such as flavonoids, polyphenols and anthocyanins, and that this is connected to the type and duration of treatment.

According to [34] heat treatment of the phenolic compounds increased the free fraction of phenolic acids, whereas it decreased the ester, glycoside, and ester-bound fractions, leading to an increase in free phenol forms.

Heat treatment has a large influence on flavonoid availability, dependent on the magnitude and duration of treatment, their sensitivity to heat, and the physicochemical food environment.

During heat treatment, total flavonoids content increases and decreases in food products depending on the processing conditions [35].

[36] compared the phonolic acids and flavonoids in black garlic at different thermal processing steps, humidity conditions and time. Total phenolic content (TPC) of black garlic samples at different thermal processing steps was significantly ($p< 0.05$) higher than fresh garlic. The TPC was increased by about 4-10 fold in the black garlic compared with fresh garlic. In addition total flavonoid content was increased by about 1.1-3.5 fold in the black garlic compared with fresh garlic.

Antioxidant properties of black garlic were determined during 35 days fermentation process [25]. The total flavonoid content of black garlic (3.22 mg RE/g), was increase significantly up to the 21st day (16.26 mg RE/g) of aging ($p < 0.05$). The total polyphenol contents of black garlic also increase up after 21st day aging period from 13.91 mg GAE/g to 58.33 mg GAE/g so optimum aging period was determined as 21 day in black garlic production at 70°C and 90% relative humidity.

Table 2. Physicochemical characteristics of black garlic during aging period. [25]

Components	Fresh garlic	Black garlic
Moisture (%)	64.21 ± 1.48	29.88 ± 0.49
Total acidity (mg/kg)	0.40 ± 0.01	2.60 ± 0.03
pH	6.33 ± 0.07	3.74 ± 0.062
Reducing sugar (g/kg)	1.52 ± 0.01	16.07 ± 0.38
Color	**Fresh garlic**	**Black garlic**
L*	68.44 ± 1.66	4.33 ± 2.02
a*	−3.84 ± 0.46	2.73 ± 1.01
b*	26.59 ± 1.76	−3.86 ± 1.49

Reducing sugar content of black garlic during fermentation process depended on two factors. First of all, degradation of polysaccharide to reducing sugar; second one is consuming of reducing sugar during Mailard reaction [30] . [30] compared the reducing sugar contents at 60°C, 70°C, 80°C, 90 °C fermented black garlic products. At 60°C and 70 °C a rising trend was shown during whole process. At 80°C, 90 °C there was a remarkably increase at the early stage of process but at the later stage of high temperature a sharp decrease was observed. According to these results at low temperature fermentation process rate of formation of reducing sugar was faster than its rate of consumption but at high temperature process conditions at early stage the accumulation of reducing sugar exceeded its consumption rate and at later stage consumption rate of reducing sugar exceeding its accumulation rate.

Figure 1. Black garlic a) Garlic at the beginning, middle and end of the fermentation b) garlic color change during fermentation process

4. Medicinal Effects of Black Garlic

Several studies revealed that black garlic has free radical scavenging and powerful antioxidant characteristics [20, 37, 38, 39]. Moreover , black garlic extracts showed that anticancer activities, hypolipidemic action, anti-tumour and and antiinflammatory characteristics [40, 41, 42, 43]. Additionally, aged black garlic products exhibited hypocholesterolaemic, hypoglycaemic and hepatoprotective effects on laboratory animals feed with aged black garlic [44, 45, 46].

5. Conclusion

Black garlic exhibit superior bioactivity and antioxidant capacity than fresh garlic. Furthermore black garlic showed that hypolipidemic action, anti-tumour, antiinflammatory characteristic and anticancer activities. Nowadays, black garlic's popularity has spread around to the world as they become a sought-after ingredient used in high-end cuisine. Also in our country, there has been an increase in the importation and use of black garlic in recent years with health benefits coming to the forefront.

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