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THE EFFECT OF DELACTOSED WHEY PERMEATE ON PHYTOCHEMICAL CONTENT OF CANNED TOMATOES

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ABSTRACT:

The effect of delactosed whey permeate (DWP) treatment on antioxidant and phyto-chemical components of canned Irish plum tomatoes were investigated. Tomatoes were sterilized for 5 min (F_0) at 120 °C and stored for 6 months. The DWP treatment retained significantly ($p<0.05$) higher levels of ascorbic acid and lycopene of tomatoes. The antioxidant activity of DWP treated tomatoes was higher (7 %) than the control at the end of storage. The firmness in DWP-treated fruits was around 40 % higher than that in control. All the parameters decreased significantly ($p<0.05$) during storage except lycopene and total phenols. Lycopene content showed no significant change and total phenols increased during storage. The changes in ascorbic acid, antioxidant activity and texture were fitted well to Weibull kinetic models with high coefficients of determination (R^2) and low RMSEC (root mean sum of squared error). The results clearly indicate that DWP enhanced the retention of antioxidant compounds in tomatoes during storage.

Key words: Delactosed whey permeate; canned tomato; processing; antioxidants; Weibull.

1. Introduction

Food canning has been one classical way to provide a continuous supply of food independently of the seasonal availability of raw materials. Acidification and thermal treatment are two widely used methods in preservation of canned fruits and vegetables. Canning processes extend the shelf life of the products and make it safe for human consumption by destroying the pathogenic microorganisms. The sterilization of the canned food is usually carried out by steam heating to a temperature sufficient to kill the microorganisms. However, thermal processing of food is often considered to cause losses of micronutrients (Seybold, Fröhlich, Bitsch, Otto & Böhm, 2004). Optimum thermal sterilization of food always requires a compromise between the beneficial and destructive influences of heat on the food. On the positive side, heat destroys microbial pathogens, spoilage organisms and endogenous and introduced enzymes that would otherwise render the food inedible or unsafe. At the same time, concentrations of heat-labile vitamins, particularly thiamine, vitamin C and folate are reduced. In many foods, organoleptic quality is reduced by the heat of the sterilization process. The texture of canned vegetables is often softer than desired (Durance, 1997). Both physical and chemical changes occur during processing and, to a lesser extent, during storage, and it is these that determine the product quality in terms of its sensory properties and nutrient content. These physicochemical changes are influenced by the time and temperature of the process, the composition and properties of the food, the canning medium, and the conditions of storage (Patras, Brunton, Pieve, Butler & Downey, 2009).

Tomato (*Lycopersicon esculentum* Mill.) is a versatile vegetable that is consumed fresh as well as in the form of processed products with more than 65 % of the world tomato production being processed. It is considered as an important source of dietary antioxidants as it is rich in vitamins, carotenoids and phenolic compounds (Toor & Savage, 2005). Results from epidemiological studies have shown that high consumption of tomato fruit is

consistently correlated with a reduced risk of chronic diseases such as cardiovascular disease and certain types of cancer (Sgherri, Kadlecova, Pardossi, Navari-Izzo & Izzo, 2008). The increase in the consumers' awareness of the health benefits of tomatoes is leading to an increase of tomato consumption. Retention of the quality and shelf-life of fresh tomato and processed tomato products is now the interest of the industry and consumers.

Whey permeate is a by-product of the production of whey protein concentrate from cheese whey. The main components of whey permeate are water, lactose, peptides and minerals. Whey and whey permeate have been proposed to be used as a natural antioxidant in foods (Contreras, Hernández-Ledesma, Amigo, Martín-Álvarez & Recio, 2011). Enzyme-hydrolysed whey protein is widely used as a bioactive and nutritional ingredient in health and food products (Marshall, 2004). Previous studies have shown that whey protein hydrolysates contain a broad range of antioxidant activity in an iron-catalysed liposome oxidation system (Peña-Ramos & Xiong, 2003) or a copper-catalysed liposome emulsion (Colbert & Decker, 1991), depending on the proteases used. Whey hydrolysates applied to cooked meat pork patties could suppress lipid oxidation (Peña-Ramos & Xiong, 2003). Acidic whey permeate was successfully used for decontamination of fresh-cut lettuce and carrots during storage (Martin-Diana, Rico, Frias, Mulcahy, Henehan & Barry-Ryan, 2006). Delactosed whey permeate could enhance the antioxidant activity of the fresh-cut tomato while retaining the antioxidant components of tomatoes during storage (Ahmed, Martin-Diana, Rico & Barry-Ryan, 2011a, b, c, d).

Kinetic models are often used for an objective, fast and economic assessment of food safety and food quality. Kinetic modelling may also be employed to predict the influence of processing on critical quality parameters. Weibull distribution function has an interesting potential for describing microbial, enzymatic and chemical degradation kinetics (Cunha et al., 1998). Traditionally, the degradation of nutrients in foods during their thermal processing and

storage has been described in terms of zero, first or higher order kinetics (Taoukis et al., 1997). However, Weibull model is extremely flexible owning to the inclusion of a shape constant in addition to the rate constant.

Therefore the objective of this study was to investigate the efficacy of delactosed whey permeate treatment on retention of the phytochemical contents of canned tomatoes during storage and to model the changes in antioxidant activity, phenols, ascorbic acid, lycopene, texture and colour parameters.

2. Materials and Methods

2.1. Sampling

Irish vine ripened plum tomatoes (*Lycopersicon esculentum* L. Mill.) cv. Moneymaker were purchased from a local grower. According to the grower, the tomato plants were grown commercially in a greenhouse with a 14 h light period from February until November. The aerial environment of the greenhouse, crop irrigation and nutrition were precisely controlled. The temperature of the greenhouse was 16 - 21 °C which is optimum for lycopene synthesis in tomato fruits. The tomatoes were then brought to the food processing laboratory and stored at 4 °C before processing. The experiments were carried out between June to November 2010.

2.2. Preparation of treatment solution

Liquid delactosed whey permeate (DWP) was supplied by Glanbia Ingredients Ltd., Kilkenny, Ireland. DWP was obtained after removal of lactose crystals from cheese whey permeate. In this experiment DWP was used at 3 % (v/v) concentration as optimised in a previous research (Ahmed, Martin-Diana, Rico & Barry-Ryan, 2011b). The solution was prepared using distilled water stored at room temperature. The main components of DWP were given in Table 1.

2.3. Preparation of Tomato samples for processing

Whole tomatoes were rinsed in tap water prior to washing in order to avoid soil contamination. In order to facilitate packing and eliminate dissolved gases within the tissues, the tomatoes were water-blanched for 1 min at 100 °C in a steam-jacketed kettle and then quickly cooled in ice cold water to peel the skin. Approximately 200 g tomatoes were added to each can (75 × 110 mm, WEI/WEISS03, Germany). The tomatoes were topped with 100 ml solution (3 % DWP + 0.5 % NaCl + 0.25 % citric acid) with 6 –10 % headspace at room temperature. The control treatment was 0.5 % NaCl + 0.25 % citric acid.

2.4. Canning Experiment

The prepared cans were loaded into a pilot scale retort (Barriquand Steriflow, Roanne, France). Sample core temperature profiles and F_0 values were recorded during the process, using an Ellab E-Val TM TM9608 data module (Ellab [UK] Ltd., Norfolk, England) connected to a laptop. A standard Ellab SSA-12080-G700-TS temperature probe was inserted through an Ellab GKM-13009-C020 packing gland (20 mm) into a tomato placed in a can to record the cook cycle. Temperature was monitored every 10 s. The samples were heated to achieve a process equivalent to 121 °C for 5 min at the end of the cook-cool cycle and samples were stored for 6 months at room temperature. Prior to any canning experiment, all Ellab unit probes were calibrated against a JOFRA (ATC-155B) calibration unit at temperatures of 121 °C and the result associated with the calibration did not exceed ± 0.1 °C.

2.4. Biomarkers Analysis of Canned Tomatoes

Ascorbic acid, lycopene, total phenols, antioxidant activity (as measured by DPPH and FRAP), texture and colour parameters of canned tomatoes were monitored over 6 months stored at room temperature.

2.4.1. Ascorbic acid

Ascorbic acid in tomatoes was analysed by HPLC with a slight modification of the method described by Lee and Castle (2001). A tomato sample (1.25 g freeze-dried powder) was weighed and 25 ml of 6 % metaphosphoric acid (pH 3.0) was added to it. The sample was then homogenized for 1 min at 24,000 rpm using an Ultra-Turrax T-25 Tissue homogenizer (USA). Then the sample was shaken with a Gyratory Shaker G-2 (USA) for 2 hrs at 150 rpm and centrifuged for 15 min at 3,000 ×g at 4 °C (Sanio MSE Mistral 3000ii, UK). Following centrifugation, 10 ml of the supernatant was filtered through PTFE syringe filters (pore size 0.45 µm, Phenomenex, UK) and stored at - 20 ºC in foil covered plastic test tubes for further analysis by HPLC. The analysis of ascorbic acid content was performed with Waters 600 Satellite HPLC, with a reversed phase analytical 5 µm particle diameter, polymeric C_{18} column (150 × 4.6 mm, 5 µm) (Waters, Dublin, Ireland) with a UV-tuneable absorbance detector (Waters 486) at 230 nm. Ten µl of the tomato sample was injected. An isocratic mobile phase of 25 mM monobasic potassium phosphate (pH 3.0) with a flow rate of 1.0 ml / min was used. Five concentrations of ascorbic acid standard in 6 % metaphosphoric acid in the range 10 - 50 µg / ml were injected and peak area and height were determined.

2.4.2. Lycopene

A tomato sample (1.25 g freeze-dried powder) was weighed and transferred into a 100 ml beaker (wrapped with aluminium foil). A 50-ml volume of hexane-acetone-ethanol solution (2:1:1 v/v/v) containing 2.5 % BHT was added to solubilise the lycopene (Shi & Le Maguer, 2000). Following this the samples were homogenized with an Ultra-Turrax T-25 tissue homogenizer for 1 min at 20,500 rpm. The samples were then shaken with a Gyrotory Shaker G-2 (USA) for 2 hrs at 150 rpm followed by 10 ml of distilled water was added and stirred for additional 10 min. The polar and non-polar layers were separated, and the upper hexane layer was collected and filtered through a 0.45 µm PVDF membrane filter. It was transferred to a new 15 ml aluminium wrapped test tubes and kept at - 80 °C till analysis. The analysis of

lycopene was performed with Waters 600 Satellite HPLC, with a reversed phase analytical 5 μm particle diameter, polymeric C_{18} column (150×4.6 mm, 5 μm) (Waters, Ireland) with a UV tuneable absorbance detector (Waters 486) at 475 nm. An isocratic mobile phase of methyl t-butyl ether/methanol/ethyl acetate (40:50:10, v/v) with a flow rate of 1 ml/min was used. The column temperature and mobile phase was maintained at 25 ºC. Analyses were performed under dim light to prevent sample degradation by photo-oxidation. Three concentrations of lycopene standard in the range 0.01 - 0.03 mg / ml were injected and peak area and peak height were determined.

2.4.3. Total phenols

For extraction, 25 ml of methanol was added to 1.25 g freeze-dried powder and homogenized in a 50 ml tube with an Ultra-Turrax T-25 tissue homogenizer for 1 min at 24,000 rpm. The samples were then thoroughly mixed with a vortex mixer (V400 Multituve Vortexer, Alpha laboratories) for 2 hrs at 150 rpm. Then they were centrifuged for 15 min at 3,000 ×g using a Sanyo MSE Mistral 3000i, UK. Following centrifugation, 10 ml samples of the supernatant were filtered through PTFE syringe filters (pore size 0.45μm, Phenomenex, UK). The extracts were then stored at -20 °C in foil covered plastic test tubes for further analysis. Total phenol content of tomatoes was determined using the Folin-Ciocalteu method (Singleton, Orthofer & Lamuela-Raventos, 1999). In a 1.5 ml Eppendorf tube, 100 μl of appropriately diluted methanolic extract, 100 μl of MeOH and 100 μl of FC reagent were added and vortexed. After exactly 1 min, 700 μl of sodium carbonate (20 %) was added, and the mixture was vortexed and allowed to stand at room temperature in the dark for 20 min. Then the tubes were centrifuged at 12,720 ×g for 3 min. The absorbance of the supernatant was read at 735 nm in 1 ml plastic cuvettes. Each sample of the three batches was measured in triplicate. Results were expressed as mg/L gallic acid equivalents (GAE).

2.4.4. Antioxidant activity test

2.4.4.1. 2, 2-Diphenyl-l-picrylhydrazyl radical scavenging capacity assay (DPPH)

DPPH scavenging activity assay was performed as per the method described by Sanchez-Moreno (2002) with a slight modification. The extraction was done as per the phenol content of tomato (section 2.4.3). For DPPH assay, In a 1.5-ml Eppendorf tube 500 µl of appropriately diluted methanolic extract and 500 µl DPPH Reagent were added and vortexed. After that they were kept for 30 min in dark. The absorbance of the supernatant was read at 515 nm in 1 ml plastic cuvettes. Each sample of the three batches was measured in triplicate.

2.4.4.2. Ferric ion reducing antioxidant power assay (FRAP)

The FRAP assay was carried out as described by Stratil, Klejdus and Kuban (2006) with a slight modification. The extraction was done as per the phenol content of tomato (section 2.4.3). The FRAP reagent was prepared by mixing 38 mM sodium acetate (anhydrous) in distilled water (pH 3.6), 20 mM $FeCl_3.6H_2O$ in distilled water and 10 mM 2,4,6-tri(2-pyridyl)-s-triazine (TPTZ) in 40 mM HCl in proportions of 10:1:1. This reagent was freshly prepared before each experiment. In a 1.5 ml Eppendorf tube 100 µl of appropriately diluted methanolic extract and 900 µl FRAP Reagent were added and vortexed. After that they were kept for 40 min in the heating blocks at 37 °C, covered with aluminium foil. The absorbance of the supernatant was read at 593 nm in 1 ml plastic cuvettes. Each sample of the three batches was measured in triplicate.

2.4.5. Firmness

Firmness was measured using an Instron texture analyser (Instron 4302 Universal Testing Machine, Canton MA, USA), with a 3.5 mm diameter flat faced cylindrical probe. The maximum force (N) necessary to cause a deformation of 3 mm with a speed of 0.2 mm/s was

recorded. The puncture test was performed on the equatorial zone of each fruit. Data were analyzed with the Instron series IX software for Windows.

2.4.6. Colour

Colour was quantified using a Colour Quest XE colorimeter (HunterLab, Northants, UK). Tomatoes were placed directly on the colorimeter sensor (3.5 cm of diameter) and measured (Ahmed et al., 2011b). 20 – 30 measurements were taken per treatment and day. The L* parameter (lightness index scale) range from 0 (black) to 100 (white). The a* parameter measures the degree of red (+a*) or green (-a*) colour and the b* parameter measures the degree of yellow (+b*) or blue (-b*) colour. The CIE L* a* b* parameters were converted to Hue (arctan b*/a*) and Chroma $(a^{*2}+b^{*2})^{1/2}$.

2.4.7. Sensory analysis

Sensory analysis was performed for canned tomato samples over 6 months of storage time by a panel with an age range of 25 – 40 years. Colour, texture, aroma and general acceptability of samples were scored on a scale of 1 to 9, where a score of one indicated a product of very poor quality, etc (Ferreira, Pinho, Amaral & Martins, 2008). The evaluation was carried out in the sensory evaluation laboratory. Products were coded using random numbers to avoid bias. Products were placed in plastic cups with lid, on a white surface and judges were isolated from each-other in a booth in an odour-free environment. The sensory analysis was monitored with Compusense Five software (Release 4.4, Ontario, Canada).

2.4.8. Statistical Analysis

Data were analysed by multivariate analysis of variance (MANOVA) using Statgraphics software (version: Centurium XV; Statistical Graphics Co., Rockville, USA) for different treatments. Analysis of variance one-way (ANOVA) was used to analyse each treatment over storage. In the case of significant differences the LSD range test ($p<0.05$) was used. Data are

presented as means ± standard deviation of 3 replicates of three batches. Relative changes in AA, DPPH, FRAP and texture were described using Weibull model (Equation 1). The Weibull model represents the distribution of the breaking strength of materials and later to describe the behavior of systems or events that have some degree of variability. It is flexible owing to the inclusion of a shape constant in addition to the rate constant and has been employed to describe microbial, enzymatic and chemical degradation kinetics (Manso, Oliveira, Oliveira & Frías, 2001; Cunha, Oliveira & Oliveira, 1998).

$$C_t = C_0 \times e^{-(Kt)^{\beta}} \quad \text{Equation 1}$$

where Ct is AA, DPPH, FRAP and texture values at time t, C_0 is the initial AA, DPPH, FRAP and texture values, K is the rate constant ($month^{-1}$) and β (dimensionless) is the shape constant. Modelling and analysis of variance was performed using SAS Statistical software (SAS Version 9.1, SAS Institute, Cary, NC). The goodness of fit was assessed by regression coefficient of determination along with an analysis of residuals. The fitting ability of the tested models was also evaluated by calculating the root mean squared error (RMSE) (Equation 2) (Neter, Wasserman & Whitmore, 1992).

$$\text{RMSE} = \sqrt{\sum_{i=1}^{n_t} \frac{(y_{expi} - y_{pre})^2}{n_t - n_p}} \quad \text{Equation 2}$$

where y_{expi} are experimental observations, y_{pre} are model predictions, n_t are number of data points and n_p are number of estimated model parameters.

3. Results and Discussion

3.1.1. Ascorbic Acid

The initial content of ascorbic acid in canned tomatoes was found to be 135 -145 mg/100 g DW, which is in the range of those reported elsewhere (Patras et al., 2009). Ascorbic acid is

256 strongly affected by the various processing techniques. However, significantly ($p<0.05$)
257 higher levels of ascorbic acid was found in DWP treated samples compared to control
258 samples (NaCl +Citric acid) throughout the storage (Table 2). DWP could have prevented the
259 thermal degradation of ascorbic acid during canning by inhibiting oxidation as well as
260 forming protective layer on the tissue surface. This was accounted for the higher ascorbic
261 acid values of the DWP treated samples before the storage, ie., immediately after canning
262 than control. This was maintained throughout the storage although storage had deteriorating
263 effect on all samples. There was a significant ($p<0.05$) decrease in ascorbic acid content in
264 canned tomato over storage. In control samples the decrease was higher (~30 %) than DWP
265 treated samples (~22 %) after 6 months of storage. Tomato is a significant dietary source of
266 ascorbic acid and its retention is important for tomato products. The decreasing trend of
267 ascorbic acid was in accordance with the findings of other authors (Lavelli & Giovanelli,
268 2003; Ordonez-Santos, Vázquez-Odériz, Arbones-Maciñeira & Romero-Rodríguez, 2009).
269 The possible reason for the reduction of total ascorbic acid could be autoxidation or oxidation
270 by pro-oxidants generated from other compounds during storage. Oxidation of ascorbic acid
271 to dehydroascorbic acid is followed by hydrolysis of the latter to 2,3-diketogulonic acid,
272 which then undergoes polymerization to other nutritionally inactive products (Dewanto,
273 Adom & Liu, 2002).

274 *3.1.2. Lycopene*

275 Lycopene content of canned tomato was analyzed during 6 months of storage after treatments
276 with DWP. The initial average amount of lycopene in the samples was 117 mg/100 g DW.
277 The DWP treatment showed significant effect ($p>0.05$) on the lycopene concentration of the
278 samples (Table 2). DWP treatment might have prevented the high temperature induced
279 oxidation of lycopene during canning. Therefore, the samples treated with DWP showed
280 higher lycopene content than the control. In contrast, lycopene content of the samples did not

281 show significant ($p<0.05$) increase or decrease during storage. Tamburini, Sandei, Aldini &
282 Leoni (1999) and Ordonez-Santos et al. (2009) similarly found no significant change in
283 lycopene of tomato puree during 1-year storage and 6-month storage, respectively. It is well
284 know that lycopene in tomato is relatively resistant to thermal degradation, whereas other
285 antioxidants (ascorbic acid, amino acids and β-carotene degrade more rapidly during
286 processing and storage (Abushita, Daood & Biacs, 2000). Dewanto et al. (2002) reported
287 thermal processing increased the extractable lycopene content in processed products when
288 compared to fresh tomatoes. This is probably because lycopene is mostly attached to the skin
289 and insoluble fibre portion of tomatoes (Toor & Savage, 2005).

290 *3.1.3. Total phenols*

291 The initial concentration of total phenols in samples was approx 290-305 mg GAE/100 g DW
292 (dry weight) (Table 2). Phenolic contents reported here were within the range of those
293 reported elsewhere (Lavelli & Giovanelli, 2003; Patras et al., 2009). In the present study total
294 phenol content of the DWP treated tomatoes was significantly ($p<0.05$) higher than the
295 control samples throughout storage. DWP was reactive to FCR and therefore had total phenol
296 value although DWP did not contain any phenolic compound. This could be the reason for
297 the higher total phenolic content in the DWP treated samples than other samples. Total
298 phenol content of tomatoes increased in all samples over 6 months of storage. Lavelli and
299 Giovanelli (2003) suggested that the increased total phenol concentrations of canned tomato
300 products may be due to hydrolysis processes. Lavelli, Hippeli, Peri & Elstner (1999)
301 explained that there could be two reasons for this phenomenon: (1) the release of free
302 hydroxyl groups through hydrolysis of flavonoid glycosides, and (2) the release of phenols by
303 cell walls. The degradation of the cell-wall polysaccharide structures favour the phenol
304 release from skins, notably those phenols that are linked to the cellwall (Pinelo, Arnous &
305 Meyer, 2006).

3.1.4. Antioxidant activity test

3.1.4.1. 2, 2-Diphenyl-1-picrylhydrazyl radical scavenging activity assay (DPPH)

The global antioxidant activity as measured by DPPH radical scavenging activity differed significantly ($p<0.05$) between treatments (Table 2). The DWP treated tomato samples showed significantly ($p<0.05$) higher DPPH reduction than the control samples. The higher antioxidant activity of DWP treated samples could be associated with the intrinsic antioxidant activity of DWP (Ahmed et al., 2011a). DWP might have also helped to retain the antioxidant activity of tomatoes. These results could be related to the total phenolic content of the samples since the samples containing higher phenolic content exhibited stronger DPPH reduction and vice versa. Overall, the antioxidant activity of canned tomatoes deceased with storage time irrespective of the treatments. The average reduction of antioxidant activity of the canned tomatoes was 18 % during 6 months of storage.

3.1.4.2. Ferric ion reducing antioxidant power assay (FRAP)

Ferric ion reducing antioxidant power (FRAP) is one of the most commonly used antioxidant activity assay (Stratil, Klejdus & Kuban, 2006). DWP treated samples retained significantly ($p<0.05$) better antioxidant activity as measured by FRAP than control samples (Table 2). FRAP value of canned tomatoes decreased during storage in all three samples. This result was in agreement with the finding of Lavelli and Giovanelli (2003). In control (NaCl + citric acid) samples the decrease was higher (~18 %) than DWP treated samples (~11 %) after 6 months of storage. The FRAP values of the tomato sample followed the same trend as DPPH values in the current study. The reduction of antioxidant activity of samples during storage could be attributed to the degradation of ascorbic acid which is one of the main antioxidants in tomato.

3.1.5. Firmness

330 Firmness is the most relevant property in quality characterization of the tomatoes processed
331 in the canning industry, in particular, of canned whole tomatoes. It is related to ripeness rate
332 and the tomato susceptibility to damage during harvesting and processing (Arazuri, Jare´n,
333 Arana & Pe´rez de Ciriza, 2007). DWP treatment markedly inhibited fruit softening and
334 maintained significantly ($p<0.05$) greater firmness throughout the storage compared to the
335 control (Table 3). The firmness in DWP-treated fruits was around 40 % higher than that in
336 control fruits at the end of 6 months of storage. The presence of calcium (Ca) in DWP might
337 have contributed to maintenance of this firmness of canned tomatoes during storage (Ahmed
338 et al., 2011b). This effect of Ca can be explained by the formation of cross links between the
339 carboxyl groups of polyuronide chains found in the middle lamella of the cell wall. Ca also
340 increases cell turgor pressure and stabilizes the cell membrane (Shafiee, Taghavi & Babala,
341 2010; Martin-Diana, Rico, Frias, Barat, Henehan & Barry-Ryan, 2007). The texture of
342 canned tomatoes decreased gradually during storage.

343 *3.1.6. Colour*

344 Colour is a very important quality factor in fruit and vegetable products, since it influences
345 consumer acceptability. The colour parameters of canned tomatoes for different treatments
346 and storage time are shown in Table 3. There were significant ($p<0.05$) differences in L*, a*
347 and b* values between DWP treated and control samples. DWP treated tomatoes retained
348 brighter colour than the control. The L*, a* and b* values of the tomato samples decrease
349 regardless of the treatment during storage. This was in agreement with the findings of other
350 authors (Liu, Cao, Wang & Liao, 2010; Lana, Tijskens & Van Kooten, 2006). The decrease
351 in L* reflected the darkening of surface colour and characterized the presence of non-
352 enzymatic browning reaction during storage. The decrease in a* and b* indicated less red and
353 less yellow in canned tomato products. Hue was fairly stable but chroma decreased during
354 storage and the decrease was more prominent in control fruits.

3.1.7. Sensory analysis

Significant differences ($p<0.05$) were observed between DWP treated and control (NaCl + citric acid) canned tomato samples for colour, aroma, texture and general acceptability scores (Figure 1). DWP treated samples scored significantly higher ($p<0.05$) than the control samples. The panellists scored the aroma and colour of tomatoes treated with DWP was higher than the control samples. This was in agreement with the other physico-chemical markers of canned tomato studied. Ahmed et al. (2011d) reported that DWP treated fresh-cut tomato samples had higher acceptability than the non-treated samples. All the attributes evaluated decreased significantly ($p<0.05$) during storage for all treatments which is associated with a loss of quality. The use of whey permeate for food preservation has also been examined by Nykänen *et al.* (1998). These authors analyzed the effect of nisin-whey permeate washing solutions on total counts and sensory characteristics in rainbow trout. They found that nisin-whey treatment caused no negative effect on sensory attributes.

4. Weibull model to describe changes in texture and antioxidant composition of tomatoes during storage

The retention of texture, ascorbic acid, DPPH and FRAP values were plotted as a function of various treatments [control (NaCl + citric acid), DWP and DWP + NaCl + citric acid] and storage (Figures 2 A, B and 3 A, B). Table 4 shows the results of fitting phytochemical composition of canned tomatoes to the Weibull model distribution. The Weibull model (Eq. 1) yielded good fits to ascorbic acid, DPPH, FRAP and texture experimental data. Weibull model (Eq. 1) was adequate for describing the changes in phytochemical content of canned tomatoes (Table 3). Therefore, Weibull distribution may be suitable for predicting the changes in texture, ascorbic acid, DPPH and FRAP during storage.

Odriozola-Serrano, Soliva-Fortuny and Martín-Belloso (2009) reported that the adequacy of Weibull distribution to relate changes in anthocyanins and antioxidant capacity of fresh-cut

strawberries was consistently good in the range of studied temperatures (5–20 °C). Weibull distribution seemed to be suitable because of the high determination coefficients (R^2 adj = 0.97–0.99). The values of kinetic constants (k) and shape constants (β) of the Weibull model were obtained by fitting Eq. (1) to the experimental data. The k and β values for texture, ascorbic acid, DPPH and FRAP obtained through Weibull model were directly affected by storage and addition of NaCl + citric acid, DWP and DWP + NaCl + citric acid. For texture, values of k (0.025– 0.060 $month^{-1}$) and values for β (0.50- 0.98) are directly dependent on NaCl + citric acid, DWP and DWP + NaCl + citric acid treatments (Figure 2A). DWP exhibited better texture values than other counterparts as evidenced by kinetic parameters (Table 4).

The ascorbic acid degradation rate constants were 0.029, 0.041 & 0.047 for NaCl + citric acid, DWP and DWP + NaCl + citric acid treated tomatoes samples respectively (Figure 2B). Similarly β increased from 0.84 to 1.16. The β parameter was related to ascorbic acid degradation, the lower the β value, the faster the ascorbic acid degradation (Table 4). DPPH and FRAP degradation constants ranged 0.031- 0.045 and 0.021- 0.045 respectively for all the three treatments (Figure 3 A, B). Whereas β values ranged between from 0.93- 1.43 and 1.06- 1.27 for DPPH and FRAP respectively. The k value increased for DWP + NaCl + citric acid treated tomatoes samples during storage. The shape factor value for DPPH (Figure 3A) ($\beta<1$) indicates first order upward concavity for (NaCl + citric acid) and DWP treatments. Upward concavity ($\beta< 1$) as observed in this study indicates a decreased stability of antioxidant components during storage, whereas downward concavity ($\beta > 1$) would indicate lower degradation rates. The low RMSE values (Table 4) showed that both models gave a good fit for the experimental data analysed.

It is quite evident that that Weibull kinetic rate constants for texture, ascorbic acid, DPPH and FRAP were significantly influenced by treatments employed. It should be noted that data for

405 total phenols and lycopene did not converge and the models were not significant (data not
406 shown).

407 5. Conclusion

408 The application of DWP significantly retained the phytochemical content and maintained
409 firmness of canned tomato throughout the storage, thereby extending the shelf-life of the
410 product. The texture, ascorbic acid, lycopene and total phenol content and the antioxidant
411 activities measured by DPPH and FRAP were significantly ($p<0.05$) higher in DWP treated
412 tomato samples than the control samples during storage. Since thermal processing has an
413 adverse effect on retention of most phytochemicals, addition of natural thermo-stable
414 antioxidants like DWP is warranted in food industries. The antioxidant composition of
415 tomatoes was adequately described through a Weibull distribution. Our findings showed that
416 the model based on Weibull distribution function is likely to be a useful tool for describing
417 changes in the antioxidant properties of canned commodities. The Weibull model provided a
418 good description of the kinetics of degradation of antioxidant components in the range of
419 treatments therefore is appropriate for predictive purpose.

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Figure Legends

Figure 1. Sensory evaluation of canned Irish plum tomatoes treated with NaCl + Citric acid (▄), DWP (□), DWP+ NaCl + citric acid (▲) during the 6 months storage. Results are expressed as independent determinations from three replicate analyses (mean of three repetitions). Colour (9 = bright red, 1 = darkened); Aroma (9 = strawberry like, 1 = fermented); Texture (9 = very crispy, 1 = soft); General acceptability (9 = excellent, 1 = poor).

Figure 2. Changes in texture (A) and ascorbic acid (B) of canned Irish plum tomatoes treated with NaCl + Citric acid (▄), DWP (□), DWP+ NaCl + citric acid (▲) during the 6 months storage as modeled by Weibull approach. Results are expressed as independent determinations from three replicate analyses (mean of three repetitions). Plotted lines correspond to the values estimated from the Weibull model from three replicate analyses.

Figure 3. Changes in antioxidant activity - DPPH (A) and FRAP (B) of canned Irish plum tomatoes treated with NaCl + Citric acid (▄), DWP (□), DWP+ NaCl + citric acid (▲) during the 6 months storage as modeled by Weibull approach. Results are expressed as independent determinations from three replicate analyses (mean of three repetitions). Plotted lines correspond to the values estimated from the Weibull model from three replicate analyses.

Figure 1.

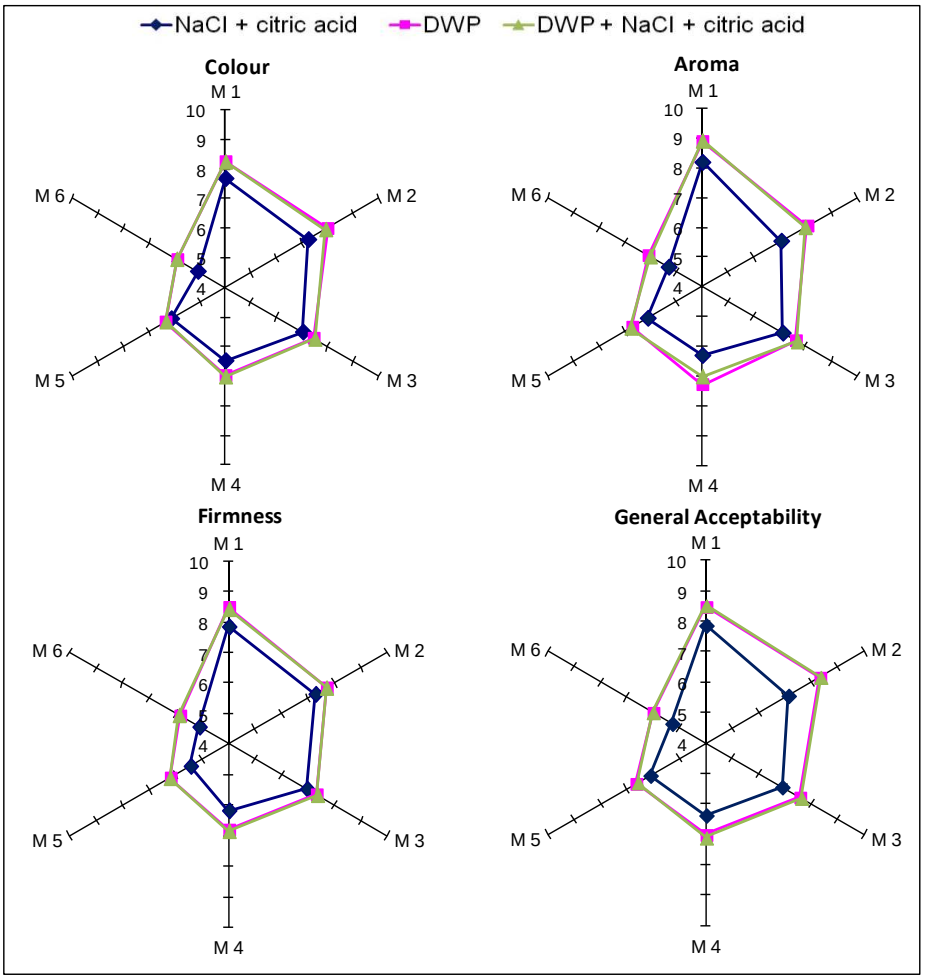
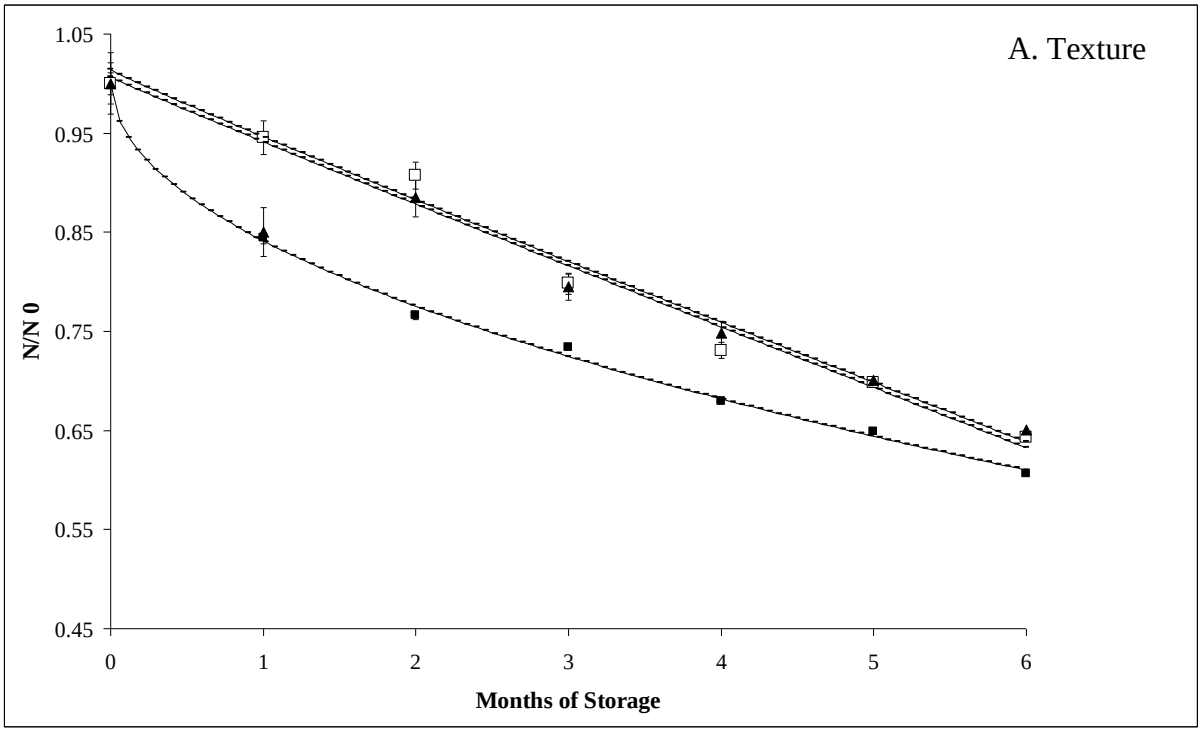

NaCl + citric acid
DWP
DWP + NaCl + citric acid
Colour
Aroma
Firmness
General Acceptability
M 1
M 2
M 3
M 4
M 5
M 6
10
9
8
7
6
5
4

Figure 2


A. Texture
1.05
0.95
0.85
0.75
0.65
0.55
0.45
N/N 0
0
1
2
3
4
5
6
Months of Storage

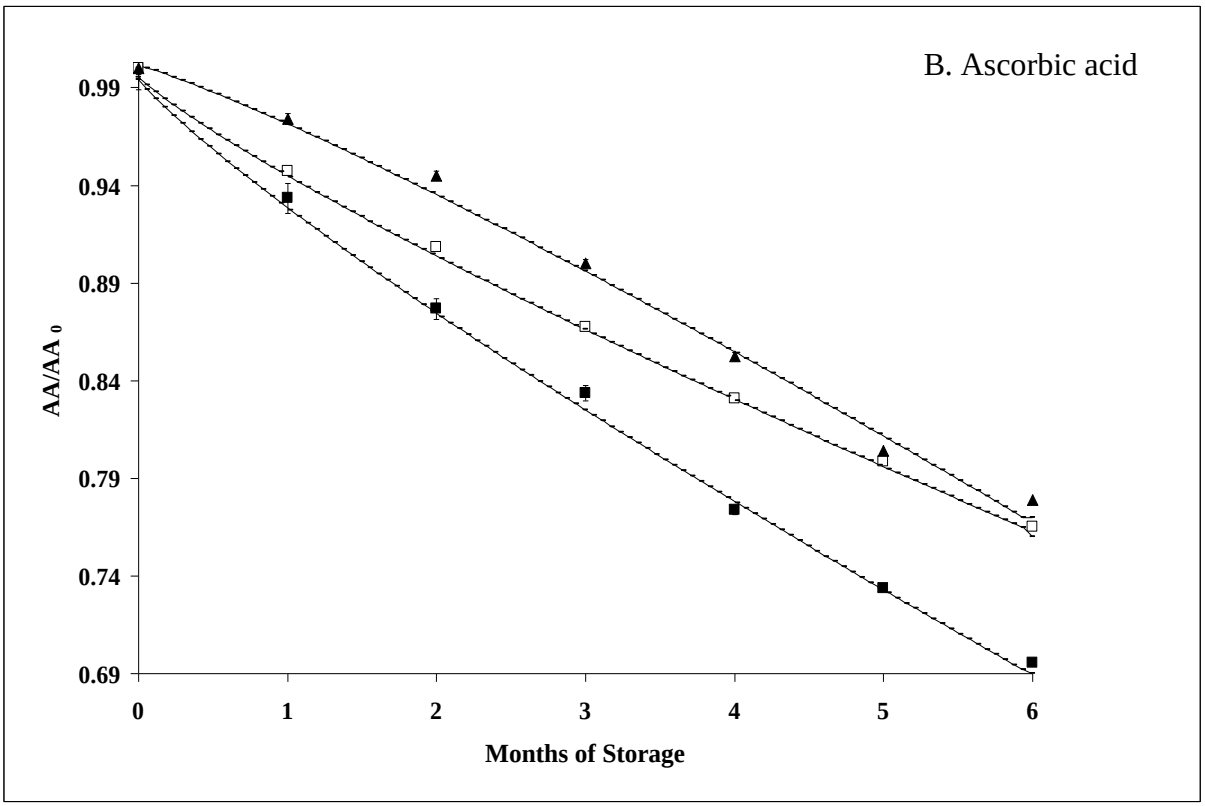
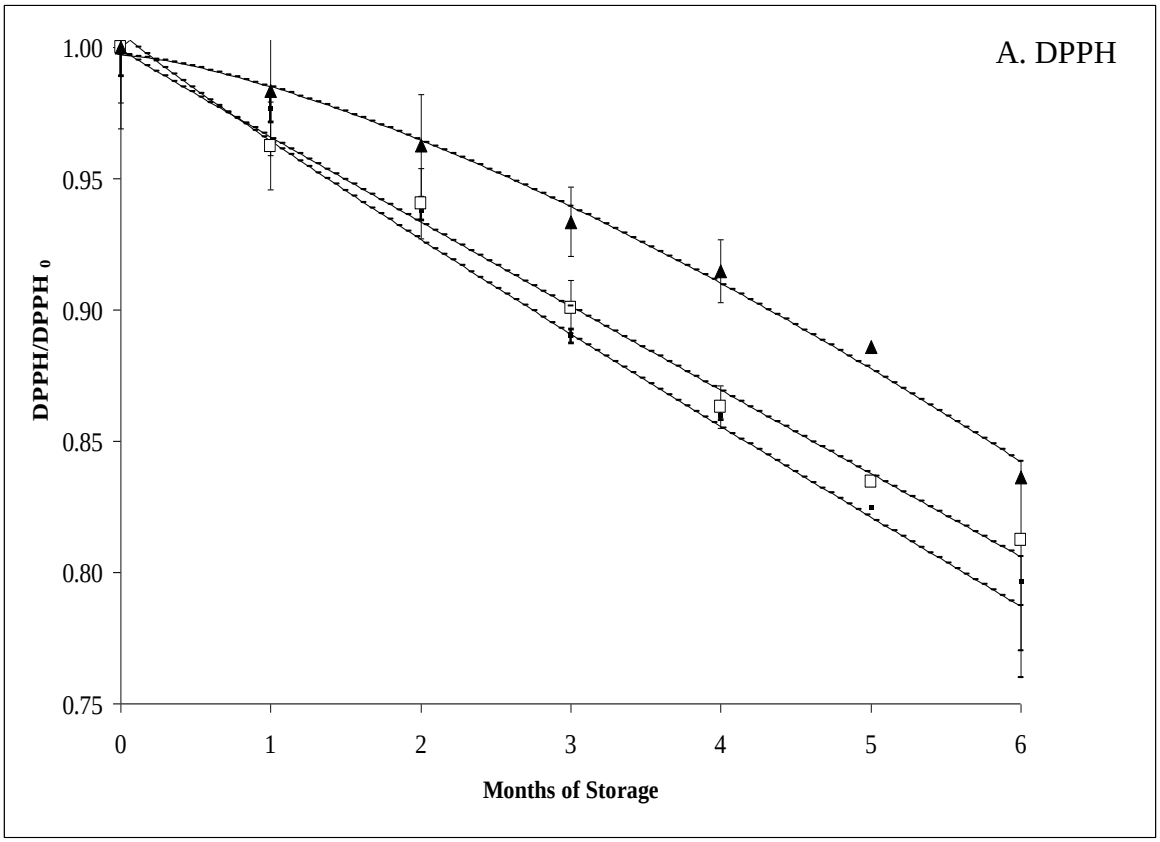

B. Ascorbic acid
0.99
0.94
0.89
0.84
0.79
0.74
0.69
AA/AA 0
0
1
2
3
4
5
6
Months of Storage

Figure 3


A. DPPH
DPPH/DPPH 0
1.00
0.95
0.90
0.85
0.80
0.75
0
1
2
3
4
5
6
Months of Storage

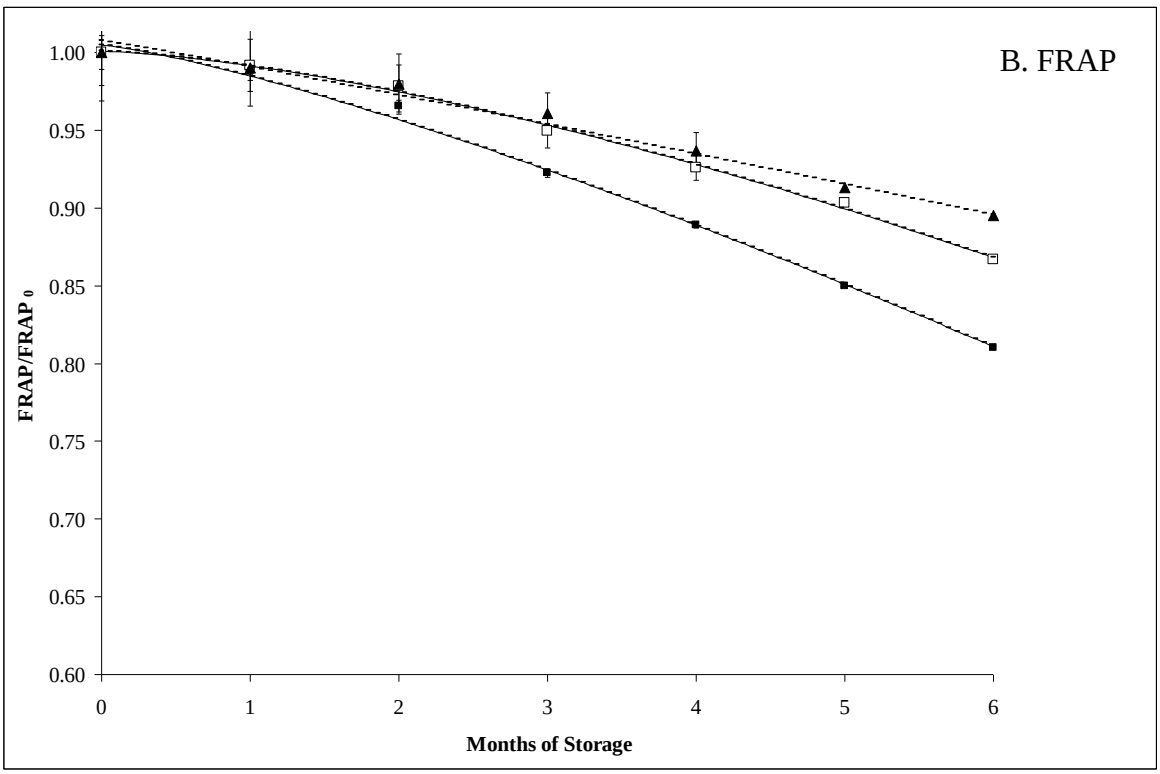

B. FRAP
FRAP/FRAP 0
1.00
0.95
0.90
0.85
0.80
0.75
0.70
0.65
0.60
0
1
2
3
4
5
6
Months of Storage

Table 1. Composition of Delactosed whey permeate (DWP).

DWP Components	Value
pH	5.0
Total Solid %	32.90
Lactose (%)	21.9
Protein %	2.83
Fat (%)	minimal
Moisture %	91.4
Ash %	8.14

Table 2. Changes in phytochemical content of canned Irish plum tomatoes treated with DWP and/or NaCl+ Citric Acid during the 6 months of storage.[1]

[1]Values designated by the different letters are significantly different ($p<0.05$). Lowercase letters are used for comparisons during storage and uppercase letters for treatment comparisons. The method used to discriminate among the means is Fisher's least significant difference (LSD) procedure.

Markers	Treatments	Significance of Difference	Storage (Months)						
			0	1	2	3	4	5	6
Ascorbic Acid	NaCl+ Citric Acid	A	130.82^{g}	122.12^{f}	114.70^{de}	109.05^{d}	101.22^{c}	95.98^{b}	91.00^{a}
	DWP	B	141.40^{h}	133.90^{g}	128.40^{fg}	122.60^{f}	117.50^{e}	112.90^{de}	108.20^{d}
	DWP + NaCl+ Citric Acid	C	143.52^{h}	139.78^{gh}	135.62^{g}	129.15^{fg}	122.32^{f}	115.38^{de}	111.77^{de}
Lycopene	NaCl+ Citric Acid	A	108.30^{b}	107.80^{b}	105.50^{ab}	106.60^{b}	104.70^{ab}	102.80^{a}	104.10^{ab}
	DWP	B	120.20^{d}	116.50^{cd}	115.80^{cd}	113.30^{c}	115.80^{cd}	115.50^{cd}	114.00^{c}
	DWP + NaCl+ Citric Acid	C	125.30^{e}	123.30^{e}	122.00^{de}	122.70^{de}	121.80^{de}	121.20^{de}	121.00^{de}
Total Phenol	NaCl+ Citric Acid	A	290.60^{a}	292.00^{ab}	294.70^{b}	295.20^{b}	297.80^{c}	298.80^{cd}	300.70^{d}
	DWP	B	304.40^{e}	305.30^{e}	306.20^{e}	308.20^{f}	310.30^{g}	311.60^{gh}	312.40^{gh}
	DWP + NaCl+ Citric Acid	C	305.30^{e}	306.20^{e}	307.40^{ef}	309.30^{f}	311.40^{gh}	312.10^{gh}	314.10^{h}
DPPH	NaCl+ Citric Acid	A	64.67^{e}	63.17^{de}	60.67^{d}	56.67^{c}	54.50^{b}	53.33^{b}	51.50^{a}
	DWP	B	75.50^{fg}	72.67^{f}	71.00^{f}	68.00^{ef}	65.17^{e}	63.00^{de}	61.33^{d}
	DWP + NaCl+ Citric Acid	C	80.33^{g}	79.00^{g}	77.33^{fg}	75.00^{fg}	73.50^{f}	71.17^{f}	67.17^{ef}
FRAP	NaCl+ Citric Acid	A	1197.30^{fg}	1182.50^{f}	1156.10^{e}	1104.50^{cd}	1064.70^{b}	1000.80^{ab}	983.80^{a}
	DWP	B	1213.80^{g}	1203.80^{fg}	1187.80^{f}	1152.50^{e}	1124.00^{d}	1096.70^{c}	1052.30^{b}
	DWP + NaCl+ Citric Acid	C	1216.50^{g}	1204.60^{fg}	1191.70^{f}	1168.80^{e}	1139.50^{d}	1110.70^{cd}	1089.20^{c}

Table 3. Changes in texture and colour of canned Irish plum tomatoes treated with DWP and/or NaCl + citric acid during the 6 months of storage.[1]

Markers	Treatments	Significance of Difference	Storage (Months) 0	1	2	3	4	5	6
Texture	NaCl+ Citric Acid	A	4.17^{fg}	3.52^{de}	3.19^{cd}	3.06^{c}	2.83^{b}	2.71^{ab}	2.53^{a}
	DWP	B	5.09^{gh}	4.81^{g}	4.62^{g}	4.06^{f}	3.72^{e}	3.56^{de}	3.27^{d}
	DWP + NaCl+ Citric Acid	C	5.45^{h}	5.35^{h}	4.82^{g}	4.33^{fg}	4.08^{f}	3.82^{e}	3.55^{de}
Colour									
L*	NaCl+ Citric Acid	A	22.20^{de}	21.95^{d}	21.36^{c}	21.16^{c}	20.78^{bc}	20.37^{b}	19.58^{a}
	DWP	B	24.82^{fg}	24.84^{fg}	24.14^{f}	23.32^{e}	22.72^{de}	22.22^{de}	21.76^{d}
	DWP + NaCl+ Citric Acid	C	25.50^{g}	24.47^{f}	24.19^{f}	23.44^{e}	23.08^{e}	22.62^{de}	22.12^{d}
a*	NaCl+ Citric Acid	A	9.49^{c}	9.26^{bc}	9.07^{bc}	8.80^{b}	8.64^{b}	8.41^{b}	8.01^{a}
	DWP	B	12.80^{f}	12.47^{ef}	12.31^{e}	12.10^{de}	12.06^{de}	11.84^{d}	11.75^{d}
	DWP + NaCl+ Citric Acid	C	13.08^{f}	12.91^{f}	12.73^{f}	12.62^{ef}	12.55^{ef}	12.41^{e}	12.22^{e}
b*	NaCl+ Citric Acid	A	23.58^{d}	23.29^{c}	23.18^{c}	22.82^{bc}	22.62^{b}	22.45^{b}	22.23^{a}
	DWP	B	25.09^{fg}	24.62^{f}	24.33^{ef}	24.10^{e}	23.79^{de}	23.60^{d}	23.29^{c}
	DWP + NaCl+ Citric Acid	C	25.87^{h}	25.55^{g}	25.31^{fg}	25.07^{fg}	24.80^{f}	24.72^{f}	24.46^{ef}
Hue	NaCl+ Citric Acid	A	68.07^{c}	68.32^{c}	68.62^{cd}	68.92^{d}	69.10^{e}	69.47^{ef}	70.19^{f}
	DWP	B	62.97^{a}	63.13^{ab}	63.16^{ab}	63.34^{b}	63.11^{ab}	63.36^{b}	63.24^{ab}
	DWP + NaCl+ Citric Acid	C	63.18^{ab}	63.19^{ab}	63.30^{ab}	63.28^{b}	63.16^{ab}	63.34^{b}	63.45^{b}
Chroma	NaCl+ Citric Acid	A	25.42^{cd}	25.07^{c}	24.89^{c}	24.46^{bc}	24.21^{bc}	23.98^{b}	23.63^{a}
	DWP	B	28.17^{fg}	27.59^{f}	27.26^{ef}	26.96^{e}	26.67^{de}	26.41^{de}	26.08^{d}
	DWP + NaCl+ Citric Acid	C	28.99^{g}	28.62^{g}	28.33^{fg}	28.07^{fg}	27.79^{f}	27.66^{f}	27.34^{ef}

[1]Values designated by the different letters are significantly different ($p<0.05$). Lowercase letters are used for comparisons during storage and uppercase letters for treatment comparisons. The method used to discriminate among the means is Fisher's least significant difference (LSD) procedure.

Table 4. Kinetic constants of Weibull distribution function (Eq. (1)) for texture, ascorbic acid, and total antioxidant activity.

Markers	Treatments	k[a] (1/month)	β[b]	R^2	R_{adj}^2	RMSE[c]
Texture	NaCl+citric acid	0.025	0.50	0.99	0.99	0.0075
	DWP	0.060	0.98	0.98	0.97	0.0218
	DWP +NaCl+ Citric acid	0.050	0.96	0.97	0.96	0.0242
Ascorbic acid	NaCl+citric acid	0.041	0.84	0.99	0.99	0.0051
	DWP	0.029	0.84	0.99	0.99	0.0014
	DWP +NaCl+ Citric acid	0.047	1.16	0.99	0.99	0.0083
DPPH[d]	NaCl+citric acid	0.032	0.93	0.97	0.96	0.9632
	DWP	0.031	0.98	0.99	0.99	0.0062
	DWP +NaCl+ Citric acid	0.045	1.43	0.99	0.98	1.1938
FRAP[e]	NaCl+citric acid	0.045	1.27	0.98	0.97	0.0107
	DWP	0.042	1.48	0.99	0.99	0.0036
	DWP +NaCl+ Citric acid	0.021	1.50	0.98	0.97	0.0064

[a] rate constant; [b] shape factor; [c]Root Mean Sum of Squared Error
[d] 2, 2-Diphenyl-l-picrylhydrazyl radical scavenging activity (% reduction)
[e]Ferric ion reducing antioxidant power (mg Trolox /100 g DW)