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Impact of a new postharvest disinfection method based on peracetic acid fogging on the phenolic profile of strawberries

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ABSTRACT

The retentions of fresh strawberry individual phenolic compounds after fogging using an environmentally friendly sanitizer based on peracetic acid (PAA) (mixture of 5% peracetic acid and 20% hydrogen peroxide) were studied and modeled as a function of the concentration (3.4, 20.0, 60.0, 100.0 and 116.6 μL PAA L^{-1} air chamber) and the treatment time (5.7, 15.0, 37.5, 60.0 and 69.3 min), using Response Surface Methodology. Information obtained from high performance liquid chromatography with photodiode array and fluorescence detection in combination with mass spectrometry was used for analyzing and quantifying the phenolics that naturally occur in strawberries (variety 'Camarosa') and to study the effects of PAA on them. Results showed that PAA fogging at certain concentrations and times caused degradation in the phenolic profile of strawberries. Anthocyanins were the most affected of the phenolic compounds, followed by proanthocyanidins with a low degree of polymerization, hydroxycinnamic acid derivatives, and the ellagitannin Sanguiin H-6. In general, pelargonidin-based anthocyanins were more susceptible to oxidation than cyanidin-based anthocyanin under the same PAA fogging conditions. In summary, the stability of strawberry individual phenolic compounds after fogging treatments was dependent on the concentration and the exposure time of PAA treatments as well as the chemical nature of them. The models developed herein allow to predict retentions of individual phenolic compounds at different fogging PAA conditions.

1. Introduction

Epidemiological studies have noted that fruit and vegetable consumption protects against degenerative diseases, including cancer, heart disease and stroke, and can contribute to control of diabetes and obesity. These benefits are linked to the optimal mix of antioxidant and anti-inflammatory phytoactive compounds present in edible produce (Alvarez-Suarez et al., 2014). Strawberry is one of the most commonly consumed fruits due to its attractive color and taste, and recognition as a very rich source of antioxidant compounds including vitamin C and phenolic compounds (da Silva Pinto et al., 2008). Phenolics contribute to both the sensory and organoleptic quality attributes of strawberry, and its health-protective value (Espín and Tomás-Barberán, 2001). Proanthocyanidins (PAC), also known as condensed tannins, are mixtures of oligomers and polymers composed of flavan-3-ol, and represent one of the main categories of phenolic compounds found in strawberries (Gu et al., 2003). The PAC concentration reported in several varieties of strawberries ranged between 53.9 and 163.2 mg 100 g^{-1} of fresh weight (FW) (Buendía et al., 2010). Glycoside derivatives from the anthocyanins, pelargonidin and cyanidin, are the main flavonoids found in strawberries with reported concentrations of up to 65 mg 100 g^{-1} FW. Anthocyanins are responsible for the red color of strawberries and represent one of the major antioxidant sources in this fruit (Crecente-Campo et al., 2012). Another interesting group of phenolic compounds in strawberry is the hydrolysable tannins (ellagitannins) (Clifford and Scalbert, 2000). Other phenolics present in lower concentrations are flavonols (quercetin and kaempferol glycosides), esters of hydroxycinnamic acids (especially of *p*-coumaric acid), ellagic acid and ellagic acid glycosides (Määttä-Riihinen et al., 2004; Buendía et al., 2010).

Like most other fruits, strawberries can be consumed fresh, which can be advantageous to consumers since nutritional losses

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due to processing can be avoided. However, the storage period and the shelf-life of this fruit are very short due to its perishability and susceptibility to the growth of rot-causing pathogens (Vardar et al., 2012). Therefore, the application of decontamination processes that can ensure microbiological safety and shelf-life extension of the product, while retaining quality attributes close to the fresh characteristics, becomes crucial for this kind of fruit (Alexandre et al., 2014). Unfortunately, strawberries can be damaged easily when traditional washing is performed in a processing line, and the drying period delays pre-cooling, which may facilitate pathogen infection (Vardar et al., 2012). Hence, the application of disinfectant agents by fogging can be an effective alternative technology since handling and wetting of the fruit is minimized (Oh et al., 2005; Vardar et al., 2012). This operation has been already used successfully for the decontamination and control of postharvest diseases of strawberries, employing chlorine dioxide, sodium hypochlorite, citric acid and ethanol as disinfectant agents (Vardar et al., 2012); and similarly figs have been treated postharvest with chlorine dioxide (Karabulut et al., 2009).

Fogging with the sanitizer based on peracetic acid (PAA) may be a promising option for controlling the microbial population and extending the storage time for up to 7 days at 2 °C of fresh whole strawberries, employing a disinfectant that is recognized for being environmentally friendly (Van de Velde et al., 2016). The commercially available PAA works with a quaternary equilibrium of acetic acid, hydrogen peroxide, peracetic acid and water, and its decomposition products are only oxygen and acetic acid. Moreover, the advantages of the use of PAA over other agents, such as chlorine, include a lack of or only negligible formation of toxic or carcinogenic compounds, and that its activity is little influenced by the presence of organic material and is not dependent on factors such as pH and temperature (Vandekinderen et al., 2009). The effectiveness of PAA solutions in reducing the initial microbiologic loads was demonstrated in the washing-disinfection of a wide range of fresh-cut fruits and vegetables (Artés et al., 2009; Van de Velde et al., 2013), and its use for fogging of lettuce leaves (Oh et al., 2005). Recently we showed that fogging with PAA was effective for reducing the total mesophilic microbial and yeast and mould loads of whole strawberries for up to 7 days of storage at 2 °C (Van de Velde et al., 2016).

Despite the well documented microbial effectiveness of PAA, these disinfectant solutions are also strong oxidants (the oxidation potentials of peracetic acid and hydrogen peroxide are close to 1.8 eV) (Pechacek et al., 2015), and phytochemicals and other nutritional compounds of strawberries, as well as quality parameters such as color, can be oxidized/affected by the treatment conditions. Özkan et al. (2005) described a degradation of anthocyanins in sour cherry nectar, strawberry and pomegranate juices following hydrogen peroxide treatments. Meanwhile, Van de Velde et al. (2013) reported that the retention of total anthocyanins and vitamin C was adversely affected after a postharvest washing-disinfection of fresh-cut strawberries using PAA solutions. Subsequently, Van de Velde et al. (2016) concluded that the fogging of whole strawberries with PAA reduced the total anthocyanin, total phenolic, and vitamin C contents, the antioxidant capacity, and the color of the fruit. The degree of postharvest loss was conditioned by the concentration and the exposure time of fogging treatments.

Therefore, considering the relevance of different individual phenolic compounds to the color and health-related properties of the fruit, it is important to determine which fogging parameters conditions would be optimal to ensure disinfection, yet minimize damage to phenolic constituents of strawberry. The aim of this work was to study and model the effects of PAA fogging, immediately after the operation, at different concentrations and contact times on the individual naturally occurring phenolic compounds of strawberries, using the complementary information from high performance liquid chromatography (HPLC) with photodiode array (PDA) and fluorescence (FLD) detection in combination with mass spectrometry (MS).

2. Materials and methods

2.1. Chemicals and reagents

Oxilac Plus, a commercial sanitizer based on peracetic acid (PAA) was obtained from Indaquim S.A. (Santa Fe, Argentina). Oxilac Plus is a stabilized mixture of 5% peracetic acid, 20% hydrogen peroxide and water. Reference compounds procyanidin B2 (PAC-B2) (PubChem CID: 122738), pelargonidin-3-*O*-glucoside (PubChem CID: 443648), cyanidin-3-*O*-glucoside (PubChem CID: 441667), ellagic acid (PubChem CID: 5281855), quercetin (PubChem CID:5280343) and *p*-coumaric acid (PubChem CID: 637542) were purchased from Chromadex (Irvine, CA, USA). All solvents were HPLC grade and obtained from VWR International (Suwanee, GA, USA).

2.2. Plant material

Cultivated strawberries (*Fragaria x ananassa* Duch.) cultivar 'Camarosa' were obtained from one planting at Arroyo Leyes (31° 27′ 0″ S, 60° 40′ 0″ W), Santa Fe, Argentina. Fruit was harvested by skilled workers at full ripeness stage (90% of the surface showing red color) and was transported 20 km directly from the field to the laboratory of the Instituto de Tecnología de Alimentos, FIQ, UNL, Argentina, and stored at 2 °C until use. Harvested fruit was selected for uniformity of size, color and absence of defects before use in experiments.

2.3. Fogging system and procedure

Treatments were set up in a 16 L plastic hermetically sealed model chamber specially designed for this experiment. The fogging was performed using an ultrasonic aerosol generator unit (Respirex, Accme, SRL, Córdoba, Argentina) that has a liquid reservoir (30 mL) for holding the liquid to be fogged and produces a fog of droplets between 0.5–8.0 μm in diameter. The small particles are carried away by the airflow and blown inside the chamber. Six round rigid plastic trays (capacity 270 cm^3), each containing 150 g of selected strawberry fruit were placed inside the chamber with the lids opened and were fogged at various PAA concentrations (μL of PAA per L of air chamber) and contact times, according to the experimental design (Section 2.4). All the fogging treatments were performed at room temperature (24 °C). The fogging system unit was turned on for nebulization of all the liquid in the reservoir (typically between 5 to 10 minutes), then the fogging system was turned off and the samples were left inside the chamber to complete the contact times according to the experimental design (Section 2.4). Treated samples were taken out of the chamber, frozen at −80 °C before lyophilization in a Flexy-dry freeze dryer (SP Scientific, NY, USA), and then analyzed.

Untreated strawberries (500 g; raw material) were used as the control and were frozen at −80 °C before lyophilization in the same way. The freeze-dried material was weighed and the dry matter content was estimated by difference in weight.

2.4. Experimental design and response modeling

Response Surface Methodology (RSM) using a Central Composite Design (CCD) was used to study the fogging operation. The CCD is the most frequent five levels fractional factorial design used for the construction of a second-order response surface model. The