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Thermal transitions of pulp and cuticle of blueberries

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ABSTRACT

The thermal transitions of two blueberries cultivars (*Duke* and *Briggitte*) were studied by differential scanning calorimetry as part of comprehensive study of blueberry conservation. Thermal transitions and texture (hardness) were determined in fresh and frozen fruits freezed at 5 °C/min and 40 °C/min. Glass transition temperatures were successfully detected in pulp and cuticle, which was associated to the soluble sugar fraction present in the fruit. Transitions associated to water crystallization and melting showed differences between both cultivars, which were explained by their soluble solids concentration. An endothermic transition at 50 °C was associated to the melting of epicuticular wax present in the cuticles. The cuticle was less affected by ice formation, which is an important feature to fruit protection at low temperatures. Hardness showed that cooling rate had not a significant effect on this quality parameter. Despite the complexity in the structure of blueberries, thermal characterization by DSC was successful.

1. Introduction

Blueberries represent a large group of high sugar content fruits for which storage stability is important. The consumption of blueberries has increased worldwide due its well known health benefits [1] by the presence of anticancer and anti-oxidants compounds and low calories associated to its components. Therefore blueberries have begun to be considered as an important component of a healthy diet [2,3]. Blueberries are little fruits, spherical in shape, blue in color, from the genus *Vaccinium* with high nutritional value and with potential anti-diseases effects but with very limited shelf-life. The opening of new markets and the retention of current ones depends on the ability to deliver a consistently high-quality product to geographically distant destinations (e.g., from south to north hemisphere). The color range of blueberry varies from light blue to deep black and depends on the cultivar and the presence of an epicuticular wax on their skin, which gives to fruit an attractive appearance [4]. Literature mentions that main quality indicators in blueberry are fruit appearance (color, size and shape), firmness as a measure of fruit's structure integrity, flavor (soluble solids, tritrable acidity and pH) and nutritive value (vitamins A, C and antioxidants) [5]. Changes on those indicators have a profound effect on consumer's acceptability. Clearly, the retention of these quality parameters is paramount to successfully compete in the fresh fruit international market.

Under refrigerated conditions at temperatures near 0 °C, shelf-life of blueberry is about 14–20 days [6,7]. Therefore, conservation methods such as freezing are required, extending the fruit shelf-life up to 18 months. An important preservation parameter is the cooling or freezing rates prior storage, which can produce an impact on the glass transition temperature and therefore on its stability [8,9] and microstructure [9]. During the freezing process, quality deterioration can occur at three well established stages: (i) nucleation, (ii) crystallization, (iii) crystal growth and recrystallization. Hence, the freezing method used for blueberries determines the possible pattern of ice formation (nucleation) in the fruit. The nucleation of ice and the number and size of ice crystals formed are dependent on the freezing rate: slower cooling rates will produce fewer nucleation, larger ice crystals and more dislocation (migration) of water molecules. Faster cooling rates will produce more nucleation, but smaller ice crystals [10,11]. Standard freezing of wild blueberries produces a significant juice loss (drip) after thawing, which appears to be caused by ice crystal damage to cell vesicles [8,9]. It is believed that frozen foods are stable when stored at −18 °C, but literature suggests that this is not entirely true due to micro-structural and quality changes can occur at this stage, related mainly to ice formation [9]. Indeed, the assessment of thermal parameters such as glass transition temperature, end point of freezing and maximal freeze-concentration conditions are considered to be relevant and important in food processing (i.e., freezing and drying) and stability under various storage conditions of temperature and moisture content [12]. Thus, a product stored at a temperature (T_s) below the glass transition temperature of the maximal freeze concentrated fraction (T_g'), it may be expected to be composed of ice and a

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freeze-concentrated phase in a glassy state and thus a long-term stability may be anticipated [13]. Moreover, only limited information is available looking a thermal transitions and stability of systems such the aforementioned fruits.

Changes in structure, solute concentration associated with the fruit ripening, as well as fruit water status can be analyzed simultaneously by DSC [14]. Thermal transitions of fruits determined by this technique have been focused mainly in water sorption, glass transition temperature and state diagram of freeze-dried in fruits such as raspberry [15], grapefruit [16], kiwifruit [17,18], freeze-dried or spray-dried juices of persimmon [19], apple [20] and tomato [21]. However, little information has been published looking at the thermal characterization of fresh fruits. Literature describes only research on unfrozen fraction of water in onion, grape, strawberry [22], apples [20] and grapefruit [16]. Meanwhile, thermal transitions of cuticles have been only partially studied, particularly in isolated cuticle (enzymatical isolation) of apple [23,24], tomato [24] and extracted cuticular waxes from grape berry [25]. The fruit cuticle is chemically heterogeneous in nature, basically consisting of a waxy fraction, soluble in organic solvents, and an insoluble cuticular matrix, the cutin, that forms the structure framework of the cuticle. Cuticular waxes constitute the main barrier limiting the transport across the plant–atmosphere interface, controlling transpiration [26], foliar uptake of xenobiotics [27,28] and the resistance against fungi [29]. This is modulated by their partial arrangement in crystalline regions, where the middle portions of the long aliphatic chains of the wax are regularly aligned, and in amorphous regions where short-chain aliphatics and cyclic compounds form clusters outside crystalline regions [30]. Those waxes can, in fact form crystalline oriented parallel to the surface of the cuticular membrane [31].

The objective of this work was to analyze thermal transitions in both cuticles and pulp of two blueberry cultivars using differential scanning calorimetry (DSC), as part of comprehensive study of blueberry conservation.

2. Materials and methods

2.1. Plant material

This study was carried out during the growing season of the summer of 2010 at the central valley of the Region Metropolitan in Chile (Curacaví, Hortifrut S.A.). Two common blueberries cultivars (*Brigitte* and *Duke*) from Highbush variety were used. Cvs. *Briggitte* and *Duke* were hand harvested and immediately packed in 230 mL plastic "clam-shell" containers (industry fruit standard containers) and transported to laboratory at the Universidad de Santiago de Chile for testing.

Prior the experimental work, fruits were selected manually, discarding those visually damaged, without peduncle or flower rest and red (unripe) fruit.

The cuticles were obtained from blueberry using a sharp scalpel separating it from the pulp of the fruit, then scraped lightly in order to remove any residual pericarp tissue [32–34]. Five fruits replicates were used for this purpose. The pulp obtained was ground and homogenized.

Epicuticular wax extraction from blueberries was achieved by soaking ten fruits (replicates) in chloroform for 30 min, where the epicuticular wax was completely solubilized [35]. Then, the solvent was evaporated at room temperature in order to obtain wax in the DSC pans for thermal measurements.

2.2. Model system

Glucose and fructose are sugars present in blueberries at significant concentrations [36]. These compounds are considered to be major vitrifying agents in plants [37,38]. Therefore, in order to identify the T_g in blueberries associated to sugar–water fraction, a model system (SMS) based on glucose and fructose with well known T_g was prepared at a concentration similar to the reported for blueberries in literature [36]. SMS solution concentration was 16% of total solids using glucose (Riedel-de Häen) and fructose (Merck) in equal ratio (1:1).

2.3. Storage conditions

Blueberries were stored at three different conditions: (i) fresh blueberries were stored at 5 °C for 22 days. Then the mechanical and thermal properties were measured by a texture analyzer and by differential scanning calorimeter (DSC), respectively. (ii) Frozen at slow rate (5 °C/min) in trays 6.0 cm deep in a storage room with slowly moving air stream at −18 °C. Fruits were stored there for 18 months. Blueberries were analyzed by mechanical analysis. For the assessment of thermal transitions, fresh blueberries (cuticle and pulp) were cooled at 5 °C/min in the DSC, taking samples of cuticle or pulp and sealing them in aluminum pans immediately before the analysis. (iii) Frozen at intermediate cooling rate (40 °C/min) by an IQF (individually quick frozen) industrial process (personal communication, Hortifrut SA, Chile) and stored at −18 °C for 18 months. After that time blueberries were analyzed by mechanical analysis.

2.4. Fruit quality indicators

The following parameters were used to assess fruit quality before storage conditions:

Water content: It was determined gravimetrically using an analytical balance (Mettler Toledo, Switzerland). Twelve blueberries were dried in an oven (Wiseven, Korea) at 105 °C for 24 h until reach constant weight [39]. The analysis was performed in triplicate. Water content was expressed in % wet basis (g water/100 g wet sample)

Fruit size: Equatorial and polar diameter was measured using a digital calliper (Bull Tools, USA) and roundness index (RI) was determined by the ratio polar diameter/equatorial diameter. A mean and standard deviation of 30 measurements were reported.

Total soluble solids content: It was determined by placing 1 mL of homogenised pulp obtained from the milling of 5 blueberries on a portable refractometer (0-32°Brix, RHB-32ATC). The analysis was performed in triplicate. The mean and standard deviation for the replicates were recorded and expressed as °Brix.

Hardness: It was defined as the fruit's stiffness; it was measured by compression test using a Texturometer (DOFBO.5TS, Zwick, Germany). Data were collected using Texture Expert Version 1.22 software (Stable Micro System Ltda.). A 12 mm diameter ball compressed each individual fruit ($n = 30$) perpendicular to its axis (equatorial height) at a rate of 1 mm/min to a threshold force of 10%. The hardness of each blueberry was measured as the Maximum Force (N) necessary to compress 10% of the initial equatorial height of the fruit. Therefore, the hardness value (N) mean of the 30 replicates was reported with their corresponding standard deviation.

2.5. Differential scanning calorimetry (DSC)

10–20 mg of the pulp, cuticle and extracted epicuticular wax were separately weighed, loaded into aluminum pans of 30 μL and subjected to thermal scans using a DSC (Pyris Diamond DSC, Perkin Elmer, USA). Prior the measurements, the DSC was calibrated using indium (melting onset temperature 156.6 ± 1.56 °C, $\Delta H = 28.6 \pm 1$ J/g). The reference used during the analysis was an empty pan. All experiments were performed in triplicate using the