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Modeling phenolic content during storage of cut fruit and vegetables: A consecutive reaction mechanism

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ABSTRACT

The changes in the phenolic content of fresh-cut produce during storage are often characterized by an initial growth caused by several abiotic stresses that promote the increase of phenylalanine ammonia-lyase (PAL) activity, which is the first step in phenylpropanoid metabolism. A kinetic model based on a mechanism involving two consecutive reactions was developed to describe the changes in the phenolic content of fresh-cut produce during storage. Experimental data for purslane stored at 0 and 5 °C, apples and broccoli stored at 5 °C, as well as literature data for 'Lisbon' lemon and 'Palazzelli' mandarin samples were used to validate the model, which is consistent with the phenol changes under all of the studied conditions. By estimating model parameters, individually or as group, the storage temperature did not affect the *de novo* synthesis of phenols but did affect the oxidative degradation for purslane samples. For apples and broccoli samples, biological variability was very important and affected the initial phenolic content and synthesis. Moreover the model also explained the phenolic variation on mandarin segments and on cut lemons. The type of cut for lemon samples had a significant effect on the rate of synthesis of phenols, with an increase of 1.8-fold being observed for the ½ slice compared to the slices. The model may be a useful tool for obtaining a better understanding of the effects of processing and storage conditions on the changes in the phenolic content and improving the shelf life prediction of fresh-cut produce.

1. Introduction

Fruits and vegetables are rich in nutritional and functional compounds, such as phenolic compounds, bioaccessible antioxidants, vitamins, minerals, carotenoids, and fibers (Kenny and O'Berine, 2010; Wootton-Beard et al., 2011). It is currently believed that an increase in the consumption of fruit and vegetables can have a beneficial impact on public health (Wootton-Beard and Ryan, 2011), even if the nature of these benefits is still unclear. The positive relationship between the consumption of fruits and vegetables and the reduction in the risks of cardiovascular diseases has been previously reported (Chobanian et al., 2003; Duthie et al., 2003; Joshipura et al., 1999; Steinmetz and Potter, 1996; Tohill et al., 2004). Due to this perception, in the last 15 years, the sales of ready-to-use fresh fruits and vegetable, which add convenience to fresh produce consumption, increased exponentially. Cook (2012), who studied the market trends of food products in the United States, reported that 56% of consumers purchase fresh-cut fruits and vegetables weekly and 55% of them consider the nutritional information as extremely or somewhat important in the purchase decision. Therefore, providing nutritional information on product labels would be very useful. To address this aim, the impact of postharvest processing and storage conditions should be taken into consideration because it is well-known that the nutritional quality profile can change during storage due to various chemical and/or enzymatic reactions. In particular, wounding promotes antioxidant degradation, resulting in oxidation of antioxidant compounds such as ascorbic acid and phenolic compounds. The degradation pathway of vitamin C has been extensively studied (Fennema, 1977; Favell, 1998; Lee and Kader, 2000; Nkhili and Brat, 2011; Serpen et al., 2007; Van Bree et al., 2012). The reactions involved during the degradation of ascorbic acid (AA) have been modeled with first order irreversible kinetics (Giannakourou and Taoukis, 2003) and first order reversible consecutive kinetics (Serpen and Gokmen, 2007; Serpen et al., 2007; Van Bree et al., 2012). Phenolic compounds are another important class of antioxidant compounds ubiquitous in plants and all derived food products (Brecht et al., 2004; Tomas-Barberan and Espin, 2001). Based on the different basic skeletons and their variations due to oxidation, rearrangements of the atoms and conjugations with other compounds, several thousand phenolic structures

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have been reported (Harbone, 1980). Phenolic compounds play an important role in several sensorial properties, such as appearance, flavor, taste, and, especially, color (Lattanzio, 2003; Tomas-Barberan and Espin, 2001). Therefore, several authors studied the changes in phenolic compounds in fresh-cut fruits and vegetables during storage. Often, a significant increase in phenolic content is observed during the first days of storage, which, in cut products, may induce further browning due to oxidation (Artes-Hernandez et al., 2007; Costa et al., 2006; Del Caro et al., 2004; Murata et al., 2004; Shiri et al., 2011). For example, Artes-Hernandez et al. (2007), who studied the effects of cutting and storage temperature on 'Lisbon' lemons, observed an increase in total phenolic compounds during the first 4 days of storage from ~90 to ~170 mg L^{-1} of lemon juice. Costa et al. (2006) observed an increase in total phenols that ranged from 0.68 g kg^{-1} to 1.18 g kg^{-1} in broccoli samples after 4 days of storage at 20 °C. Kenny and O'Berine (2010), who studied the effect of peeling methods on phytochemical compounds of fresh-cut carrots, reported a significant increase in the phenolic content from 140 to ~160 mg kg^{-1} after fine abrasion peeling. Similar results were observed for lettuce and carrots by Kang and Saltveit (2003), Surjadinata and Cisneros-Zevallos (2012) and Tomas-Barberan et al. (1997). Surjandinata and Cisneros-Zevallos, who studied the effect of wounding intensity on the phenolic content of carrots reported an ~5.6-fold increase compared to fresh samples (~45 mg 100 g^{-1}). In general, the increase in phenolic content is the response of plants to biotic and abiotic stresses, such as a pathogen attack, wounding, high levels of visible light, and cold stress. (Dixon and Paiva, 1995). However, for fresh-cut produce, wounding during postharvest processing is one of the most important causes of an increase in phenols during storage (Klaiber et al., 2005; Saltveit, 2000) even though ethylene production exhibited a significant effect in lettuce (Hyodo et al., 1978). The exact nature of the wound signals is not completely understood but several chemical compounds, such as absiscic acid, ethylene, jasmonic acid, linolenic acid and phosphatidic acid appear to be involved (Choi et al., 2005; Leon et al., 2001). However, it is recognized that wounding promotes an increase in phenylalanine ammonia-lyase (PAL EC 4.3.1.5) activity, which catalyzes the first step of phenylpropanoid metabolism (Kang and Saltveit, 2002; Murata et al., 2004; Tomas-Barberan et al., 1997). In particular, cinnamic acid obtained from phenylalanine due to PAL activity is the compound from which several phenylpropanoids are derived *via* a series of hydroxylation, methylation, and dehydration reactions (Dixon and Paiva, 1995). Due to these reactions, tartaric acid is converted into caffeoltartaric, and dicaffeoltartaric acids and quinic acid are converted into chlorogenic acid (Saltveit, 2000; Tomas-Barberan et al., 1997). The increase in PAL activity is recognized as the limiting factor in the browning of fresh-cut lettuce, which turns brown after several days during which the *de novo* biosynthesis of polyphenols occurs due to wounding (Campos-Vargas and Saltveit, 2002; Kang and Saltveit, 2003; Murata et al., 2004). The effects of processing and packaging conditions on the activity of PAL and phenolic content (Cisneros-Zevallos, 2003; Kang and Saltveit, 2003; Loaiza-Velarde and Saltveit, 2001; Saltveit, 2000) and the kinetics of enymatic browning of several fruit and vegetables (Falguera et al., 2010; Gomez et al., 2006; Quevedo et al., 2009; Soliva-Fortuny et al., 2002) have been previously investigated. Falguera et al. (2010), who modeled the browning of mushrooms and took into account the autocatalytic reaction of L-tyrosinase for the production of melanin, reported that the rate constants of these reactions decreased as the concentration of the enzyme increased. Nevertheless, no models are available to describe the kinetics of phenolic changes during storage to be used as a predictive tool to minimize the loss of phenol compounds during storage, to add nutritional information of the fresh-cut produce and to sort cut products based on phenolic content and fate for online systems. Based on these considerations, the aim of this paper was to develop and validate a kinetic model able to describe the changes in the phenolic content in fresh-cut produce during storage.

2. Material and methods

2.1. Plant material

Data related to changes in the phenolic content were obtained both from specific experimental trials performed on purslane (previously published in Rinaldi et al., 2010), apples, and broccoli as well as from literature data (lemon and mandarin). Broccoli heads and purslane plants were harvested and transported within 1 h to the postharvest laboratory at the University of Foggia where they were processed by detaching the fully expanded leaves from the stems for purslane and by detaching small florets from the broccoli heads. Three replicates consisting of five 25 g samples of purslane leaves were stored at 0 and at 5 °C in 8 L containers under a continuous flow of humidified air, which prevented dehydration while avoiding CO_2 accumulation and O_2 depletion in the containers. Broccoli florets were prepared from 12 individual heads (single replicates), which were stored at 5 °C.

Finally, 'Stark Red' apples were purchased locally and transported to the postharvest laboratory at the University of Foggia. After washing in NaClO (100 ppm of active chlorine), unpeeled apples were sliced and cut into cubes; 5 apples were used for each replicate, for a total of 12 replicates. Each replicate was stored at 5 °C under a constant flow of humidified air.

The literature data for 'Lisbon' lemon samples, which were cut into slices and ½ slices and stored at 5 °C, and 'Palazzelli' mandarin samples, which were stored at 4 °C for 12 days, were obtained from Artes-Hernandez et al. (2007) and Del Caro et al. (2004), respectively. For mandarin samples, the values were reported in tables, whereas the values for lemon samples were obtained from the figures using Image Pro-Discovery software ver. 6.0 (Media Cybernetics, USA).

2.2. Phenolic content determination

The phenolic content was measured at 0, 3, 14, and 17 days of storage for purslane leaves, at 0, 3, 6, 8, and 10 days of storage for broccoli and at 1, 2, 5, and 7 days for apples. Five grams of fresh tissue were homogenized in a 2 mM NaF methanol:water solution (80:20) for 1 min followed by centrifugation at 5 °C and 12,000*g* for 10 min. The pellet was discarded, and the supernatant was retained and used as the extract. The total phenolic content was determined according to the method reported by Singleton and Rossi (1965). Each extract (100 μL), which was appropriately diluted, was mixed with 1.58 mL water, 100 μL of Folin–Ciocalteau's reagent and 300 μL of a sodium carbonate solution (200 g L^{-1}). After 2 h of standing in closed cuvettes, the absorbance was read at 725 nm against a blank with a spectrophotometer (Shimadzu UV-1700, Jiangsu, China). The total phenol content was calculated based on the calibration curves of gallic acid and expressed as mg of gallic acid equivalents per 100 g of fresh weight.

2.3. Model development and parameter estimation

As previously reported, during storage, several stresses may promote an increase in the PAL activity resulting in the *de novo* synthesis of phenols. Then, these compounds may be oxidized by PPO enzymes (Lopez-Galvez et al., 1996; Murata et al., 2004; Saltveit, 2000). Assuming that the complete description of the phenylpropanoid metabolism would be very complicated, we