

Biogenic amines in foods

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Abstract Biogenic amines are produced by bacterial decarboxylation of corresponding amino acids in foods. Concentration of biogenic amines in fermented food products is affected by several factors in the manufacturing process, including hygienic of raw materials, microbial composition, fermentation condition, and the duration of fermentation. Intake of low amount of biogenic amines normally does not have harmful effect on human health. However, when their amount in food is too high and detoxification ability is inhibited or disturbed, biogenic amines could cause problem. To control concentration of BAs in food, decarboxylase activity for amino acids can be regulated. Levels of BAs can be reduced by several methods such as packaging, additives, hydrostatic pressure, irradiation, pasteurization, smoking, starter culture, oxidizing formed biogenic amine, and temperature. The objective of this review paper was to collect, summarize, and discuss necessary information or useful data based on previous studies in terms of BAs in various foods.

Keywords Biogenic amines formation · Biogenic amines control

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Introduction

Biogenic amine (BA)s are nitrogenous, and organic compounds and can be found in some fermented foods such as cheese, sausage, fermented vegetable, wine, and fish [1, 2]. Main interest in BAs is due to their potential toxicity to human health and indicators of food quality. Normally, small amounts of BAs could be detoxified by intestine amine oxidases [3, 4]. However, when the detoxification ability of amine oxidases is disturbed or inhibited due to high amounts of BA ingestion, serious health problems can occur [5].

Numerous studies have identified that histamine is the cause of scombroid food poisoning [6] which can occur consuming fish or fish products with histamine level at more than 1000 ppm [7]. Histamine concentrations in tuna fillet in oil, tuna and fresh yellow fin tuna loin are 4398, 3110, and 1774 mg/Kg, respectively [8]. It has been shown that cadaverine and putrescine can enhance the toxicity of histamine and react with nitrite to form carcinogenic nitrosamines [9]. Overall, BAs could cause nausea, vomit, diarrhea, abdominal pain, causing rash, itching, headache, and hypertension [10]. Their toxicity levels vary depending on the amount of BAs ingested and sensitivity of human [11].

Ladero et al. [12] and Silla Santos [1] have reported that the maximum total BA intake by human is less than 1000 mg/kg. BAs production can be monitored by several methods. Nieto-Arribas et al. [13] reported that BA accumulation in food can be inhibited by using high quality raw material, controlled temperature, and amine-negative starter cultures. However, Tapingkae et al. [14] and Shalaby [15] have reported that BAs are heat stable compounds, and slightly reduced or not significantly changed by boiling.

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There are two ways to detect BAs, first; by detecting microorganisms that possess the ability to produce BAs, second; by directly quantifying BAs. The formation of BA can be verified by changes in medium color and pH [16]. Most detection methods for BAs have been developed based on chromatography technology. HPLC with fluorescence detection, UV detection, or mass spectrometry detection after derivatization of benzoyl chloride [17], dansyl chloride [18], and o-phthalaldehyde [19] have been successfully used.

Many reviews are available on BAs focusing on different domains such as review of BAs in raw and processed seafood [11], dairy products [20], fish [9], meat and meat product [21], dry fermented sausage [22], analytical method [23], control method [24], and factor influence on accumulation [25]. The purpose of this review paper was to collect, summarize, and discuss necessary information or useful data based on previous studies in terms of BAs in various foods.

Biogenic amine formation

BAs can be classified as aromatic, aliphatic, and heterocyclic based on their chemical structure, or also can be divided into monoamines and diamines based on the number of amine groups. During decarboxylation, α -carboxyl group is removed from amino acids, giving corresponding amines [26].

BAs in foods are principally produced by bacterial decarboxylation of corresponding amino acids through substrate-specific decarboxylase enzymes. While histamine can be formed by converting histidine via histidine decarboxylase and lysine can be converted to cadaverine via lysine decarboxylase, tyrosine decarboxylase can convert tyrosine and phenylalanine to tyramine and phenylethylamine, respectively. Putrescine can be formed by two different pathways. First, under the action of ornithine decarboxylase, ornithine can be converted to putrescine [27]. Second, the formation of putrescine through deamination of agmatine. Spermine and spermidine are polyamines derived from putrescine [28]. Agmatine system consists of three enzymes: agmatine deiminase, putrescine carbamoyltransferase, and carbamate kinase.

Factors affecting the formation of biogenic amines in foods

Concentration of BAs in foods, especially fermented food products, is affected by several factors in the manufacturing process, including hygienic of raw materials, microbial composition, condition and duration of fermentation.

Hygienic condition of raw materials

It has been reported that BAs are naturally present in grapes [29], raw meats [30], and fresh milk [31] before being fermented. It has been reported that poor hygienic meat used in sausage can significantly reduce the capacity of amino acid decarboxylase negative strain *L. saki* CTC494 [32]. It has been reported high amounts of spermidine, putrescine, and cadaverine have appeared in the pericarp of berries during wine making process [33], and high concentrations of spermidine, putrescine, and cardaverine have appeared in the set also been found in seeds of grape berries [34]. Those originated from fresh Indian anchovy contained lower amounts of BAs compare to those stored at 35 °C for 8 and 16 h before being used to produce fish sauce, with anchovy stored for 16 h showing the highest level of biogenic amines [35].

Microorganisms with biogenic amines producing ability

Several microbial groups have been identified to possess decarboxylase activity [36]. It has been shown that some microorganisms such as Lactobacilli [37], Pseudomonads [38], Enterobacteriaceae [39], and Enterococci [40] present in meat products possess decarboxylase activity. Cadaverine and putrescine can be produced considerably by most yeasts. However, only a few yeasts such as Debaryomyces hansenii and Yarrowia lipolytica isolated from cheese can produce histamine and tyramine [41]. Some bacteria species isolated from seafood have been verified as histamine producers, including Staphylococcus xylosus isolated from salted semi-preserved anchovies [42], Morganella morganii, Hafnia alvei, and Klebsiella pneumoniae isolated from tuna [43], and Aeromonas hydrophila isolated from mackerel [44]. Pessione et al. [45] have reported that Lactobacillus sp. 30a and Lactobacillus sp. w53 isolated from wine are histamine, putrescine, and cadaverine producers. In yogurt, the formation of BAs, especially tyramine and histamine, is due to Streptococcus thermophilus [46]. A number of studies have demonstrate histamine producing bacteria in soybean fermented products, including Staphylococcus pasteuri, Bacillus amyloliquefaciens, Bacillus subtilis, and Bacillus megaterium in miso [47], Bacillus subtilis in sufu [48], Bacillus subtilis and Staphylococcus pasteuri in natto [49], and Bacillus subtilis, Staphylococcus pasteuri, and Staphylocuccus capitis in douchi [50].

Temperature and pH

Increasing temperature during prolonged storage or process can significantly affect the formation of BA in food products [26]. In fish, 25 °C has been found to be the ideal temperature for *Morganella morgani* to produce histamine. Tyramine content in meat-fat mixture produced by *Carnobacterium divergens* at 25 °C is higher than that produced at 15 °C [51]. Moreover, BAs can be produced by mesophilic bacteria significantly at temperature ranging from 20 to 37 °C [52]. Marcobal et al. [53] have shown that tyramine content produced by bacteria such as *L. brevis* and *Enterococcus faecium* is higher when temperature is higher. Krizek et al. [54] have found that content of BAs in carp meat is increased when storage temperature is increased.

Moreno-Arribas et al. [55] have reported that the optimum pH for decarboxylation activity is around 5.0. However, in wine manufacturing, increasing pH levels can increase the accumulation of biogenic amines [56]. It has been suggested that histamine production in sausage is related to insufficient decrease in pH during the first day of the ripening process [57]. Similarly, Masson et al. [51] have demonstrated that *C. divergens* can form more amount of tyramine in meat-fat mixture at pH 5.3 than that at pH 4.9.

Biogenic amines in foods

Levels of BAs presented in foods are different depending on the type of food products (Table 1). They are also influenced by the nature and availability of microorganisms in foods [2]. Large amounts of BAs can be found in foods such as cheese, fermented vegetables, fish and fish products, wine, dried meat products, and sausages [59]. Several studies have reported high levels of BAs in foods, particularly in cheese and fish. Most food poisoning cases of BAs are believed to be caused by histamine and tyramine [60]. Due to its vasoactive characteristic, histamine could cause flushing, abdominal cramps, headache, and hypertension [61].

Fish and fish products

Histamine, tyramine, cadaverine, and putrescine are the most common BAs formed in seafoods [4]. Histidine has been found naturally in fish muscles of many fish species belonging to Scombridae family [62], and histamine could be formed by histidine decarboxylase bacteria at any time after harvesting [63]. Generally, the formation of BAs in fish products is mainly affected by storage duration and temperature [64]. Klausen and Lund [65] have reported that histamine, cadaverine, putrescine, and spermidine amounts in herring and mackerel stored at 10 °C are 2–20 times higher than those in samples stored at 2 °C with the same storage duration. However, Staruszkiewicz et al. [66] have

reported that BAs could accumulate at any stages including catching or handling.

Abundant amount of histamine has been detected in fish products such as fish sauce [35], fish paste [67], shrimp paste [68], anchovies fermented [58], dried fish [69], and lightly cured horse mackerel [70]. The maximum level of histamine in fish products was set at 50 ppm by FDA [71] and 200 ppm by EC [72].

Sausage

Starter cultures such as lactic acid bacteria, coagulase negative cocci, yeast, and mold used in sausage fermentation have ability to develop BAs [73]. Tyramine and putrescine are the most abundant BAs present in dry sausages [74]. It has been found that tyramine is produced by lactic acid bacteria and coagulase negative staphylococci [75]. Latorre-Moratalla et al. [76] have reported that 48% of lactic acid bacteria and 13% of staphylococci isolated from spontaneously fermented sausages are able to decarboxylate amino acids. Concentrations of BAs in sausages vary depending on the type of products and manufacturers. Main factors associated with such variation include biological quality of raw materials, ingredients, additives, diameter of sausage [77] and ripening technique.

Cheese

The process of cheese making provides an ideal condition for the formation of BAs [78]. The amino acid decarboxylase activities of bacteria in raw material could generate BAs during cheese making [25]. Formation of BAs in cheese might occur during ripening step in which casein is degraded and free amino could be transformed into BAs by microbial decarboxylases [26]. Other factors such as the use of starter culture and enzymes, milk treatment, pH, amount of proteolysis, temperature and period of ripening, presence of oxygen, water activity, relative humidity, and the availability of microorganisms might have influence the formation of BAs [79]. The maximum level of BAs in cheese could be more than 2000 ppm [80].

Fermented soybean products and fermented vegetable

Since soy sauce is produced through hydrolysis of soybean protein, it also contains high levels of BAs such histamine and tyramine [81]. Kim et al. [82] reported that Korean fermented soybean products also contain tyramine, histamine, putrescine, cadaverine, spermine, spermidine, β -phenylethylamine, agmatine and tryptamine. Kim et al. [83] have reported that natto contains tyramine and β -phenylethylamine with levels exceeding toxicity dose.

Table 1 Biogenic amines contents in food products

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Fish sauce394Shrimp paste382		117.3	308.2	685.5	3.7	9.9	NA	30.5	Yongsawatdigul et al. [35]
		9.4	24	89	52	9	3.8	87	Tsai et al. [68]
		3.7	40	80	43	36	30	67	Tsai et al. [68]
Fish paste 263		8.8	12	58	60	15	ND	70	Tsai et al. [68]
		< 5	114.53	280.51	329.32	79.93	18.48	ND	Naila et al. [24]
Red wine 8.76		4.88	25.03	1.87	NA	NA	0.13	ND	García-Marino et al. (2010)
Red wine 3.65		1.93	8.5	0.4	0.07	2.08	0.61	0.03	Mayr and Schieberle [153]
Red wine 2.91		5.22	7.88	0.11	ND	ND	ND	NA	Martuscelli et al. [151]
Rosé wine 0.58		0.76	3.28	0.9	ND	0.09	0.16	NA	Martuscelli et al. [151]
White wine 0.18		0.41	2.24	0.79	ND	ND	ND	NA	Martuscelli et al. [151]
Sauv Blanc (2009 Maipo) 1.36	(ND	5.87	0.62	0.12	0.46	0.72	NA	Henríquez-Aedo et al. [85]
Cab Sauvignon (2009 Maipo) 8.39		2.61	19.81	5.21	0.67	4.21	ND	NA	Henríquez-Aedo et al. [85]
Merlot (2009 Maipo) 6.83	1	2.51	10.03	1.93	1.94	4.6	ND	NA	Henríquez-Aedo et al. [85]
Carménère (2009 Maipo) 9.21	1		20.09	3.85	0.99	4.0 5.41	0.17	NA	Henríquez-Aedo et al. [85]

Sauerkraut, produced by fermentation of cabbage and a good source of minerals and vitamins, also contain histamine, tyramine, putrescine, cadaverine, spermine, and spermidine [84].

Wine

Histamine. phenylethylamine, tyramine, putrescine. cadaverine, spermidine, spermine, serotine, tryptamine, and agamatine are BAs most commonly found in wine [3]. It has been reported that putrescine is the most abundant BA in wine [85]. Spermidine and putrescine have been identified as two dominant amines in grape and must [86]. Another parameter related to raw material is the availability of free amino acid in must and grape which could have also influence on BAs content in wine [87]. In the process of vinification, BAs could be accumulated during alcoholic fermentation and malolactic fermentation. During alcoholic fermentation, metabolism of yeast strains can produce some BAs [88]. Growth of lactic acid bacteria during malolactic fermentation can also optimize the formation of BAs [89]. It has been discovered that white wine generally contains lower levels of BAs than red ones because malolactic fermentation does not occur in the process of making white wine [90]. Henríquez-Aedo et al. [91] have shown that level of total BAs in white wine was the lower compare to that of red wines.

Effect of biogenic amines on human health

Intake of a low amount of BAs through food is normally not harmful for health as it can be detoxified by amino oxidases present in the gut. The enzymes including monoamine oxidase (MAO), diamine oxidase (DAO), and histamine N-methyltransferase (HNMT) can metabolize dietary BA in healthy person [92]. However, BAs could be transformed to toxic metabolites responsible for serious human health problem when its amount in food is too high or when detoxification ability is inhibited or disturbed in human [93]. Ingestion of BA for more than 40 mg per meal can significantly increase the risk of food poisoning [94]. It has been found that weak enzymatic amine degradation activity due to genetic factor or impaired function of MAO, DAO, and HNMT can increase a person's sensitivity to BAs [93]. Gastrointestinal diseases, genetic predisposition, and medication with DAO inhibitor can inhibit amino oxidase [95]. The action of MAO or DAO can be inhibited by ethanol and acetaldehyde compounds present in wine [3]. Therefore, consumption of wine, beer, and alcohol beverages can increase toxicity risk of BAs.

Food poisoning due to consumption of fish containing high amounts of histamine causes dizziness, faintness, burning sensation in the mouth, inability to swallow, and itching [96]. Symptoms of poisoning can appear within several minutes to 3 h after ingestion of fish containing histamine at levels higher than 1 mg/g [7]. Tyramine, phenylethylamine, and tryptamine are mainly cause hypertension, headache, pupil dilatation, palpebral tissue dilatation, respiration increasing, and blood pressure increasing [10].

Most cases of food poisoning due to tyramine are associated with cheese followed by other foods such as pickled herring, meat products, avocados, soy sauce, miso, chicken livers, beef livers, and caviar [97]. The presence of putrescine and cadaverine along with tyramine and histamine in food has been found to be responsible for their toxic effect on human [98]. Furthermore, cadaverine, putrescine, spermine, and spermidine can form carcinogenic nitrosoamines by reacting with nitrite [99]. Brink et al. [2] have reported that levels of histamine at more than 500 ppm are toxic to human. The histamine in food at 8-40 mg can cause slight poisoning [74], and 1080 ppm of tyramine is considered very harmful to adults [2]. On the other hand, with intake of monoamine oxidase inhibitor (MAOI) drugs, tyramine concentration at 100-250 ppm can cause hypertension. It has been shown that phenyethylamine at dose of 3 mg can significantly produce symptoms of migraine [100]. Currently no data is available for the dose-response effects of putrescine or cadaverine on human.

Biogenic amine reduction

Packaging

Carbon dioxide in modified atmosphere packaging (MAP) plays an important role in extension of food shelf-life by inhibiting microbial growth of histamine forming bacteria [101]. Yassoralipour et al. [102] have reported that the CO_2 at 75-100% in MAP can significantly reduce the level of BA in barramundi fillets. Furthermore, with vacuum packaging stored at 4 °C has shown lower content of BAs than that of package without vacuum and stored in air [101]. Packaging the Seer fish has in the absence of oxygen or when oxygen is removed by oxygen scavengers can result in lower levels of BA, and shelf life has improved compared to air packaging [103]. The precooked chicken stored in MAP at 4 °C for up to 23 days, suppressed the formation of tyramine and putrescine compared to that of air packaging [104]. Özogul et al. [105] reported that the level of histamine is 197 ppm in MAP, 284 ppm in vacuum packaging, and 396 ppm in air packaging after storage at 2 °C for 16 days. However, some researchers have presented evidence that MAP fails to reduce levels of BAs [106]. Ruiz-Capillas and Moral [107] have found that there is no significantly difference in BA amount between MAP and air storage.

Additives

It has been reported that the use of preservative and additives in food can inhibit the formation of biogenic amines. Mackerel stored at 25 °C for 10 days with addition of Dsorbitol, succinic acid, malic acid, and ascorbic acid can inhibit decarboxylase activity and prevent histamine formation [10]. Yuecel and Ueren [108] have reported that 1% of citric acid can lower the level of biogenic amines in pickled cabbage during fermentation. Potassium sorbate and ascorbic acid can also significantly reduce the aggregation of biogenic amines in sausages [109]. Moreover, BA concentration in fermented sausage has decreased significantly when selected starter culture containing 0.5 or 1% sugar [110].

Mah et al. [111] have found that the addition of 5% garlic extract in fermented anchovy reduced amount of BA by approximately 8.7%. Roseiro et al. [112] have reported that 6% salt can reduce levels of tyramine, putrescine, cadaverine, and phenylethylamine in sausages. Furthermore, the use of NaCl at concentration between 3.5 and 5.5% could prevent the formation of BA in miso [113]. The efficacy of salt on BA control has also been discovered in cheese manufacturing [79].

However, in some cases, the use of NaCl might optimize the formation of BA. For example, it has been reported that the level of histamine in Spanish Mackerel is increased when higher concentration of salt is used, reaching the highest or toxic level when 13–15% salt is used [114].

Hydrostatic pressure

High hydrostatic pressure reduces bacteria population and BA accumulation in raw material and final food products [24]. Lanciotti et al. [115] have proved that cheese made from high pressure treated milk contains around 2.5 times lower level of BA than that of raw milk. Pressurizing meat at 200 MPa for 10 min at 17 °C inhibits the growth of Enterobacteria [116]. Similarly, Ruiz-Capillas et al. [117] have reported that the formation of putrescine, cadaverine, and tyramine in frankfurter packed with vacuum and hydrostatic pressure treatment is inhibited significantly. Furthermore, Simon-Sarkadi et al. [26] have shown that high hydrostatic pressure treatment applied to sausage can inhibit the formation of cadaverine and putrescine, and enhanced the formation of spermine and tyramine formation. Generally, the efficacy of BA reduction depends on the intensity of the pressure applied [118].

Irradiation

There are some applications of irradiation in food processing for BA reduction. It is reported that gamma irradiation of blue jack mackerel reduces the levels of histamine, tyramine, cadaverine, and putrescine [119], significantly reduced the level of histamine in Bonito [120], and effectively reduced BA formation in soybean paste [121]. Levels of BAs in irradiated sausages were also lower compare to those in non-irradiated sausages [122], and BA levels in ripened sausages irradiated were dropped [123]. In addition, chicken, beef and pork treated with irradiation have showed dramatic reduction of BA contents compared to that of untreated control [124]. The application of gamma irradiation on blue cheese during storage is also effective in decreasing the amount of BA compare to that in the control [125].

Pasteurization

It has been suggested that pasteurization can also prevent the formation of biogenic amines in processed food products [126]. The thermal processing and pasteurizing milk before making cheese has shown decrease of BA content [126]. Pasteurization not only can reduce levels of BAs, but also can reduce their producer strains. Pasteurization of carp has shown positive effect on sensory quality, shelf life extension, and BA reduction [127].

Smoking

The smoking was successfully reduced the level of histamine, tyramine, cadaverine, putrescine, spermine, and spermidine compared to that of non-smoked samples [127]. Smoking process can yield products with aseptic characteristics, thus decreasing the level of BA by inhibiting the growth of amine-decarboxylating bacteria [128]. Smoked cooked sausage contains very low levels of BA compared to ordinarily fermented sausages [129].

Starter culture

Different starter cultures can influence BA formation differently. Besides BA producing strains, there are also strains that possess negative decarboxylase activity or enzymes with ability to oxidize biogenic amines in food [130]. The use of selected starter culture in some products such as sausage [131], wine [132], fish sauce [133], and cheese fermentation [13] has inhibited the accumulation of biogenic amines. González-Fernández et al. [110] have reported that *L. sakei* K29 reduce tyramine, cadaverine, and putrescine in chorizo dry sausages. Ayhan et al. [134] have shown that *L. sakei* + *P. pentosaceous* + *S. carnosus* + *S.* *xylosus* used in Turkish Soudjoucks reduce putrescine. Lu et al. [135] have reported that the combination of *L. farciminis* and *S. saprophyticus* in Xinese fermented sausage reduce tyramine, histamine, cadaverine, and putrescine. However, Dominguez et al. have reported that sausages inoculated with *P. pentosaceus* + S. xylosus displayed the highest accumulation of total biogenic amines [136].

Oxidizing formed biogenic amine

Oxidizing agents have been applied to degrade to formed BAs as an alternative method to reducing BAs in food. *Natrinema gari* [14], *Vergibacillus sp* SK33 [137], *Micrococcus varians* [138], *L. sakei, Lactobacillus curvatus* [139], *S. xylosus* [140], and *Brevibacterium linen* [141] are the well-known oxidizers of BAs. Cueva et al. [142] have isolated fungi from grapevine and vineyard soil, which can degrade histamine, tyramine, and putrescine in wine.

Temperature

The processing and storage temperature are important measures for preventing or inhibiting the formation of BA in foods. Bunková et al. [143] have demonstrated that levels of putrescine, tyramine, and cadaverine in Edamcheese ripened at 5 °C are lower than that of cheese ripened at 10 °C. Base on hazard analysis and critical control points (HACCP) by FDA [71], 4.4 °C or lower temperature has been recommended for processing and storage to prevent histamine formation in fish.

Biogenic amine detection methods

BA detection methods can be classified in two categories. The first is based on detection of BAs themselves. The other one is based on the detection of amino acid decarboxylase microorganisms [144].

Amino acid decarboxylase microorganism based detection

Use of growth media consisting of pH indicator and substrates can be used to identify BA aggregation based on change of medium color [144]. However, methods based on culture media have been found to be unreliable and time-consuming due to the development of false positives and negatives, and polymerase chain reaction (PCR) can detect potential BA producer bacterial strains at any step of the food processing process in a short time with reliable results [145].

Biogenic amine based detection

The high-performance liquid chromatography (HPLC) [145], gas chromatography (GC) [146], thin-layer chromatography (TLC) [147], ion exchange chromatography [148], biosensors [149], and capillary electrophoresis (CE) [150] are the method used for detection of BAs. It has been applied to wines [151], soybean paste [152], and pepperoni sausage [136] to determine BA levels. To provide a chromophore for UV or fluorescence detection, their polarity needs to be reduced. This process is generally done by derivatization [153]. Dansyl chloride [154], benzoyl chloride [155], and o-phthalaldehyde [156] are generally used for derivatization. Extraction is one practical step used in most BA detection techniques.

Tang et al. [157] have reported the detection of BAs in sufu through HPLC with solid-phase extraction (SPE) and pre-column derivatization. HPLC with direct derivatization of acid extract has been used to quantify BAs in cheese [154]. To determine BAs in Port wine and grape juice, Fernandes and Ferreira [158] have employed gas chromatographic-mass spectrophotometric method in selected ion-monitoring mode using heptafluorobutyric anhydride as a derivatization reagent. Capillary electrophoresis with conductometric detection has been used to detect BAs in food without any derivatization steps [159].

Competitive direct-enzyme linked immunosorbent assay (CD-ELISA) is a non-complex and rapid method used to detect histamine in food products such as cheese [160] and wine [161]. Dadakova et al. [162] have demonstrated a rapid ultra-performance liquid chromatography (UPLC) to detect BAs. Ultra-high pressure liquid chromatography-electrospray tandem mass spectrometry (UHPLC-ESI-MS/MS) has been used to determine BAs in Cheonggukjang [163]. In addition, an enzyme sensor array has been proposed to simultaneously determine several types of BAs with less time required [164].

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