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A critical overview on the chemistry, clean-up and recent advances in analysis of biogenic amines in foodstuffs

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ABSTRACT

In the past few years, we have seen intense interest grow in chemistry, toxicity and analysis of biogenic amines (BAs). Thus, a comprehensive review on clean-up and recent advances in analysis of biogenic amines (BAs) in human body and dairy products of foodstuffs are presented. Liquid-liquid extraction, solid phase extraction, solid phase microextraction, dispersive liquid-liquid microextraction (DLLME), cloud point extraction and hollow fiber-liquid phase microextraction represent the most common preconcentration techniques for BAs. HPLC, GC, TLC, spectrofluorimetry, capillary zone electrophoresis coupled with mass spectrometry are the most common analytical techniques used for analysis of BAs. DLLME techniques offer benefits over centrifugation, filtration and solid-phase extraction. The milestones and combination of nanotechniques in the DLLMEs field and green aspects of BAs in literature; advantages and drawbacks are addressed. A major focus on analysis of BAs revealed no use of coupling DLLME techniques with electroanalytical techniques in particular stripping voltammetry. Thus, voltammetric techniques at surface modified electrodes implemented with DLLME techniques is highly recommended for developing low cost and precise methods for analysis of BAs at ultra trace levels in foodstuffs. Conclusions have been drawn for future research is proposed.

Contents

1. Classifications of BAs

BAs are basic nitrogenous compounds formed mainly by decarboxylation of amino acids or by amination and transamination of aldehydes and ketones [1]. BAs are natural compounds which can be produced by bacteria during amino acids decarboxylation in living cells [2]. All kinds of foodstuffs that contain proteins or free amino acids represent important tasks to be subjected to conditions enabling microbial or biochemical activity of BAs. The total amount of different amines formed strongly depends on the nature of food and the microorganisms present [3]. Foods likely to contain high levels of these compounds are dairy products, fish and fish products, meat and meat products, fermented vegetables and soy products, and fermented beverages such as wine and beer [4]. High concentrations of BAs have been found in fermented foods as a result of a contaminating microfloraexhibiting amino acid decarboxylase activity [3]. The main BAs encountered in foods and beverages are histamine, tyramine, putrescine, and cadaverine [4]. Secondary amines such as putrescine and cadaverine play an important

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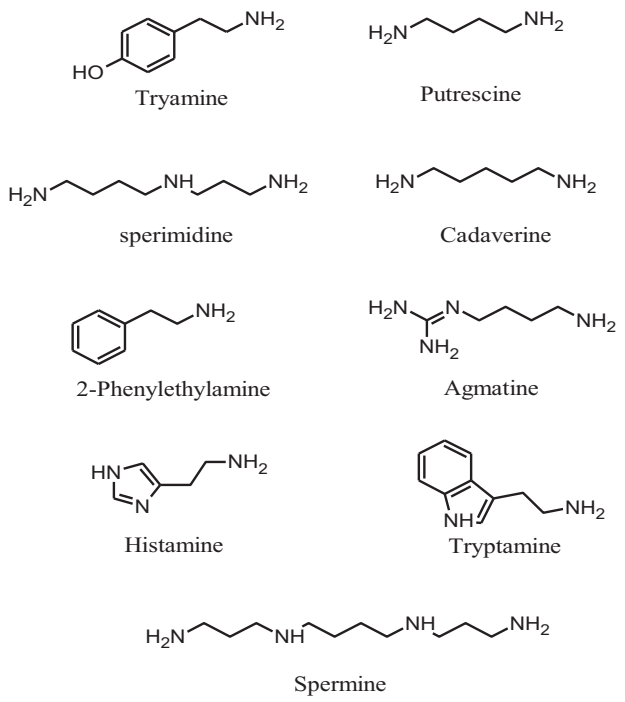

Fig. 1. Chemical structures of different BAs.

role in food poisoning as they can potentiate the toxicity of histamine. The quantity of BAs is also considered as a marker of the level of microbiological contamination in food. For these reasons, it is important to monitor BAs levels in food [5].

The chemical structures of BAs can be either aliphatic (e.g. putrescine, cadaverine, agmatine, spermine, spermidine), aromatic (e.g. tyramine, phenylethylamine), heterocyclic (e.g. histamine, tryptamine), or volatile (e.g. methylamine, pyrrolidone, morpholine, isoamylamine, ethylamine, hexylamine, isopropylamine, isobutylamine, n-butylamine, n-amylamine, dimethylamine, n-propylamine, ethanolamine, 3-methylpropylamine) [6]. Based on the number of amines, these compounds can also be classified into monoamines (e.g. phenylethylamine and tyramine), diamines (e.g. cadaverine and putrescine) and polyamines (e.g. spermidine and spermine) [2]. However, several authors have classified cadaverine, putrescine, spermine, and spermidine among the class of polyamines [7,8]. Fig. 1 shows the chemical structures of selected BAs with biological activity which are classified according to their physiological effects on humans as psychoactive and/or vasoactive. Vasoactive amines such as tyramine, tryptamine and β-phenylanine act on the vascular system, while psychoactive amines such as histamine, putrescine, and cadaverine act on the nervous system [9].

2. Occurrence of BAs in foods

Biogenically active amines are compounds formed and broken down by usual metabolic processes in the cells of living organisms including growth regulation (spermine, spermidine and cadaverine), neural transmission (catecholamines and serotonin) and as mediators of inflammation (histamine and tyramine). The most common monoamines (histamine, tyramine and tryptamine) and diamines or polyamines (putrescine, *β*-phenylethylamine, cadaverine) are formed from histidine, tyrosine, tryptophan, ornithine, phenylethylalanine and lysine, respectively. Polyamines e.g. spermidine and spermine arise from putrescine [5,10]. The biosynthesis pathways of BAs are demonstrated in Fig. 2. In plants and some microorganisms, putrescine can also be produced from arginine metabolism together with agmatine [11,12].

Polyamines are ubiquitous constituents occurring in microbial, plant and animal cells. Mammalian biosynthetic pathways were reviewed by Hillary et al. [13]. Their biosynthesis is very highly regulated by the activities of two key enzymes, ornithine decarboxylase (ODC) and S-adenosylmethionine decarboxylase (AdoMetDC). The major pathway for putrescine formation in mammalian cells is via the activity of ornithine decarboxylase. Methionine provides the aminopropyl groups needed to convert putrescine into the higher polyamines. The synthesis is carried out by two aminopropyl-transferase enzymes, spermidine synthase and spermine synthase [14]. BAs can be produced during storage or processing of the products by thermal or bacterial enzymatic decarboxylation of free amino acids by *Bacillus*, *Clostridium*, *Hafnia*, *Klebsiella*, *Morganella morganii*, *Proteus, Lactobacillus* such as *Lactobacillus buchneri* and *Lactobacillus delbrueckii* in cheese, Enterobacteriaceae and Enterococcus growing on fish, meat and their products. They are also found in fermented food, like cheese, camembert, wine, beer, sauerkraut and yeast extract [5].

In non fermented foods, these compounds were found as useful indicators and markers for food decomposition. Spoiled foods are also rich in BAs and usually contain high levels of putrescine and cadaverine [11]. Histamine presents in many living tissues as a normal constituent of the body and has multiple effects in different mammalian and invertebrate organs. In humans, it is found in different concentrations in the brain, lung, stomach, small and large intestine, uterus and the urethras. It is produced and stored predominantly in mast cells, circulating basophiles and neurons [10]. BAs found in certain foods along with the bacteria responsible for their production in such foods are given in Table 1. It is of interest to mention that amine levels vary extensively not only between different food varieties but also within the varieties themselves [15].

3. Clean-up and pretreatment of BAs

BAs are determined in food for two reasons: the first one is concerned with their potential toxicity and the second is the possibility of using BAs as food quality markers [5]. The major applications of determination of BAs are the quality of raw materials, intermediates and final products, monitoring fermentation processes, process control and research and development [5]. Analysis of BAs in food is problematic not only because of their low concentration levels but also due to the complexity of the matrix. Thus, sample clean-up plays an important role for proper isolation and enrichment of BAs prior to their analytical determination. Common clean-up and pretreatment techniques are liquid–liquid extraction (LLE) [16,17], solid phase extraction (SPE) [18], solid phase microextraction (SPME) [19], cloud point extraction (CPE) [20] and hollow fiber liquid phase microextraction (HF-LPME) [21–23]. LLE technique is not recommended because it involves long extraction procedures and often uses harmful organic solvents. Moreover, low recoveries for some BAs are sometimes found [17,24]. SPE represents a good alternative approach for BAs preconcentration instead to the LLE technique, especially by virtue of the wide commercial availability of sorbent materials and also due to the fact that the need to dispose organic solvents is to a large extent minimized [25]. Sorbent materials based on anionic [26] and cationic [27] exchangers or non-polar functional groups (e.g., octadecylsilane groups (C_{18})) [18] often show better extraction efficiencies than the LLE counterpart.

Even though SPE technique requires moderately small volume of organic solvents, however, the manual version is tedious, time consuming, and meanwhile automated SPE is expensive [28]. More recently, HF-LPME represents interesting developments in extraction technique [23]. This technique is simple and inexpensive, with a further advantage that the fiber is disposed after use due to its