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Phase transition of apple cuticles: a DSC study

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Abstract

Apple and capsicum cuticles were isolated enzymatically from mature fruits and the effect of storage temperature on phase transition of the lipid components in the cuticle was examined using differential scanning calorimetry (DSC). It was found that the cuticular membrane underwent an endothermic transition attributed to melting of the waxes present in the cuticle. On storage at low temperatures the cuticular membrane underwent a change in structure and the melting enthalpy of the waxes present decreased as seen by DSC. \odot 2001 Elsevier Science B.V. All rights reserved.

Keywords: Apple cuticles; Differential scanning calorimetry; Phase transition

1. Introduction

When fruits and vegetables are stored at low temperatures for various periods of time, they run the risk of physical changes due to chilling injury. The symptoms of chilling injury are surface pitting, discoloration, internal breakdown and decay. It has been shown earlier that the factors responsible for chilling injury are located in the membrane [1]. However, the cuticular region may also influence the onset of injury. This is important during food storage. It has been shown earlier that this may be due to the contents of unsaturated fatty acids that may be responsible for protecting the plant against chilling injury and may undergo changes due to the decrease in temperature [2-4]. Since the cuticle of plants is considered as the first barrier against mechanical and physical damage, temperature changes that may effect the polymer matrix of the cuticle were examined.

The cuticle of plants is like a protective barrier, protecting the plant against evaporation and mechanical damage. It is a lipophilic polymeric membrane,

which covers the aerial parts of the plants and limits passive water loss [5,6]. It consists of an insoluble biopolymer cutin and wax-like lipids which are deposited within the polymer membrane and on the cuticle surface. The waxes are long-chain aliphatic and cyclic components including primary alcohol, secondary alcohol, hydrocarbon, and fatty acids. The non-lipid components of cuticles are cellulose, pectin and phenolics [7,8]. In this investigation, in order to observe the effect of low temperature on the polymer matrix [9] and the epicuticular waxes present in the cuticular membrane of apples and capsicum, the cuticles from mature ripe untreated apples and capsicum were isolated. These samples were stored at low temperature to simulate frost damage conditions seeking evidence if any of the changes in the cuticular membrane is due to low temperature storage, after which the samples were heated in a controlled atmosphere using differential scanning calorimetry (DSC), which is a device which can be used to obtain information on the phase transition of the cuticular waxes due to changes in temperature [10].

2. Materials and methods

The cuticles were prepared from mature apples and capsicums purchased from the market, fresh golden delicious apples were used. The pulp and fleshy portions were separated from the skin by using a peeler. The cuticle was separated from the rest of the skin enzymatically [11] using pectinase and cellulase. The isolated cuticles were stored under dry conditions at room temperature until used. For the low temperature samples, the cuticles were cut into tiny discs and stored at -30° C. Samples kept at room temperature were used as control. After incubation at the respective temperature for 48 h, the apple cuticles were weighed into aluminum pans

and sealed. An empty pan was used as reference material. These samples were then loaded on the DSC system, cooled to -40° C, held there for 5 min and then heated to 95° C at a heating rate of 10° C min⁻¹. DSC analysis on the apple cuticles was performed using a Perkin-Elmer DSC-7 Robotic system (Perkin-Elmer, Norwalk, CT) equipped with an Intercooler II for subambient conditions. In the case of the capsicum cuticle, the samples were loaded into the steel sample holders of the microcalorimeter Micro DSC III manufactured by Setaram (Setaram, Caluire, France) since no thermal transitions were visible with the conventional DSC system. The temperature scan used was from 25 to 95° C at a heating rate of 2° C min⁻¹.

Fig. 1. DSC plot of apple cuticle.

3. Results and discussion

As can be seen from the plot (Fig. 1), a typical DSC scan of apple cuticles heated to 95° C shows the occurrence of an endothermic transition due to the melting of the waxes present in the cuticular membrane. The transition commences at around 54° C. As seen, the endotherm is not a single peak but consists of at least three overlapping peaks, indicating the melting of multiple components. These occur at 54.8, 63.5 and 71.4° C, respectively. The transition is also quite broad. These results are consistent with cuticle behavior. Cuticular waxes are crystalline at physiological temperatures [12]. They do not have a distinct melting point but melt over a wide melting range from 60 to 90° C, indicating that the waxes are not single

components but mixtures. The energy involved in this transition was 22 J g^{-1} . Similar observations were also made on the apple cuticles that had been stored at -30° C (Fig. 2). It showed the presence of at least three distinct components with a peak melting temperature of 54.3, 62.4 and 68.6° C showing a slight shift of the transition temperature to the lower end. The energy required for this transition is also lower at 19 J g^{-1} as compared to the control which is 22 J g^{-1} . On storage of this sample at -30° C for 1 month, the effect on the transition energy is further decreased to 17 J g^{-1} . In the case of the capsicum cuticle, it also shows the occurrence of an endothermic transition (Fig. 3) which commences at 57° C with a peak transition temperature of 70.3° C. In this case there is a single broad peak observed indicating that the

Fig. 2. Apple cuticle stored at -30° C.

Fig. 3. Micro DSC plot of capsicum cuticle.

major component is one type of wax family. The sample stored at -30° C similarly showed the lowering of the transition temperature and a slight decrease of the enthalpy value from 3 J g^{-1} seen for the sample at ambient temperature to 1.7 J g^{-1} for the sample at lower temperature. These results indicate that there may be some physical changes taking place in the cuticular membrane of fruits and vegetables $[13-15]$ stored at low temperatures which can be demonstrated by examination using thermal techniques.

4. Conclusions

In this study it was demonstrated that the cuticular membrane of apple and capsicum is influenced by storage at low temperature. Storage at low temperature

causes a shift of the phase transition on the lower end. This may indicate that the cuticle of fruits may participate in chilling injury caused in plants due to cold storage.

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