Oven-dried table olives: textural properties as related to pectic composition

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Abstract: The effects of processing treatments on the microscopic structure, pectic fractions and firmness of ripe olives (*Olea europaea* L Cassanese variety), processed by the 'Ferrandina' method for oven-dried table olive production, were studied. The process included a first heating step, a salting step and a final oven-drying process. Scanning electron microscopic observations of olive tissue structure revealed that heat treatment was highly damaging, affecting the intercellular pectic substances and producing cell separation. Epicuticular waxes were barely affected and limited the shrivelling of the fruit during the oven dehydration process. The pectin content was higher in the oven-dried olives than in the fresh samples. The sodium hydroxide-soluble fraction was the main pectin fraction in the olive tissues. Its content decreased markedly after the heating step, while it increased after the oven dehydration step. The softening of the olive tissues increased after heat treatment, and a correlation was found between protopectin content and firmness. In oven-dried olives a firming of the olive tissues was observed due to the de-esterification of pectin and to its decreased solubility resulting from an increase in cell wall calcium bridging.

Keywords: olives; *Olea europaea* L; oven-drying process; texture; pectin; scanning electron microscopy (SEM)

INTRODUCTION

The world production of table olives is around 10^6 t, with approximately 80% coming from countries of the Mediterranean area. From available data[1] it can be estimated that approximately 45% and 34% of the production are made up of green and black olives respectively, while the remainder is constituted of cherry colour olives.

Table olives are consumed on a large scale all over the world, and their consumption is expanding owing to the increasing popularity of the Mediterranean diet. Nowadays there are three main types of table olives: Spanish green olives, Greek-style ripe olives and Californian-style ripe olives. Other marketable products, such as oven-dried and dry-salted olives, are less common.

It is well known that the physicochemical properties of olive fruit are modified by processing,[2–5] and the texture[6,7] is one of the organoleptic characteristics most affected by alkali treatment with dilute NaOH (lye) currently used to hydrolyse oleuropein,[8,9] considered the main compound responsible for the bitter taste of the fruit.

Many physical and chemical changes occurring in the fruit, such as the loss of soluble constituents and nutrients (sugars, organic acids, salts, amino acids, etc) responsible for the typical properties of table olives, are perceived by the consumer as a loss of quality of the final product.

However, most processing technologies are well known and methods to control the characteristics of the olives are available. On the other hand, fermentation processes are still spontaneous, while processing technologies of oven-dried and dry-salted table olives remain completely empirical.

However, the increasing interest of the consumer in 'natural' products involves the use and diffusion of technologies which can offer a guarantee of preservation, hygiene and genuineness of food products. This may arouse the interest of the industry in preparing oven-dried table olives variously seasoned with olive oil and natural aromatic herbs. In view of the continuing consumer interest, these products may represent a success to meet the consumer demand in terms of dietetical, gustative, social and cultural expectations.

As far as we know, there is no published report on the characteristics of oven-dried table olives. Therefore it is important to carry out investigations to study the changes in physicochemical properties of the olives due to the technological transformation process in order to assess the quality of the final product. The opportunity was offered by the EC programme FAIR CT97-3053 (Olitext-Project), whose aim is the improvement of the textural characteristics of some European olive fruit varieties suitable for table olive purposes.

The present work was performed to study the

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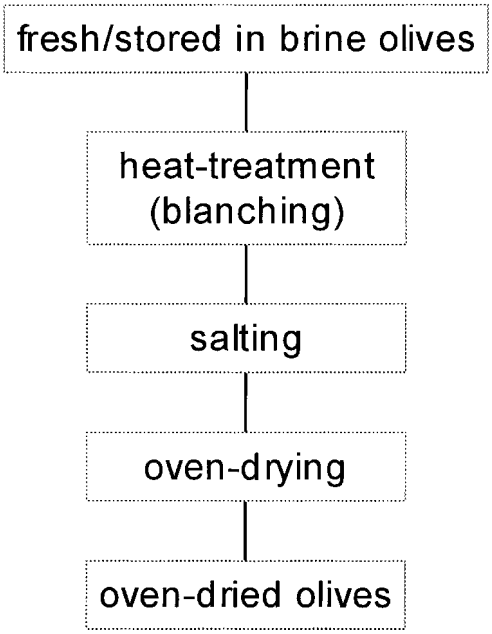

Figure 1. Oven-dried black olive processing flow diagram ('Ferrandina' method).

physicochemical changes occurring in oven-dried olive tissues during each processing step. Therefore pectin and texture were analysed, and furthermore, the changes that took place in the olive tissues during processing were visualised by scanning electron microscopy.

MATERIALS AND METHODS

Plant material and process

Olive fruits (*Olea europaea* L Cassanese variety) were harvested at an advanced stage of ripening from the orchard of Istituto Sperimentale Elaiotecnica (Olive and Olive Oil Research Institute) in Pescara (Italy). Olives, after 1 month of storage in brine, were processed by the 'Ferrandina' method, whose processing flow diagram is shown in Fig 1. The process included three main steps: (i) heat treatment (blanching) of the fruits contained in a perforated vat and immersed in a water bath at approximately 90 °C for 6 min, mainly depending on the ripeness of the fruit; (ii) salting of the fruits with sodium chloride (100 g kg^{-1}) for 3 days; and (iii) drying of the fruits on a wooden trellis in an air oven at approximately 50 °C for 17 h.

Moisture content

Moisture was determined by drying a weighed olive flesh sample at 105 °C in an air oven for 24 h.

Temperature assay

During heating, temperature was monitored by inserting a thermosensor inside the flesh of an olive fruit located in the central zone of the vat.

Extraction of pectic substances

According to the procedure described in a previous work,[3] pectic fractions were sequentially and selectively extracted from alcohol-insoluble solids with distilled water, sodium hexametaphosphate and sodium hydroxide, using the opportunely adapted Dietz and Rouse[10] method. Fractions were collected and monitored for galacturonic acid by spectrophotometric determination at 525 nm using the *m*-hydroxydiphenyl colorimetric method.[11]

Firmness measurement

Firmness of the olive tissues was measured by an Effegi pressure tester on 10 uniformly sized olive fruits. The results, expressed as percentage of deformation (ratio of the decrease in the fruit pulp height to the initial height), were the means of 10 readings for each sample. Operating conditions were the same as described previously.[3]

Scanning electron microscopy

Tissue blocks (approx $3 \times 3 \times 1.5\,mm^3$ in size) of fresh and processed olive tissues were fractured to reveal the epicarp and mesocarp in longitudinal view. The fracture face was cut away from the rest of the slice and fixed by 30 g glutaraldehyde l^{-1} 0.05 M cacodylate buffer (pH 7.2) for 4 h at room temperature. The samples were washed with the same buffer, dehydrated in an alcohol series (100, 200, 300, 400, 500, 600, 700, 800, 900 and 1000 ml ethanol l^{-1} water) and critical point dried. The dry tissues were then mounted, fracture surface upwards, onto aluminium stubs using silver conducting paint and coated with gold (25 nm thick) in a sputter coater. Representative specimens were examined with a Philips XL 20 scanning electron microscope and photographed.

RESULTS AND DISCUSSION

The time–temperature profile of olive fruits during heat treatment is presented in Fig 2. The temperature

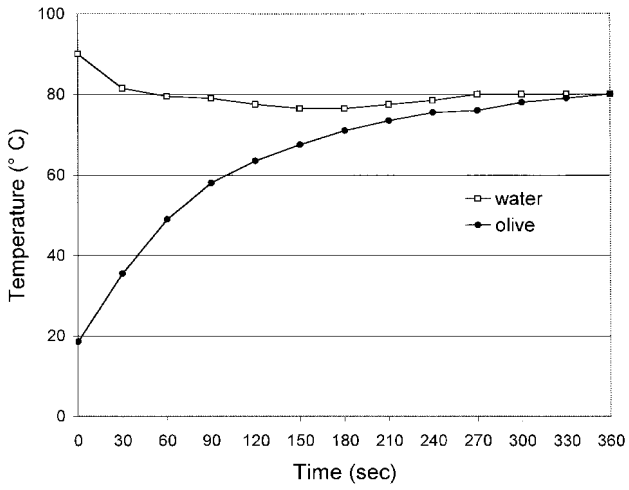

Figure 2. Time–temperature profile of olive fruits during heating.

profile indicated that the olive fruit temperature progressively increased and equilibrated with the water temperature after approximately 3–4 min of heating. The duration of heat treatment was 6 min, but the olives suffered a temperature higher than 70 °C for 3 min.

Moisture content remained practically stable during the heating and salting steps, but decreased slightly (−3%) in olive tissues after the drying process. Longer drying times are needed to obtain partially shrivelled olive fruits, because epicuticular waxes, composed of a complex mixture of long-chain apolar compounds,[12] are present on the fruit surface as an amorphous film, on which crystalline structures may be dispersed (Figs 3A and 3B), acting as a sort of physical barrier to the loss of water from the fruit. The morphology of these crystalline structures depends on their chemical composition,[13] varying with cultivar and ontogeny of the plant and also according to climatic conditions.

During heating, most of the waxy material remained *in situ* (Figs 3C and 3D), but some changes in the nature of the waxes occurred and a continuous varnish-like covering of oxidised waxy substances caused by air exposure was formed on the cuticle. Oven-dried olives presented a different wax mass picture that evidenced some prominent filamentous and curved wax structures projecting from the epidermis (Figs 3E and 3F).

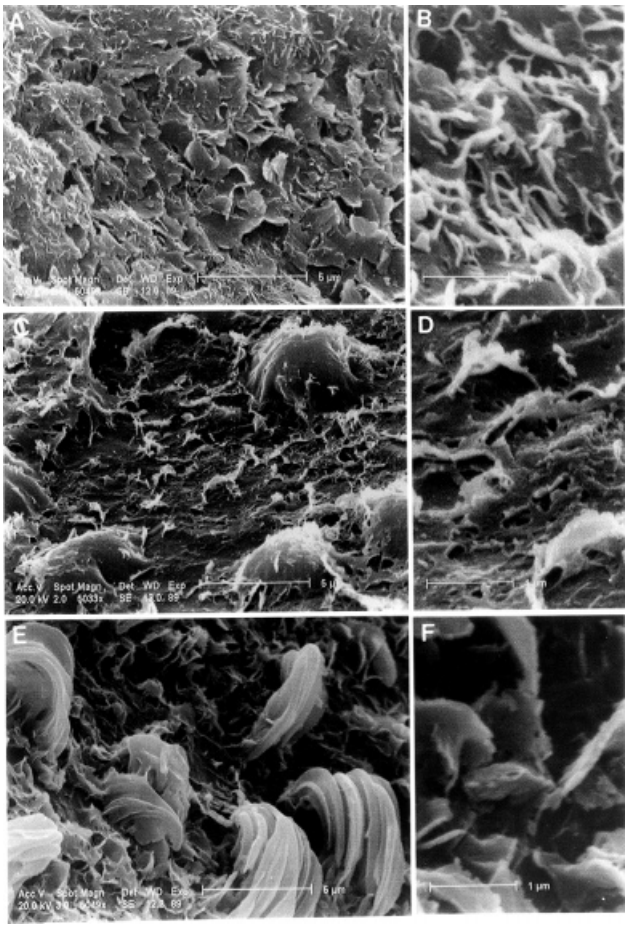

Figure 3. SEM images of (A, B) fresh olives, (C, D) heated olives and (E, F) oven-dried olives. (A, C, E) Surface of olive fruit showing epicuticular wax covering. (B, D, F) Epicuticular wax details.

Furthermore, fresh olive tissues revealed uniform and tightly thin-walled parenchyma cells, since pectic substances between as well as within the matrices of adjacent cell walls form a middle lamella which contains more of the insoluble pectins (or protopectins) mainly responsible for adhesion between cells and firm texture (Figs 4A–4C). Heat treatment caused gross changes in the parenchyma tissue structure of the fruit (Fig 4D) as a result of changes in the chemical constitution of the middle lamella which affected its adhesive properties,[14,15] thus permitting cell separation to occur (Figs 4E and 4F). Examination of fracture surfaces showed that most cells remained intact, suggesting that tissue failure occurred by cell-to-cell debonding and that the resulting decrease in firmness of olive fruit was related to the formation of soluble pectins. Oven-dried olive tissues clearly showed cell wall disruption[16] and the presence of some cavities (Figs 4G–4I), explained as a gelation process of the network of cellulose microfibrils, hemicelluloses and polysaccharides based on pectins.[17]

Quantifications of the microscopic observations are given by chemical characterisation of the pectic substances isolated from fresh and oven-dried olive tissues at each processing step (Fig 5). Fresh samples presented a total pectin content of 1.16 g kg^{-1} (on a dry weight basis), of which the sodium hydroxide fraction (protopectins) corresponded to 52%. The pectin fraction extracted by sodium hexametaphosphate (pectates) corresponded to 37% of the total pectins, while the water-soluble pectins were present in small concentrations.

During heating, total pectins decreased to 0.749 g kg^{-1} (−36%), of which protopectins and pectates corresponded to 27% and 65% respectively. Total pectin content remained stable during the salting step, but the protopectins increased and, in parallel, the pectates decreased. In oven-dried olive tissues, total pectins increased to 1.92 g kg^{-1}, of which protopectins and pectates corresponded to 65% and 32% respectively. Therefore many changes took place in pectin fractions during processing due to the changes in their solubility characteristics.[18]

Correlated with the hydrolysis of protopectin to form pectin was an increase in softening of the olive tissues (Fig 6). Data evidenced a general correspondence of firmness with pectin content at various processing steps. Heat treatment induced firmness loss in comparison with fresh samples, while during salting, firmness increased slightly. The oven-drying step brought about further firming of the tissues.

A high correlation coefficient between firmness and protopectins ($r = -0.959$; $P < 0.05$) was found, while pectin water fraction and pectates were not correlated (Fig 7). Therefore a decrease both in total pectin and in the size of the pectin fractions plays an important

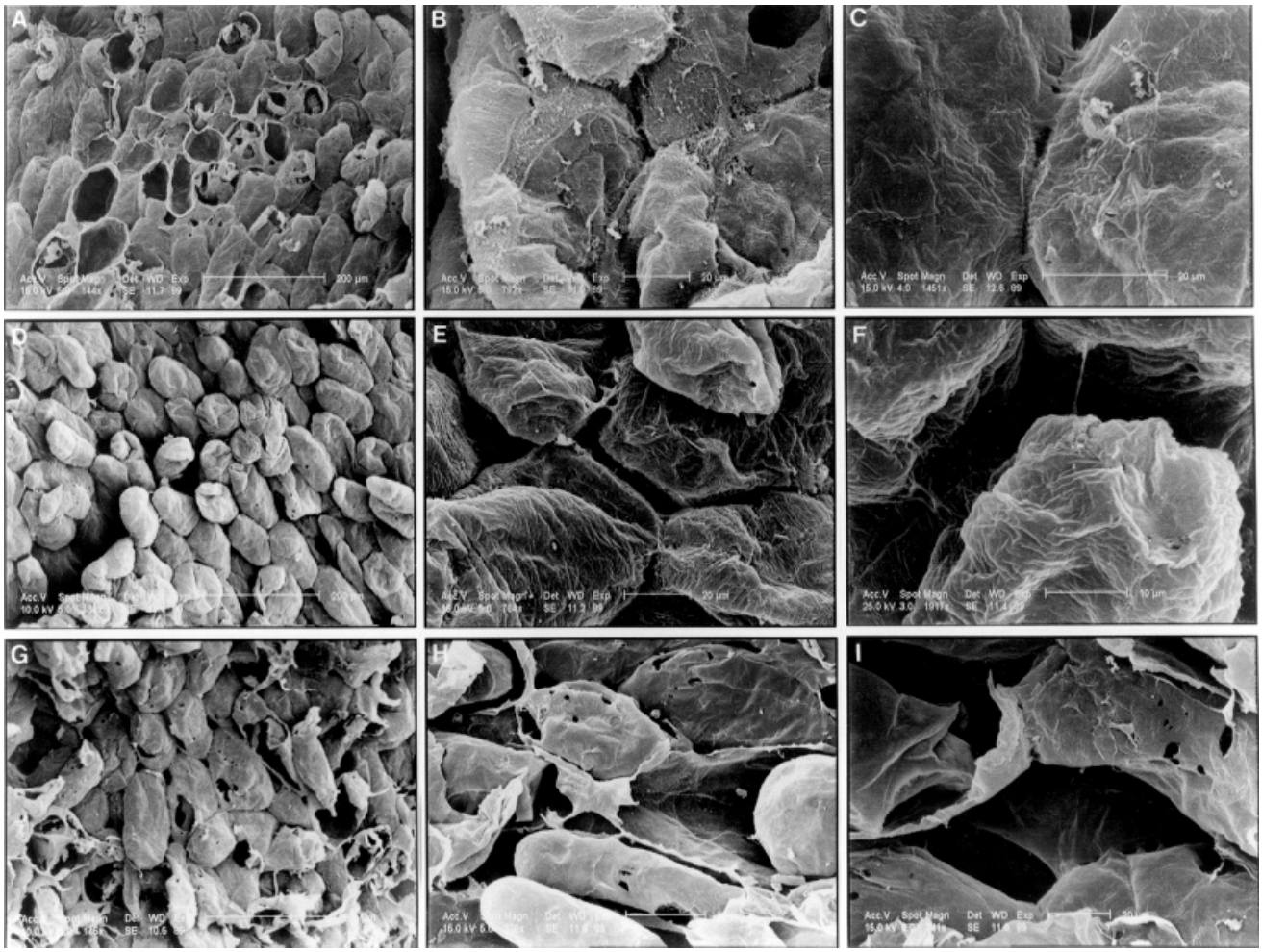

Figure 4. (A, B, C) SEM images of fresh olives. (A) Overview, showing tissues fracturing through the cells. (B, C) Details of parenchyma cells tightly packed (cell adhesion). (D, E, F) SEM images of heated olives. (D) Overview, showing tissues fracturing along the middle lamellae. (E, F) Details of the parenchyma, showing the dissolution of pectopolysaccharides (cell separation). (G, H, I) SEM images of oven-dried olives. (G) Overview, showing tissues damaged. (H, I) Details of the parenchyma, showing the dissolution of pectocellulosic walls (cell disruption).

role in the softening of the fruits during the heating step.

It is well known that pectolytic enzymes occur in vegetable and fruit tissues and are concerned with pectin changes.[19,20] As shown in Fig 8A, enzymatic degradation of α-1,4 linkages can occur in pectin by de-esterification and depolymerisation processes catalysed by the combined action of pectinmethylesterase (PME; EC 3.1.1.11) and polygalacturonase (PG; EC 3.2.1.15).[21,22] PME removes methyl groups from the cell wall pectin, which can then be depolymerised by PG, reducing intercellular adhesiveness and tissue rigidity. A *trans*-elimination reaction, recognised as *β*-elimination catalysed by several cations and anions, can occur in plant tissues, forming methylgalacturonides with unsaturated bonds between carbon atoms 4 and 5 in the glycosidic residue of the galacturonic acid molecule (Fig 8B). The latter special type of pectin depolymerisation takes place under alkaline or neutral conditions; however, it has been used to explain the degradation of heated plant pectin under pH (5.0–6.5) conditions found in most processed vegetables.[23–28] Bearing in mind the weakly acidic pH around 5.5 of the olive tissue, the resulting decrease in firmness of olive fruits, blanched by high temperatures affecting the enzyme activities, may be mainly related

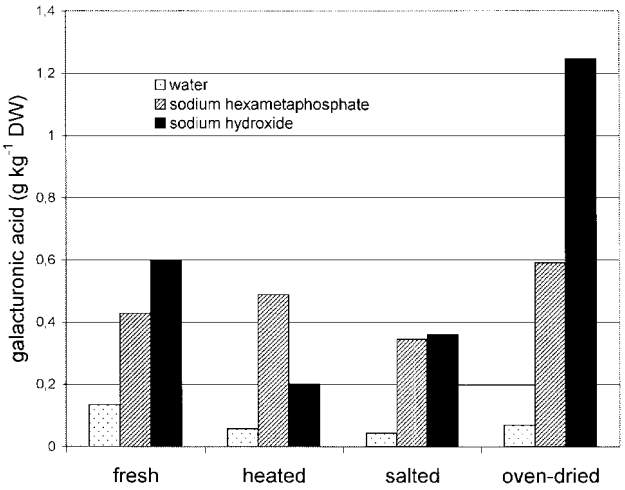

Figure 5. Pectin fractions content (as galacturonic acid) of olive tissues at various processing steps.

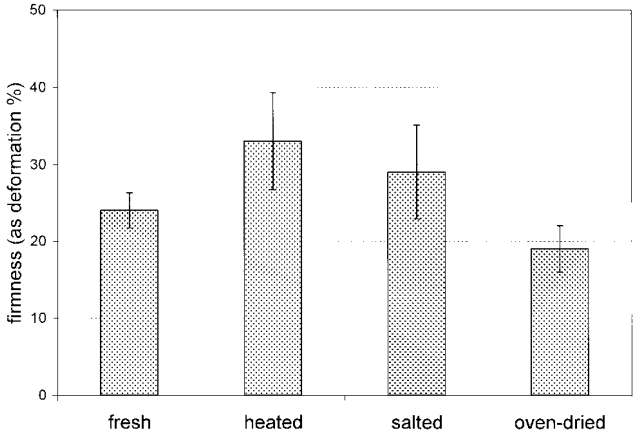

Figure 6. Firmness of olive tissues at various processing steps.

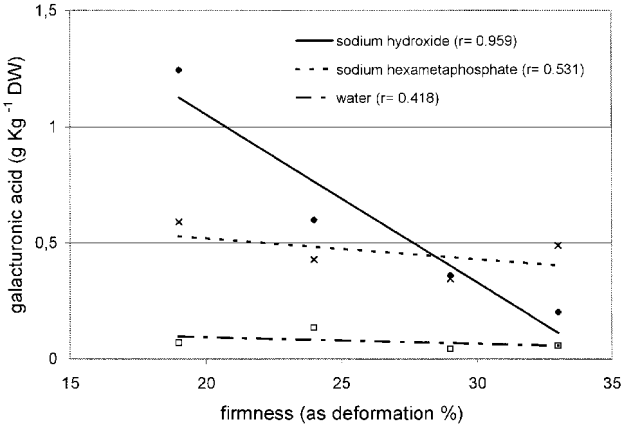

Figure 7. Relationships between firmness and pectin fractions of olive tissues (means and standard deviations for $n = 10$).

to the β-elimination degradation of methylated pectins. Under the mild heating temperature of our experiments the heat-activated PME system was primarily responsible for the pectin degradation. Heat treatment affects the selective permeability in the plasma membrane of the fruit, giving rise to diffusion of cations, probably Ca^{2+}, to the cell wall. The increased number of cations will activate PME isoforms, increasing de-esterification and promoting the formation of divalent bridges between residues of galacturonic acid belonging to adjacent pectic chains (Fig 8C). The divalent ion–pectin complex thus formed acts as an intercellular cement to lend firmness to olive tissues during oven dehydration.[29] Therefore the firmness in heated olive tissues can be influenced not only by heating times and temperatures, but also by the hardness of the water boiling, and addition of Ca^{2+} should result in toughening of olive fruits due to Ca^{2+} interaction with cell wall pectin.

However, more research is necessary for a lucid interpretation and clarification of the role of pectin and its changes in olive tissue texture. Moreover, processing conditions to obtain oven-dried table olives need to be better defined to minimise undesirable compositional changes in the fruit. These conditions should be determined separately for different olive cultivars and for different lots of olives.

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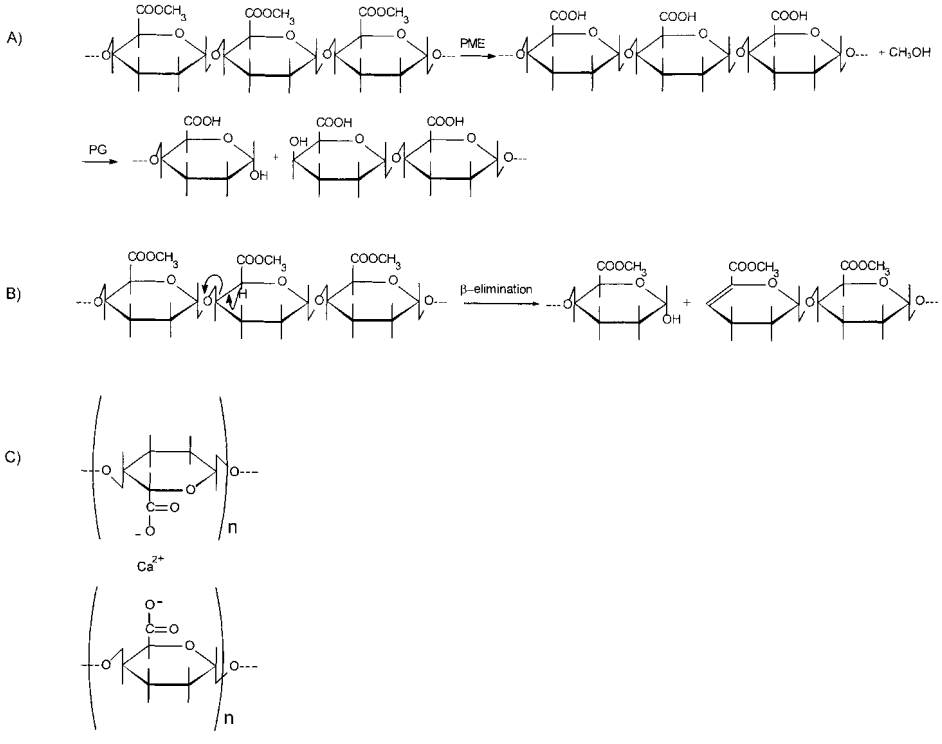

Figure 8. (A, B) Degradation pathways of plant pectin and (C) Ca^{2+} bridging between residues of galacturonic acid of adjacent pectic chains.

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