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Diffusion and thermal stability of phenolic compounds during fortified rice rehydration process

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ABSTRACT

The diffusivity of phenolic constituents in rice as well as the kinetics of their leaching in boiling water were studied during fortified rice rehydration. Phenolic concentrations in fortified rice grains during cooking were modeled using a Fickian diffusion model and seemed to be in good agreement with the calculated data. The apparent diffusivity of 4 specific phenolic compounds was estimated to be in the range of $4.90–16.97*10^{-10}$ m^2/s and the retention of these compounds in rehydrated rice was found to be at least 24% of their amount in dry fortified rice. This indicates that a significant amount of antioxidants was not released even after intense thermal processing in excess water and this may be a result of strong interactions between rice macromolecules and phenolic antioxidants. Moreover, a great thermal stability of individual phenolic compounds in fortified rice was observed during rehydration at boiling temperatures.

1. Introduction

Rehydration of dry food products is a very common process which aims to restore the properties of the fresh product by bringing dehydrated food in contact with a liquid phase (Cox et al., 2012). Though, one of the main drawbacks of this process, except for inducing minor or even severe changes to the microstructure and sensory characteristics of the final product, is the leaching of part of soluble constituents from the dry product to the rehydrating medium which is often used in excess quantities. For example, significant amounts of soluble solids made up of components like sugars, minerals and vitamins were found to have been lost in the aqueous solution after rehydration of dry vegetables and fruits such as carrots, onions, pineapples and seaweeds (Cox et al., 2012; Debnath et al., 2004; Rastogi et al., 2000, 2004). In particular, the solutes' diffusion in water could be sufficiently described in most cases by Fick's 2nd law for diffusion and was mainly affected by the nature of each product, as well as the selected conditions and methods of dehydration and rehydration. Another factor that influences leaching of solutes during rehydration is the product porosity. Normally, high porosity in dry food structure would be expected to increase the amount of imbibed water and also promote leaching of solutes (Marabi et al., 2004), though there are certain studies in literature that contradict the positive effect of high porosity on solute leaching (Saca and Lozano, 1992; Mate et al., 1999).

Thermal processes such as boiling and blanching also induce leaching of soluble constituents from plant tissues into hot water and it has been found that diffusion could be the predominant cause of solute loss when compared to solute thermal degradation (Selman, 1994; Abdel-Kader, 1991; Delchier et al., 2012). To our knowledge, there is a rather large number of studies in literature which deal with the thermal stability of specific components i.e. vitamins, proteins, sugars, etc. and their leaching in hot water at the end of thermal treatment, but only few of them focus on the estimation of apparent diffusion coefficients of specific compounds released in hot water due to leaching. The results of these studies could be used for the optimization of specific hydrothermal techniques, such as boiling and blanching of raw vegetables and legumes, by taking into account the correlations between solute apparent diffusivities with heating temperatures as well as with water volumes used for each application (De Maria et al., 1998; Arroqui et al., 2001; Selman et al., 1983; Abdel-Kader, 1991).

Fortification of rice products has been extensively applied in some countries, so that people could cope with their dietary deficiencies, mainly in traces and minerals, such as Fe and Zn (Pooniya

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Nomenclature

t	rehydration – boiling time (s)
D_{app}	apparent diffusion coefficient (m^2/s)
k_c	kinetic constant (s^{-1})
r	radius of fortified rice grain cylinder (m)
x	any position in the sample where the concentration is C (m)
a_n	the nth root of $J_0(x) = 0$ where J_0 is the zero order Bessel function
n	the number of roots
C(x,t)	phenolic compound concentration at any point inside rice grain (ng/g dry rice)
C_0	concentration of specific phenolic constituents in rice at the start of rehydration process (ng/g dry rice)
C_{ph}	average concentration of individual phenolic compounds in cylindric rice grains as a function of boiling time (ng/g dry rice)
C_∞	calculated equilibrium concentration of specific phenolic compounds in rice grains after rehydration (ng/g dry rice)
C(t), C(t+Δt)	concentration of each phenolic compound in rice grains at boiling times t and t+Δt respectively (ng/g dry rice)
a	Empirical constant (s^{-1})
B	Empirical constant (non dimensional)

and Shivay, 2013; Wei et al., 2013). In one of our recent studies (Igoumenidis et al., 2016), a technique for rice fortification with antioxidants was described and the use of the proposed method resulted in a green-color, fortified, ready-to-eat rice product which presented increased nutritional attributes compared to cooked white milled rice. The final product of that study, after being dried under optimum conditions in order to increase its shelf life, could be used for the production of quick-cooking fortified rice.

The most common methods for preparation of rice meals are i) cooking rice in fixed water-to-rice ratios and ii) cooking rice in excess water. The main aim of the present research was to study the diffusivity of individual phenolic compounds in fortified rice kernels during rehydration under prolonged hydrothermal treatment conditions, using excess water at boiling temperatures. The diffusivity of these constituents was modeled by applying Fick's 2nd law for diffusion. Another aim of this work was to investigate the thermal stability of these compounds at the end of fortified rice rehydration in the case of using fixed rice-to-water volume ratios. In general, rice hydration during boiling or soaking in hot water and dehydration have been studied extensively in terms of modeling moisture diffusion inside the kernels, but literature concerning the diffusion of phytochemicals in rice grains during cooking, rehydration or even hydrothermal processes remains scarce. The modeling of phenolic compound diffusivity could offer new knowledge about fortified rice microstructure and stability, as well as promote other fortification attempts by combining natural extracts with starchy foods, which could be applied in food industry.

2. Materials and methods

2.1. Chemical reagents

Caffeic, protocatechuic, and 3,4-dihydroxyphenylacetic acid standards were purchased from Fluka (Steinheim, Germany), while gallic acid standard was purchased from Sigma (Steinheim, Germany) and naringenin standard from Extrasynthese (Genay-Cedex, France). Analytical grade methanol (MeOH) and Folin–Ciocalteu reagent were obtained from Merck (Darmstadt, Germany). Bis-(trimethylsilyl)-trifluoroacetamide reagent (BSTFA) and 3-(4-hydroxyphenyl)-1-propanol were purchased from Aldrich Chemie GmbH (Steinheim, Germany).

2.2. Fortified rice grain characteristics and rehydration process

The milled rice grains used in this study were of “nychaki” type and had average dimensions of 6.73 mm × 1.67 mm (Length X Diameter), measured using a Vernier caliper.

White milled rice (200 g) was fortified by being boiled for 15 min in excess quantity (3 L) of *Mentha spicata* (*MS*) leaves' aqueous extract produced following the procedure described in our previous study (Igoumenidis et al., 2016). After drying the whole quantity of boiled fortified rice, part of it (100 g) was used for the study of individual phenolic compound desorption after rehydration by acquiring a 20 min reboiling process in excess of pure water (3 L). In particular, rice samples were obtained at specific time intervals during boiling (t = 2, 4, 6, 8, 10, 12, 15, 20 min) and freeze dried for further extraction and analyses. Another portion (50 g) of dry fortified rice was used in order to study its thermal stability, concerning phenolic content, after heating and rehydrating using fixed water-to-rice volume ratio (1.5:1 v/v).

2.3. Chemical analyses

All rehydrated rice samples were freeze dried and underwent methanolic extraction (4 repeated cycles), using 20 ml MeOH/sample in total, in order to extract their phenolic compounds (Igoumenidis et al., 2016). Afterwards, MeOH extracts of rice samples were further examined by photometric (Folin–Ciocalteu) and Gas Chromatography/Mass Spectroscopy (GC/MS) methods.

Total polyphenol content (TPC) of rehydrated fortified rice methanolic extracts was determined using the Folin–Ciocalteu method as described by Arnous et al. (2002) after being adapted to microscale. Gallic acid was used as calibration standard and results were expressed as μg Gallic Acid Equivalents (GAE)/g dry rice.

The amount of individual phenolic compounds in rehydrated rice sample MeOH extracts was determined as trimethylsilylethers by employing GC/MS analysis as described by Kalogeropoulos et al. (2009). Briefly, a Selective Ion Monitoring (SIM) method was developed for the analysis of 4 target phenolic compounds and the detection of phenolics was based on the ±0.05 RT (Retention Time) presence of target and qualifier ions of standard phenolic compounds at the predetermined ratios. Meanwhile, the quantification of 4 phenolic compounds in extracts of fortified rice samples was made by acquiring 3-(4-hydroxyphenyl)-1-propanol as internal standard and final results were expressed as ng phenolic compound/g dry rice.

2.4. The diffusion model

The two contributions to the total resistance to phenolic mass transfer during rehydration of rice grains in excess boiling water are the surface resistance due to convection and the internal resistance due to mass diffusion. These two can be represented by Fick's first and second laws together with a mass balance at the interface, though in case there is sufficient agitation of the boiling media, surface resistance becomes small and it can be assumed that the only contribution to total resistance is that of internal resistance. Then, Fick's 2nd law can be solely applied (Selman et al., 1983):