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Functional potential of tropical fruits with respect to free bioactive amines

Paula Santiago-Silva, Renata A. Labanca, M. Beatriz A. Gloria *

Laboratório de Bioquímica de Alimentos, Departamento de Alimentos, FAFAR, Universidade Federal de Minas Gerais, Av. Antonio Carlos 6627, bloco 3, sala 2091, Belo Horizonte, MG, Brazil 31.270-901

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ABSTRACT

The profile and levels of 10 bioactive amines were determined in five tropical fruits, among them, pineapple, guava, papaya, mango and passion fruit. The amines were extracted from the Brazilian fruits with 1 *N* HCl and analyzed by ion-pair HPLC, post-column derivatization with *o*-phthalaldehyde and fluorimetric detection. Five amines were found in the fruits (spermidine, spermine, putrescine, serotonin and agmatine). Total amines levels varied from 0.77 mg/100 g in mango up to 7.53 mg/100 g in passion fruit. Spermidine was detected in every fruit whereas putrescine and spermine were found in most of them. Agmatine was detected in some samples of pineapple, papaya and passion fruit and serotonin was present in pineapple and passion fruit. Passion fruit is a good source of the polyamines spermidine and spermine (3.05 and 2.43 mg/100 g, respectively) and, therefore, could play an important role in growth, health, antioxidant activity and membrane permeability. Papaya is a good source of serotonin (0.99 mg/100 g), which has been associated with enabling the gut to mediate reflex activity and also with decreasing the risk of thrombosis. Histamine, a peripheral vasodilator, and the vasoconstrictors tyramine, tryptamine and phenylethylamine, as well as cadaverine were not detected in any of the fruits analyzed. Due to the diversity of amines in these fruits, they can provide different functional properties and, therefore, can be used for different nutritional needs.

1. Introduction

Today's society is characterized by an increasing health consciousness and growing interest in the role of food for maintaining and improving human well-being and health (Ragaert, Verbeke, Devlieguere, & Debevere, 2004). Associated with the new consumer's profile of less time for cooking and increasing out-of-home food consumption, there is a demand for natural products which could contribute for a healthier diet and better quality of life (Martín-Diana et al., 2007).

Among the new trends, the consumption of fruits and vegetables is growing rapidly. Fruits and vegetables are important sources of a wide range of vital nutrients including vitamins, minerals, fibers, some phytochemicals, as well as other biologically active compounds. Epidemiologic studies have demonstrated inverse relationships between the intake of fruits and vegetables and the risk of developing cardiovascular diseases, hypertension, and some cancers (Kim & Holowaty, 2003; Knai, Pomerleau, Lock, & McKee, 2006; Boffetta, Couto, Wichmann, Ferrari et al., 2010; Campos-Veja, Loarca-Pina, & Oomah, 2010).

Fruits also contain bioactive amines, which are formed during normal metabolic processes and fulfill a number of important metabolic and physiological functions in all living organisms. They are low molecular weight organic bases which express high biological activity. They are known for centuries and still attract considerable interest in biomedical researchers. Due to the modern technical approaches and new detection methods, the knowledge about amines and their role in health and disease are better understood (Fogel, 2009).

The bioactive amines can be classified in different ways: on the basis of the number of amine groups, chemical structure, and biosynthesis or physiological functions. The latter is the most widely used. Based upon this criterion they are classified as polyamines and biogenic amines. The polyamines spermine and spermidine play important role in cell division, organogenesis, response to stress and inhibition of lipid oxidation. The biogenic amines histamine, tyramine, tryptamine, serotonin, putrescine, cadaverine and phenylethylamine are neuroactive or vasoactive. Biogenic amines are mainly formed by decarboxylation of precursor amino acids. Polyamine synthesis is a more complex process, although the first few steps also include decarboxylation reactions in the formation of putrescine, which is an obligate intermediate. Methionine is responsible for providing an aminopropyl group to putrescine forming spermidine and to spermidine forming spermine (Gloria, 2005).

Some amines occur naturally in fruits and vegetables where they exert essential metabolic functions. The polyamines spermidine and spermine are involved in the growth, renovation, and metabolism of cells (Bardócz, Grant, Brown, Ralph, & Pusztai, 1993). Serotonin, histamine and tryptamine act as protective agents against predators (Smith, 1985). Other amines are formed by the action of decarboxylating enzymes from microorganisms, and may be used as index of

* Corresponding author. Tel.: +55 31 3409 6926; fax: +55 31 3409 6911.
E-mail address: mbeatriz@ufmg.br (M.B.A. Gloria).

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quality or hygienic conditions of products (Gloria, 2005; Galgano, Favati, Bonadio, Lorusso, & Romano, 2009).

The bioactive amines are important components of mammalian organisms. They regulate virtually all processes. Amines transmit internal and external signals, trigger responses; contract or relax vessels and muscles, stimulate or inhibit secretory activity, affect the mood and support life, health, disease and reproduction (Fogel, 2009). Amines present in foods are rapidly metabolized in the organism by means of aminoxidases. The absorbed amines may have beneficial functional properties as indicated above. However, when consumed in larger quantities, they can cause adverse effects to human health (Shalaby, 1996). Large concentrations of biogenic amines can cause nausea, erithema, migraine, and also hypertensive crisis in individuals under monoaminoxidase inhibitor (MAOI) therapy. The polyamines, like some other growth factors, can accelerate the growth of tumors. They can also react with nitrite in acidic conditions and form N-nitrosamines which are potential carcinogens (Bardócz, 1995; Silla-Santos, 1996).

Therefore, the knowledge of the types and levels of amines in foods is important in the formulation of diets. Patients with cancer should be exposed to diets with reduced levels of polyamines (Eliassen, Reistad, Risoen, & Ronning, 2002). Individuals under MAOI drugs (antituberculosis and antidepressant drugs) should avoid foods which are rich in monoamines (Gloria, 2005). Information on the types and levels of bioactive amines in fruits and vegetables is scarce, especially in fruits from tropical countries. Therefore, the objective of this study was to determine the types, levels and potential functional properties of 10 bioactive amines in some typical tropical Brazilian fruits, which have become popular throughout the world.

2. Material and methods

2.1. Samples

Different types of tropical Brazilian fruits (Table 1) were purchased at grocery stores from Belo Horizonte, MG, Brazil. The fruits had good quality and full development with regard to size, flavor and color. They were fresh, compact, firm, and free of diseases and insects. The fruits were purchased during the specific seasons. Seven different lots of the fruits were purchased (at least three units of each fruit represented a lot, which represents a minimum of 21 unities of each fruit).

At the moment of analysis, the fruits were washed thoroughly. The edible parts of the fruits were ground in a food processor (Walita Master Plus, Walita, São Paulo, SP, Brazil), and homogenized thoroughly. The larger fruits, like pineapple, were quartered prior to grinding.

2.2. Reagents

Bioactive amine standards were purchased from Sigma Chemical Co. (St. Louis, MO, USA). They included spermine tetrahydrochloride, spermidine trihydrochloride, putrescine dihydrochloride, agmatine sulfate, cadaverine dihydrochloride, 5-hydroxitryptamine (serotonin), histamine dihydrochloride, tyramine hydrochloride, 2-phenylethylamine hydrochloride and tryptamine. o-Phthaldehyde was also purchased from Sigma Chemical Co.

Table 1
Characterization of some tropical fruits selected for analysis.

Fruit	Family*	Species*	Variety	Part analyzed
Mango	Anacardiaceae	*Mangifera indica* L.	Tommy	Pulp
Pineapple	Bromeliaceae	*Ananas comosus* L.	Pérola	Pulp and core
Papaya	Caricaceae	*Carica papaya* L.	Papaya	Pulp
Guava	Myrtaceae	*Psidium guajava* L.	Red	Whole
Passion fruit	Passifloraceae	*Passiflora alata* Dryand	Azedo	Pulp and seed

* Source: IBGE (Instituto Brasileiro de Geografia e Estatística), 1980.

All reagents were of analytical grade, except HPLC reagents which were chromatographic grade. Ultrapure water was obtained from a Milli-Q System (Millipore Corp., Milford, MA, USA). The mobile phases were filtered through HAWP and HVWP membranes (47 mm diameter and 0.45 µm pore size, Millipore Corp., Milford, MA, USA), used for aqueous and organic solvents, respectively.

2.3. Screening of bioactive amines in the tropical fruits

The edible parts of the fruits were analyzed for the profile and levels of bioactive amines. The same samples were analyzed for some physico-chemical characteristics, among them, total soluble solids, pH and total titratable acidity.

2.4. Determination of the levels of bioactive amines in passion fruit pulp prepared by different ways

Passion fruit pulp was prepared by the two most commonly used methods: (i) grinding of the pulp and seeds, and (ii) extraction of the pulp without breaking the seeds. The first was obtained by grinding the whole pulp in a blender. The second one was mixed thoroughly without breaking the seeds and passed through the strainer. The different pulps were submitted to analysis of bioactive amines.

2.5. Determination of bioactive amines

Amines were extracted from 5 g samples with 7 mL of 1 *N* hydrochloric acid (HCl). After vortexing for 5 min, the slurry was centrifuged at 11,180 *g* for 10 min at 4 °C, and the supernatant was collected. The solid residue was extracted twice more with 7 and 6 mL of 1 *N* HCl. The supernatants were combined and filtered through a 0.45 µm pore size membrane. Because of the high water content, the pineapple samples were extracted with a total of 10 mL of 1 *N* HCl.

The amines were separated by ion-pair reverse phase HPLC and quantified by fluorescence detection after post-column derivatization with *o*-phthaladehyde (Cirilo et al., 2003). Liquid chromatography was performed with a LC-10 AD system connected to a RF-551 spectrofluorimetric detector at 340 and 445 nm of excitation and emission, respectively, and to a CBM-10 AD controller (Shimadzu, Kyoto, Japan). A reversed-phase µBondapak C18 column, 300 x 3.9 mm i.d., 10 µm, was used with a µBondapak C18 guard-pak insert (Waters, Milford, MA). The mobile phases were: A) solution of 0.2 *M* sodium acetate and 10 m*M* 1-octanesulfonic acid sodium salt adjusted to pH 4.9 with acetic acid and B) acetonitrile. The flow rate was set at 0.8 mL/min and the gradient was: 13 min at 11% B, 19 min at 30%, 24 min at 11% and 45 min at 11%. The post-column derivatization reagent was delivered at 0.4 mL/min. It consisted of 1.5 mL Brij-35, 1.5 mL mercaptoethanol and 0.2 g *o*-phthalaldehyde dissolved in a 500 mL solution of 25 g of boric acid and 22 g of KOH (pH adjusted to 10.5 with 30 g/L KOH). The column and the post-column reaction apparatus were kept at 23 ± 1 °C.

The identification of the amines was performed by comparison of the retention times of amines in the samples to those of standard solutions and also by addition of the suspect amine to the sample. Quantification was accomplished by direct interpolation in a standard curve and the levels were expressed in mg/100 g. The method was validated for fruits providing recoveries of $93 \pm 2\%$. Repeatability was adequate ($CV \leq 5.2\%$). The determination limits were 0.01 mg/100 g for spermidine, spermine and putrescine, 0.03 mg/100 g for histamine and tyramine, 0.05 mg/100 g for agmatine and 0.08 mg/100 g for serotonin.

2.6. Determination of the physico-chemical characteristics

The fruits were also analyzed for some physico-chemical parameters, among them, pH, titratable acidity and total soluble solids. The pH values were determined by means of a pH meter (Digimed, Sao Paulo,