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ARTICLE

# Effect of Temperature and Cultivar on Polyphenol Retention and Mass Transfer during Osmotic Dehydration of Apples

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Several cultivars of apples (*Malus domestica*) were chosen for their variable concentrations and compositions in phenolic compounds. Cubed samples (1 $cm^3$) were subjected to osmotic dehydration, and the effect of temperature was studied at 45 and 60 °C. Water loss, sucrose impregnation, and the evolution of some natural components of the product were followed to quantify mass transfer. Ascorbic acid and polyphenols were quantified by HPLC for several osmotic dehydration times and regardless of the quantity of impregnated sugar. Changes in antioxidant components differed as a function of the nature of molecules. Their concentrations decreased in line with temperature, and few differences were observed between cultivars. Processing at a lower temperature (45 °C) caused a total loss in ascorbic acid but allowed the retention of between 74 and 85% of initial polyphenols, depending on the cultivar. Cultivars containing highly polymerized procyanidins (such as Guillevic) experienced less loss. Hydroxycinnamic acids and monomeric catechins displayed the most marked changes. Leaching with water into the soaking solution was the principal mechanism retained to explain these losses.

**KEYWORDS: Diffusion; hydroxycinnamic acids; monomeric catechins; oxidation; procyanidins**

## INTRODUCTION

Osmotic dehydration, also called "dehydration−impregnation by soaking" (DIS) (*1*), is widely employed to remove water from pieces of fruits or vegetables by immersing the product in a relatively concentrated aqueous solution of sugar or salt, or both, without any phase change. This process is mainly used for the partial removal of water, but it also leads to the penetration of solute into the product and the leaching of some natural solutes (sugars, acids, minerals, etc.) from the product into the soaking solution. The composition of the solution, and the selection of process conditions, can be optimized to maximize water removal and minimize all other transports. The cross-diffusion of natural solutes is low in quantitative terms but may have important effects on product quality (*2*). Moreover, when compared to conventional drying processes, osmotic dehydration is characterized by a formulation effect. However, the final products generally contain too much moisture to be shelf-stable and need to be processed, for example, using convective drying. Partially dehydrated fruits can be included in foods such as ice cream, desserts, yogurt, dairy, cereals, and confectionery and bakery products or consumed at snacking occasions (*3*).

Fruit is an important component of a healthy diet. Meta-analyses of studies linking fruit intake to disease risk have all concluded that eating fruit can help to prevent major diseases such as cardiovascular diseases and certain cancers, principally of the digestive system (*4*). According to the World Health Report 2002 (*5*), a low intake of fruits and vegetables (< 400 g $day^{-1}$) was estimated to cause, worldwide and annually, about 31% of ischemic heart disease, 11% of stroke, and 19% of gastrointestinal cancers. The dried fruit market is promising because it can provide what consumers are looking for: products combining convenience, pleasure, and health (*6*). In France, during the year 2006, this sector recorded the second highest annual growth rate in fruit transformation, with an increase of 15.6% (*7*). Thus, dried fruits can contribute to increase the fruit consumption as recommended in recent studies (*8*). Fruit provides a good source of fibers and biologically active compounds, especially ascorbic acid and polyphenols, which are known to act as natural antioxidants (*8*). Antioxidant activity is positively correlated with the total polyphenol content (*9*−*11*). Moreover, phenolic compounds are also relevant with respect to fruit quality, because they are important to the visual appearance (browning), taste (bitterness and astringency), and health-promoting properties of fresh fruits and their derived products (*12*). Several polyphenols have been identified in apples. Hydroxycinnamic acids, flavan-3-ols (including monomeric catechins and procyanidins), and dihydrochalcones can be found in all parts of fruits, whereas flavonols are essentially located in the peel. Procyanidins are the most abundant polyphenols in apples. They are oligomers and polymers of catechins and are characterized by an average degree of polymerization (DPn), which corresponds to the number of catechin

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units in the procyanidin molecule (*13*). Furthermore, the concentration and average degree of procyanidin polymerization are related to organoleptic properties such as bitterness and astringency (*14*). Procyanidins also appear to be related to nutritional properties and, particularly, to bioavailability (*15*). Absorption, antioxidant capacity, and bioavailability of polyphenols have been studied in both animals and humans, but most of the studies reported in the literature refer to extractable polyphenols analyzed in aqueous−organic extracts. However, an important fraction of procyanidins is nonextractable, even if they may exert antioxidant activity, and their contribution is not taken into account in nutritional studies (*9*, *16*). It is therefore interesting to fully quantify the phenolic profile by specific analysis (*16*, *17*) to provide data for further nutritional and biological studies.

Polyphenols in fresh pome fruits have often been reported and displayed considerable variability as a function of cultivar (*18*,*19*). Fruit maturity, season, geographic location, and storage conditions are also known to affect the composition in polyphenols (*20*−*22*). The influence on mass transfers of DIS processing variables such as temperature, the type and concentration of the osmotic solution, agitation, or sample size and shape has also been widely studied on fruits (*1*, *2*, *23*−*29*). However, no result on osmotic dehydration of cider apple cultivars can be found in the literature, and very few studies have focused on the impact of fruit processing on antioxidant levels. In pome fruits, conventional boiling (*30*) and sun drying (*31*) have been studied in pears and vacuum impregnation (*32*) and puree preparation (*33*, *34*) in apples. To our knowledge, no study has been performed to date on the impact of osmotic dehydration on antioxidants, except for studies on ascorbic acid loss during the osmotic dehydration of tropical fruits (*2*, *23*, *27*).

The aim of this work was therefore to determine the effects of soaking temperature and processing time on ascorbic acid and phenolic compounds in several cider or dessert apple cultivars chosen for their different antioxidant concentrations and profiles. It was necessary to adapt the method used to analyze polyphenols from an existing technique (*17*) for high sugar levels. To obtain full information on the impregnation process, changes to fructose, glucose, and sucrose concentrations were monitored during the process.

## MATERIALS AND METHODS

**Solvents and Reagents.** Food grade, commercial sucrose was used for the osmotic solution (CEEW02, from Saint Louis, Paris, France). Anhydrous citric acid (99.5% purity), calcium chloride ($CaCl_2 \cdot 2H_2O$, analytical grade), L-ascorbic acid, sodium fluoride, and metaphosphoric acid were all purchased from VWR International (Fontenay-sous-Bois, France).

Chromatographic grade ethanol, methanol, acetonitrile, and glacial acetic acid were purchased from Merck (Darmstadt, Germany). Ultrapure water was obtained using a Milli-Q Elix 3 water purification system (Millipore Corp., Bedford, MA).

**Standards.** All standards were of analytical grade. Glucose, fructose, and sucrose (99% purity) were purchased from Panreac (Barcelona, Spain). L-Ascorbic acid, (+)-catechin, (−)-epicatechin, chlorogenic acid (5-caffeoylquinic acid), and phloridzin were obtained from Sigma-Aldrich, Inc. (Bellefonte, PA). *p*-Coumaroylquinic acid was obtained as described by Sanoner et al. (*18*). (+)-Catechin benzylthioethers and (−)-epicatechin benzylthioethers were produced as already described by Guyot et al. (*35*). Procyanidins B1, B2, and B5 were available from INRA, UR117 (Le Rheu, France) and prepared as already described by Nunes et al. (*12*).

**Plant Materials.** Cultivar Guillevic and Marie Menard cider apples were purchased from IFPC (Institut Français des Productions Cidricoles − French Institute for Cider Production, Sees, France). Cider cultivars are known for their much higher polyphenol contents when compared to dessert ones (*19*). Moreover, Guillevic is known to have an atypical phenolic profile for a cider apple, inducing a lower sensitivity to enzymatic browning (*18*), whereas Marie Menard has a more standard one, but in higher concentrations. Both cultivars also differ if one considers the average degree of polymerization of procyanidins: Marie Menard has a standard one (around 5), whereas Guillevic has a very high one (10-fold higher) (*18*), inducing different interaction with cell-wall components (*36*). Cultivar Gala dessert apples were provided by the CTIFL (Centre Technique Interprofessionnel des Fruits et Légumes − Interprofessional Technical Centre for Fruit and Vegetables, Lanxade, France). This cultivar was selected as a reference to compare with cider apples. This was the second most important variety produced in France in 2007 (*37*), and it has been less extensively studied than Golden Delicious. Each cultivar was cropped in a single orchard and harvested at maturity (12% dry matter) in 2007. The apples were stored at 4 °C until processing.

**Osmotic Dehydration.** *Sample and Solution Preparation*. The apples were peeled and cored by hand and cut into cubes (1 cm × 1 cm × 1 cm, initial dimensions) with a manual KitchenAid device allowing dimensions of the cubes and mass transfers to be controlled. To have a representative sample, about 500 g of apple cubes was needed. As the cutting operation could last up to 2 h, the apples cubes were pretreated by spraying them with a solution of 6% (w/v) citric acid, 3% (w/v) calcium chloride, and 1% (w/v) ascorbic acid to prevent enzymatic browning phenomena during cutting (*38*, *39*), which may alter the content and composition in polyphenols. Nicolas et al. reviewed different methods for controlling the browning of apple tissues and described ascorbic acid as the most effective and frequently used chemical product (*40*). Ascorbic acid reduces the *o*-quinones formed by polyphenol oxidase to the original diphenols. Its effect is temporary (*40*), so oxidation reactions that may occur during processing will not be inhibited. The spraying solution was then removed by rinsing with cold tap water (2 L $min^{-1}$) for 1 min at the end of the cutting.

The hypertonic soaking solution was a 60 °Brix sucrose solution. Sucrose is the most popular osmotic agent because of its relatively low cost (*3*), and contrary to monosaccharide, sucrose favors water loss instead of solute gain (*25*). Moreover, Rashmi et al. have studied the impact of the concentration of the sucrose solution in the range of 50−70 °Brix and have demonstrated that the maximal dry fruit yield, micronutrients retention, and sensory score were obtained with a 60 °Brix solution (*41*). The solution was prepared by blending sucrose with boiling Ultrapure water under agitation until complete dissolution and then placed in an ultrasonic tank for 15 min to remove any air before the soaking experiments.

*Soaking Experiments*. Osmotic treatments were conducted in 650 mL opaque containers fitted with hermetic lids, which were placed in an agitated, temperature-controlled water bath (SW 22, Julabo, Colmar, France). At time $t$ = 0, about 22 g (± 0.5 g) of rinsed apple cubes was immersed in about 440 g (± 0.5 g) of solution, previously heated to the set-point temperature. Two temperatures were tested: 45 °C, considered to be a moderate one, and 60 °C, considered to be a high one, at which cell membranes lose their selectivity and diffusion and chemical reaction rates increase (*24*). A plastic grid fixed under the lid ensured the complete immersion of the apple cubes. A 20:1 (w/w) ratio of osmotic solution/apple cubes was chosen to ensure only negligible changes to the concentration of the solution during the experiment (*24*). The containers were agitated continuously (140 rpm) in the bath. At time $t$ (15, 30, 90, and 180 min), three to five containers were removed from the water bath and the cubes were drained, quickly rinsed with cold tap water (2 L $min^{-1}$, 30 s), drained again, gently blotted with paper to remove surface solution, weighed, and used for chemical analyses.

**Moisture Content.** Moisture content was determined by weight loss after drying in a ventilated oven (UFE 500, Memmert, Schwabach, Germany) at 70 °C, until a constant weight was obtained (approximately 24 h) (*24*). The measurements were repeated three times on 5 g (± 0.1 mg) samples of raw or soaked apples. The relative standard deviation of the measurement was 4% ($n$ = 7).

Moisture content ($X_w$), expressed on a wet basis in grams per 100 g of fruit, and water loss (WL), expressed in grams per 100 g of initial fresh fruit (FW), were calculated versus time as in eq 1:

$$\mathrm{WL}(t) = X_w(0) - X_w(t) \times \frac{m(t)}{m(0)} \quad (1)$$

$X_w(0)$ = initial moisture content (wet basis; g 100 $g^{-1}$ FW), $X_w(t)$ = moisture content (wet basis) at time $t$ (g 100 $g^{-1}$ of fruit at time t), and $m(t)$ = sample weight at time $t$ (g), and $m(0)$ = initial sample weight (g).

**Ascorbic Acid and Sugars.** *Extraction of Ascorbic Acid.* The method was derived from that described previously by Cocci et al. (*42*). At the initial time and at each sampling time, 20 g of apple cubes was accurately weighed (± 0.1 mg) and ground with 25 mL of a metaphosphoric acid solution (4% w/v, prepared extemporaneously) using a Stomacher Lab-Blender 80 (Laboratoire Humeau, La Chapelle-sur-Erdre, France). The volume was then adjusted to 75 mL with Ultrapure water, and the extract was filtered twice through microfiber and nylon filters (1.6 μm, GF/A, and 0.45 μm, Mini-UniPrep, Whatman, Versailles, France). The filtrate was then stored at 4 °C until analysis. A preliminary test had shown that ascorbic acid remained stable in a metaphosphoric acid solution for 48 h at 4 °C. All analyses were then performed during the first 48 h after grinding.

*Extraction of Sugars.* The method was adapted from that described previously by Chardonnet et al. (*43*). At the same time as the extraction described above, 10 g of crushed apples was accurately weighed (± 0.1 mg), blended with ethanol (80:20, v/v), boiled under reflux for 30 min, and then placed in an ultrasonic tank for 10 min. The final volume was adjusted to 500 mL with Ultrapure water, and the solution was then filtered twice, as previously described for ascorbic acid. Finally, the filtrate was stored at 4 °C until analysis.

*Characterization and Quantification of Ascorbic Acid and Sugars.* A method was developed for the simultaneous analysis of ascorbic acid and sugars using high-pressure liquid chromatography (HPLC). The device included an autosampler 465 automatic HPLC injector (Biotek Kontron Instruments, Colmar, France), an Aminex HPX 87 H column (300 × 7.8 mm i.d., 9 μm, ion exclusion column, Bio-Rad Laboratories., Watford, U.K.), which were placed in an Igloo-cil oven (Cluzeau Info Labo, Courbevoie, France) heated at 25 °C and preceded by a microguard Cation H Refill Cartridge (Bio-Rad Laboratories), and a Gilson 321 injection pump (Gilson, Roissy en France, France). A Waters 410 refractometer (Waters, Guyancourt, France) was used for sugar detection, and a Waters 996 photodiode array detector was used at a wavelength of 242 nm for ascorbic acid detection. The mobile phase was an aqueous solution of sulfuric acid at a concentration of $5 \times 10^{-4}$ mol $L^{-1}$. The flow rate was constant and fixed at 0.5 mL $min^{-1}$, whereas the run time was 27 min. Data were acquired and processed by Empower 2 (Build 2154) software (Waters).

Compounds were identified on chromatograms by comparing their retention times with standards. The compounds thus identified were quantified using external calibration curves obtained for L-ascorbic acid (0−0.3 g $L^{-1}$; 8%), glucose (0−2 g $L^{-1}$; 13%), fructose (0−2 g $L^{-1}$; 8%), and sucrose (0−8 g $L^{-1}$; 13%), the percentage values in brackets referring to the relative standard deviation of the analysis ($n$ = 5). The limits of detection (LOD) of ascorbic acid and sugars were 9.9 μg $L^{-1}$ and 4.8 mg $L^{-1}$, respectively, and the limit of quantification (LOQ) can be calculated by multiplying the LOD by 10/3.

Results were expressed in milligrams or grams per gram of initial dry matter (DM). Gains in sucrose (SuG) and losses in natural components (CL, for ascorbic acid or fructose or glucose) were calculated as below (eqs 2 and 3, respectively) and expressed as a percentage (w/w) of the initial compound.

$$\mathrm{SuG}(t) = \frac{(\mathrm{Su}(t) - \mathrm{Su}(0))}{\mathrm{Su}(0)} \times 100 \quad (2)$$

Su (0) = initial sucrose content (g $g^{-1}$ of initial DM) and Su ($t$) = sucrose content at time $t$ (g $g^{-1}$ of initial DM).

$$\mathrm{CL}(t) = \frac{(C(0) - C(t))}{C(0)} \times 100 \quad (3)$$

$C(0)$ = initial compound content (g or mg $g^{-1}$ of initial DM), and $C(t)$ = compound content at time $t$ (g or mg $g^{-1}$ of initial DM).

**Polyphenols.** To analyze polyphenols using HPLC, it was necessary for the product to be reduced to a powder prior to extraction (*17*). Because the apples were impregnated with variable and relatively high sucrose contents, classic grinding with steel balls after freeze-drying (*17*) was not appropriate. It was therefore necessary to develop an original method (described in the section below). This method was compared with the standard technique for raw, nonimpregnated apples and produced identical results.

*Sample Preparation.* Five grams of fresh or soaked apple cubes was ground in 15 mL of a sodium fluoride (0.2 g $L^{-1}$) and acetic acid (2.5%, v/v) solution (*44*) using an Ultraturrax T25 blender (IKa Labortechnik, Staufen, Germany), fitted with an S25N-10G stem, to obtain complete dissolution (45 s). Mixed samples were then frozen at −80 °C and freeze-dried at −20 °C for 24 h, at −15 °C for 17 h, at −5 °C for 4 h, at 5 °C for 5 h, and at 15 °C for 2 h. Homogeneous powders were then obtained by crushing the freeze-dried tissues, which were stored in desiccators to prevent any hydration prior to extraction or thiolysis.

*Crude Solvent Extraction and Thiolysis.* To obtain full information on polyphenol contents, two types of extraction were performed in parallel. The crude solvent extraction enabled access to all single (or nonpolymerized) phenolic compounds. On the other hand, the thiolysis reaction led to the depolymerization of procyanidin oligomers and polymers, thus enabling their quantification as equivalent of monomeric flavanols and providing structural information on their average degree of polymerization (*17*). Thus, the thiolysis allows accessing all the procyanidins, even the nonextractable ones that cannot be quantified after a crude solvent extraction (*17*).

Crude solvent extraction and thiolysis were performed as previously described by Guyot et al. (*17*). The crude solvent extraction is realized by adding acidic methanol before sonication and filtration. For the thiolysis, acidic methanol and toluene α-thiol are directly added to the freeze-dried powder, splitting the procyanidin structures and liberating the terminal units as monomeric flavanols (*17*). Only a filtration is needed before analysis.

Because osmotic dehydration was found to cause an increase in the sucrose concentration of samples, the corresponding freeze-dried powders became increasingly hygroscopic, and it was necessary to verify the possible impact of this on the efficiency of the thiolysis reaction. Scientists had indeed shown previously that the thiolysis yield might be reduced in the presence of water (*45*). A calibration range was therefore determined in triplicate. For a given amount of apple (5 g, cv. Marie Ménard), increasing quantities of sucrose were added, up to the highest concentration obtained during DIS experiments (i.e., 0.58 g of sucrose $g^{-1}$ of FW). The samples were then ground with sodium fluoride, freeze-dried, and subjected to thiolysis or crude solvent extraction prior to HPLC analysis. The mean of the three repetitions for each compound detected is shown in **Table 1**, with particular focus on flavan-3-ols (including catechins and procyanidins), which could be quantified only by thiolysis. The other phenolic compounds were quantified by both thiolysis and crude solvent extraction, and the results were identical.

The concentration in flavan-3-ols resulted from the sum of the concentrations of the four components shown in **Table 1**. The two isomers of (−)-epicatechin benzylthioether resulted from the cleavage of procyanidin interflavan linkages by the thiolysis reaction and corresponded to adducts between toluene α-thiol and extension units of procyanidins. (+)-catechin and (−)-epicatechin were the sum of the terminal units of procyanidins (mainly made up of (−)-epicatechin) and monomeric catechins. (+)-catechin and 4(*S*)-(−)-epicatechin benzylthioether concentrations remained significantly unchanged. As for 4(*R*)-(−)-epicatechin benzylthioether and (−)-epicatechin, a slight reduction was observed when the sucrose concentration increased, but this reduction was of the same order of magnitude as the standard deviation. Overall, flavan-3-ols concentrations versus sucrose concentrations remained within the confidence interval. The statistical significance of a linear relationship between flavan-3-ols concentration and sucrose concentration was tested. The confidence interval on the estimation of the regression coefficient overlapped zero at 98% confidence level, thus proving that under these conditions, sucrose can be considered as having no effect on the flavan-3-ols concentration.

It could therefore be concluded that within the range of 0.02−0.59 g of sucrose $g^{-1}$ of FW, thiolysis could be used to measure the flavan-3-ols concentration in raw and soaked apples, without it being necessary to apply any corrective term.

*Characterization and Quantification of Polyphenols.* The crude methanol extract and the thiolysis-derived compounds were analyzed using reverse-phase high-performance liquid chromatography (RP-HPLC), under the conditions already described by Guyot et al. (*17*). The Waters system was equipped with a 717 autosampler with a cooling module set at 4 °C to increase the stability of thiolysis derivatives.

**Table 1.** Influence of the Sucrose Concentration on Flavan-3-ol Compounds (in Milligrams per Gram of Dry Matter of Apple without Added Sucrose) after Thiolysis

| | sucrose concn | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 0.02 g g$^{-1}$ of FW | 0.15 g g$^{-1}$ of FW | 0.24 g g$^{-1}$ of FW | 0.32 g g$^{-1}$ of FW | 0.39 g g$^{-1}$ of FW | 0.48 g g$^{-1}$ of FW | 0.59 g g$^{-1}$ of FW | mean | SD[a] |
| (+)-catechin | 0.94 | 0.91 | 0.82 | 0.81 | 0.72 | 0.82 | 0.82 | 0.83 | 0.13 |
| (−)-epicatechin | 9.54 | 9.84 | 9.24 | 9.24 | 7.44 | 8.52 | 8.12 | 8.85 | 0.95 |
| 4(*R*)-(−)-epicatechin benzylthioether | 1.55 | 1.71 | 1.27 | 1.41 | 0.97 | 1.14 | 1.06 | 1.30 | 0.17 |
| 4(*S*)-(−)-epicatechin benzylthioether | 24.76 | 26.17 | 25.52 | 26.45 | 23.61 | 23.49 | 22.10 | 24.59 | 3.21 |
| flavan-3-ols | 36.79 | 38.63 | 36.85 | 37.91 | 32.74 | 33.97 | 32.10 | 35.57 | 4.06 |

[a] SD, mean standard deviation.

The column was a Purospher RP18 end-capped column, 250 × 4 mm, 5 μm (Merck, Darmstadt, Germany). The solvent system was a gradient of 2.5% (v/v) acetic acid in water (solvent A) and acetonitrile (solvent B), degassed continuously with helium. The following gradient was applied: 3% B, 0−5 min; 9% B, linear; 5−15 min, 16% B linear; 15−45 min, 50% B linear; 45−48 min, 90% B linear; 48−51 min, 90% B isocratic; and 51−55 min, 3% B linear, followed by washing and reconditioning of the column. The data acquisition and remote control of the HPLC system were done by Millennium 32 version 3.20 software.

Phenolic compounds, for which standards were available, were identified by chromatograms, as shown by Guyot et al. (*17*), as a function of their retention times and UV−vis spectra. Chlorogenic acid and *p*-coumaroylquinic acid were detected and quantified at 320 nm, and monomeric catechins, (+)-catechin and (−)-epicatechin, at 280 nm. Procyanidins were also detected and quantified at 280 nm as (−)-epicatechin equivalent, except for procyanidins B1, B2, and B5, which were expressed as B2 equivalent. Dihydrochalcones (phloridzin and phloretin xyloglucoside) were detected and quantified at 280 nm as phloridzin equivalent. Calibration curves were available for each of these compounds, and response factors were applied to the areas of the chromatographic peak corresponding to compound, and accordance with their UV−visible spectrum was checked.

The calibration range was the same as that published by Nunes et al. (*12*) for phloridzin; it was within the range of 0.05−0.1 mg mL$^{-1}$. The relative standard deviation of the analysis was 5% ($n$ = 5).

Results were expressed in milligrams per grams of initial DM. Losses of polyphenol compounds were calculated as below (eq 4) and expressed as percentage (w/w) of the initial compound:

$$\mathrm{PPL}(t) = \frac{(\mathrm{PP}(0) - \mathrm{PP}(t))}{\mathrm{PP}(0)} \times 100 \quad (4)$$

PP(0) = initial compound content (mg g$^{-1}$ of DM) and PP($t$) = compound content at time $t$ (mg g$^{-1}$ of DM).

The average degree of polymerization was calculated using the molar ratios of all flavan-3-ol units (thioether adducts + terminal units) to (−)-epicatechin and (+)-catechin, corresponding to terminal units (*35*).

## RESULTS AND DISCUSSION

**Initial Compositions of Different Apple Cultivars.** The initial compositions of the cortex of the three cultivars considered during this study are presented in **Table 2**.

The moisture contents of all cultivars were about the same. Sugar contents were higher in Gala than in cider cultivars, especially in terms of sucrose and fructose (the main sugar in apples), with 68 g kg$^{-1}$ of FW for Gala to about 50 g kg$^{-1}$ of FW for Guillevic or Marie Menard. Cider cultivars displayed antioxidant contents that were 5-fold higher than those found in dessert apples, with a small quantity (1%) corresponding to ascorbic acid in fresh apples (called "natural ascorbic acid" in **Table 2**), which varied from 4 mg kg$^{-1}$ of FW for Gala (in accordance with the findings of Vrhovsek et al. (*19*)) to 26 mg kg$^{-1}$ for Marie Menard. Even though the apples were drained before the experiments, ascorbic acid levels rose after the spraying of antibrowning solution during cutting. This increase multiplied the ascorbic acid content (called "initial ascorbic acid" in **Table 2**) from 5- to 17-fold and was very irregular in different experiments. Polyphenols were also found to be 3−7-fold more concentrated in cider cultivars, as described by Sanoner et al. (*18*). However, the values measured for Guillevic and Gala were lower than those found in the literature (*18* and *19*, respectively). A marked difference in the polyphenol content was also measured between cider cultivars: Marie Menard was about twice as concentrated as Guillevic, which is in accordance with the classification of these varieties into bitter and sharp cider varieties, respectively (*14*).

**Table 2.** Average Initial Composition of the Cortex for the Studied Cultivars[a]

| | Gala | Guillevic | Marie Menard |
|---|---|---|---|
| moisture content (g 100 g$^{-1}$ of FW) | 88.6 ± 0.4 | 87.8 ± 0.5 | 88.1 ± 0.9 |
| glucose (g kg$^{-1}$ of FW) | 14 ± 1 | 18 ± 0.5 | 20 ± 2 |
| fructose (g kg$^{-1}$ of FW) | 68 ± 4 | 48 ± 1 | 50 ± 4 |
| sucrose (g kg$^{-1}$ of FW) | 25 ± 2 | 17 ± 1 | 20 ± 3 |
| natural ascorbic acid[b] (mg kg$^{-1}$ of FW) | 4 ± 1 | 17 ± 1 | 26 ± 2 |
| initial ascorbic acid[c] (mg kg$^{-1}$ of FW) | 67 ± 30 | 124 ± 39 | 134 ± 70 |
| polyphenols (mg kg$^{-1}$ of FW) | 492 ± 76 | 1378 ± 57 | 3359 ± 590 |

[a] Mean ± standard deviation ($n$ = 4 for Gala and Guillevic and $n$ = 5 for Marie Menard). [b] Ascorbic acid present in fresh apples. [c] Ascorbic acid at $t$ = 0 after rinsing the sprayed antibrowning solution.

Polyphenol compounds were analyzed separately (**Table 3**) and then pooled in four groups (in bold type in **Table 3**) for a more convenient analysis of the results. Among the procyanidins, dimers were quantified separately after crude solvent extraction, and the whole procyanidins (polymerized flavan-3-ols) were assessed after thiolysis.

The apple cortex contains three main classes of polyphenols: the flavan-3-ols, including monomeric catechins and procyanidins, the hydroxycinnamic acids, and the dihydrochalcones, which are specific to apples. Regardless of the concentrations, Gala and Marie Menard had similar phenolic profiles and the same average degree of polymerization of procyanidins.

As observed by many other authors working on apples (*13*, *17*−*19*, *21*, *22*, *30*, *35*, *36*, *46*−*48*), procyanidins were the principal phenolic compounds found. They represented 60% in Marie Menard and Gala and 85% in Guillevic. The predominant procyanidin detected was procyanidin B2, at a concentration of 442 mg kg$^{-1}$ in Marie Menard. Guillevic had a very high DP$n$, as already mentioned (*18*), when compared to Marie Menard or Gala. During a different study, a slightly lower DP$n$ (at around 4) had been found for Gala (*22*). The second most important group was the hydroxycinnamic acids, which accounted for about 28% in Gala and Marie Menard and only half in Guillevic. The predominant compound in this group of cultivars was chlorogenic acid (90% in Marie Menard, 75% in Gala, and about 50% in Guillevic), although the *p*-coumaroylquinic acid content was also high in Guillevic. Because chlorogenic acid is the preferential substrate for polyphenol oxidase (*49*), it renders Marie Menard much more susceptible to enzymatic browning than the other

**Table 3.** Concentrations of Phenolic Compounds in the Cortex of Apple Cultivars[a]

| | mg kg$^{-1}$ of FW | | |
|---|---|---|---|
| | Gala | Guillevic | Marie Menard |
| phloretin xyloglucoside | 7 ± 1 | 8 ± 1 | 25 ± 6 |
| phloridzin | 4 ± 1 | 3 ± 1 | 18 ± 5 |
| **dihydrochalcones** | **11 ± 1** | **12 ± 2** | **46 ± 13** |
| chlorogenic acid | 101 ± 17 | 106 ± 3 | 851 ± 116 |
| *p*-coumaroylquinic acid | 19 ± 4 | 79 ± 3 | 32 ± 9 |
| **hydroxycinnamic acids** | **134 ± 30** | **199 ± 3** | **939 ± 129** |
| (+)-catechin | 10 ± 3 | nd | 24 ± 6 |
| (−)-epicatechin | 37 ± 1 | nd | 390 ± 38 |
| **monomeric catechins** | **47 ± 3** | **nd** | **415 ± 33** |
| procyanidin B1 | 5 ± 1 | 3 ± 0.5 | 27 ± 5 |
| procyanidin B2 | 30 ± 5 | 16 ± 3 | 442 ± 126 |
| procyanidin B5 | nd | 3 ± 0.5 | 33 ± 7 |
| **procyanidins** | **300 ± 43** | **1168 ± 53** | **1960 ± 460** |
| DP*n* | 5.0 ± 0.5 | 48.5 ± 12.5 | 4.5 ± 0.5 |

[a] Mean ± standard deviation ($n$ = 4 for Gala and Guillevic and $n$ = 5 for Marie Menard). nd, not detected; DP*n*, average degree of polymerization.

cultivars. Monomeric catechins accounted for about 10%, mainly in the form of (−)-epicatechin, but were lacking in Guillevic, as previously observed (*18*). Finally, dihydrochalcones (mainly phloretin xyloglucoside) represented only around 2% in Gala and Marie Menard and < 1% in Guillevic. This low percentage could be explained by their higher concentration in seeds, which were eliminated when the apple cubes were prepared.

**Effect of Soaking Solution Temperature on Mass Transfer.** The apples were soaked in a 60 °Brix sucrose solution at either 45 or 60 °C. Each experiment was duplicated except for cv. Marie Menard at 45 °C, which was performed in triplicate so that a standard deviation could be calculated for the whole experiment from the mean of the variance at each sampling time point.

To assess mass transfers, mean water and sugar concentrations were analyzed at each sampling time on whole apple cubes. No distinction was made between the surface of the product in contact with the solution and its inner parts, as had been done in some studies (*28*, *50*). The results regarding water loss are plotted in **Figure 1**.

Water loss increased exponentially over time and was accelerated by a higher temperature. Most transfers occurred during the first 30 min of the process, as classically observed by many other authors (*24*, *26*), and temperature-related differences also appeared during this period. After 30 min of osmotic dehydration, 53% of water had disappeared at 45 °C and > 60% at 60 °C. This observation could explained by the promoting effect of temperature on the swelling and plasticizing of cell membranes, a greater diffusion of water within the product, and an increased mass transfer at the product surface because of the weaker viscosity of the osmotic solution (*29*, *51*). Nevertheless, this difference tended to be smaller with long soaking times, the final water loss at equilibrium being relatively independent of temperature (*28*). The cultivar impact was less important than that of temperature. At 45 °C, all cultivars were similarly dehydrated, whereas at 60 °C a slight difference could be observed for Gala, which dehydrated slightly more rapidly. Whatever the cultivars, the kinetics were comparable with those published in the literature on tropical fruits (*2*, *23*, *27*) or on apple (*25*).

**Figure 2** illustrates sucrose gains (%, w/w) and fructose losses (%, w/w) as a function of processing time or moisture content

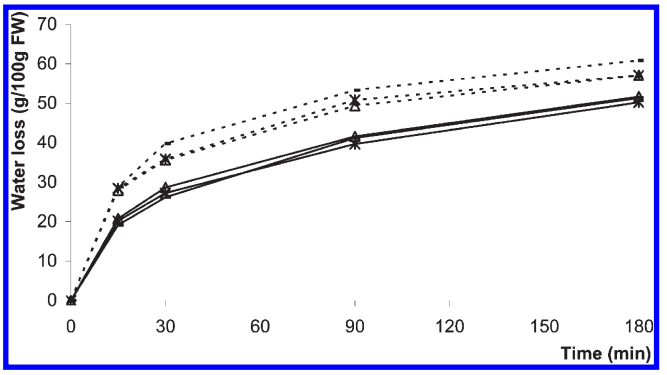


**Figure 1.** Water loss during osmotic dehydration at 45 °C (full line) and at 60 °C (dotted line) in Marie Menard (△), Guillevic (∗), and Gala (—). Standard deviation = 1.0 g 100 g$^{-1}$ of FW.

under both operating temperatures and in the three selected cultivars.

As observed for water loss, sucrose gain and fructose loss mainly occurred during the first 30 min of osmotic dehydration. The sucrose content was multiplied 10-fold at 45 °C and 16-fold at 60 °C, and an increase in temperature enhanced the sucrose gain whatever the cultivar. However, this gain was not directly due to temperature but due to the increase in water loss caused by temperature. The results plotted in **Figure 2b** show that the sucrose gain versus water content was about the same whatever the soaking temperature in both cider cultivars. The same behavior had been observed during a recent study on pineapples osmo-dehydrated in a sucrose solution at 60 °Brix, when the sucrose concentration versus moisture content fitted the same linear function whatever the temperature applied within the range of 30−50 °C (*28*). The cultivar impact on sucrose gains was difficult to quantify; indeed, at 45 °C, Gala and Marie Menard reacted in the same way, whereas at 60 °C it was the two cider apples that reacted similarly (**Figure 2a**,**b**). Nor was the 15 °C increase perceived in the same way. After 30 min, the difference in solute gain between the two temperatures was 5 times higher in Marie Menard than in Gala. As shown in **Figure 2c**,**d**, fructose losses were significantly increased by temperature. After 180 min of osmotic dehydration, one-third of the initial fructose was lost at 45 °C and more than twice as much at 60 °C (two-thirds). However, fructose losses were relatively proportional to water losses, and the coefficient of proportionality increased with temperature. No clear cultivar effect could be observed with respect to fructose loss. Glucose was also monitored throughout the process, and the same trend was observed as for fructose. However, the final loss after 3 h of osmotic dehydration was less considerable (28% at 45 °C and around 50% at 60 °C). Ramallo and Mascheroni (*28*) had also observed that glucose and fructose losses were enhanced by temperature and also found a higher fructose loss. As previously proposed by Saurel et al. (*24*), they suggested that this resulted from diffusion due to the difference in concentration between the solution and the product and by leaching with water, the flux of which increased with temperature.

**Effect of Soaking Solution Temperature on Ascorbic Acid and Polyphenol Retention.** Like the water and sugar contents in the previous section, ascorbic acid and phenolic contents were monitored throughout osmotic dehydration under the same conditions of temperature and in the same cultivars. Ascorbic acid losses were extremely rapid, whether based on time or water content. The losses were temperature-dependent, the cultivar having very little effect. At 45 °C, around 80% of ascorbic acid disappeared during the first 15 min of osmotic dehydration and 100% at 60 °C. During previous studies on the osmotic dehydration of

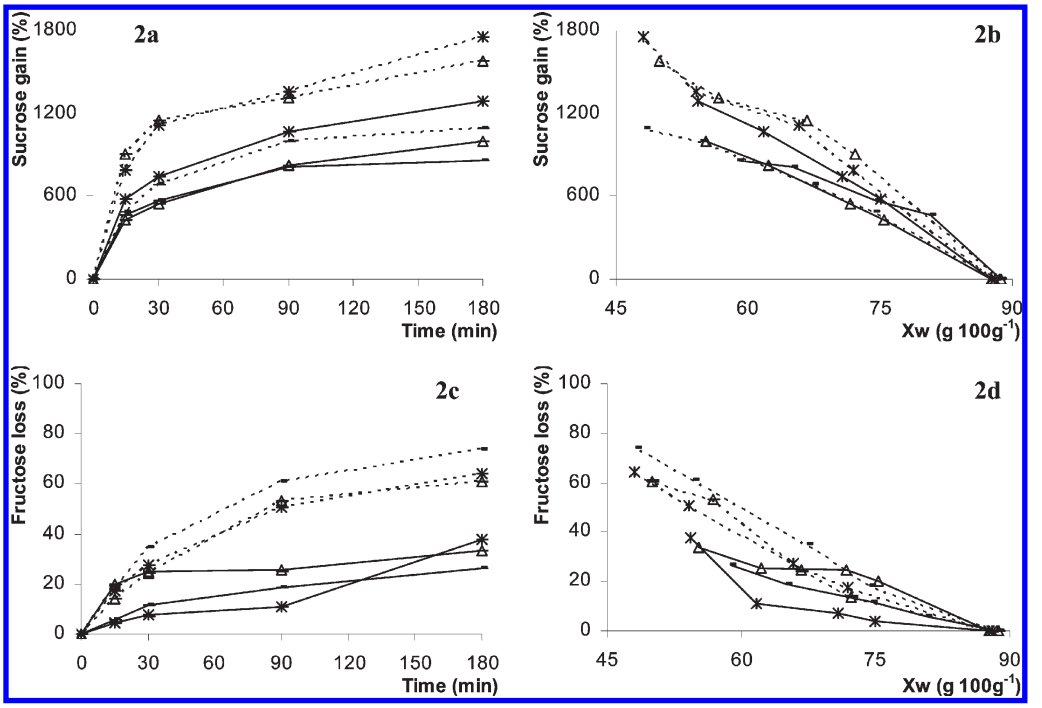


**Figure 2.** Sucrose gain and fructose loss during osmotic dehydration at 45 °C (full line) or 60 °C (dotted line) in Marie Menard (△), Guillevic (∗), and Gala (—); (**a**, **c**) versus time; (**b**, **d**) versus mean moisture content. Standard deviation = 205 and 10% for sucrose and fructose, respectively.

papaya and kiwi, temperature had also been found to be a very important factor, but ascorbic acid losses were much less marked in these cases (*2*, *23*). As an example, the loss was only 30% after 3.5 h of osmotic dehydration of the kiwi at 40 °C, but reached 90% at 50 °C (*23*). However, the kiwi contains higher levels of ascorbic acid than the apple, its concentration in raw fruit being around 600 mg $kg^{-1}$ (*23*), or 25−150-fold higher, which could explain why ascorbic acid losses during osmotic dehydration of the kiwi were slower. Furthermore, for the same water content of 70 g 100 $g^{-1}$, reached after 15 min of soaking at 60 °C, in our conditions, the loss of ascorbic acid was 10% higher. At 45 °C and for a processing time of > 15 min, this loss decreased in line with the soaking time. This could be explained by a combination of two factors: leaching with water diffusion (a rapid phenomenon, predominant at low temperatures and due to the high degree of ascorbic acid solubility in water) and chemical degradation (enhanced by temperature) (*2*). One important point that may explain the difference from previous studies on tropical fruits at low temperature is that during the present study, the apple cubes were sprayed with an antibrowning solution containing ascorbic acid; even if the cubes were rinsed before soaking, the ascorbic acid content measured (initial ascorbic acid in **Table 2**) was the sum of the sprayed ascorbic acid that had diffused into outer layers of the cubes and the natural ascorbic acid of the apples. Spraying thus increased the initial ascorbic acid content, as shown in **Table 2**, within the range 150−4000% depending on the experiment, and was mainly located on the surface of the apple cubes. This supplementary ascorbic acid would leach first and very rapidly with water, thus explaining the drastic percentage reduction observed as from the temperature of 45 °C. Another explanation could be that ascorbic acid plays an important role in regeneration of the *o*-quinones that result from the oxidation of phenols (chlorogenic acid or monomeric catechin) by polyphenol oxidase (enzymatic browning); under this hypothesis, ascorbic acid could be oxidized to dehydroascorbic acid (*52*).

**Figure 3** shows the losses affecting several polyphenol groups of compounds versus processing time and moisture content.

Panels **a** and **b** of **Figure 3** show the results for hydroxycinnamic acids. Losses were low at 45 °C: 27% in Gala and around 40% in cider apples after 180 min of soaking. At 60 °C, losses increased: 78% for Gala and around 60% for cider cultivars (**Figure 3a**). When plotted versus water content (**Figure 3b**), the loss of hydroxycinnamic acids appeared to be approximately proportional to the water content. As for fructose, temperature acted indirectly by increasing the water flux. No cultivar effect was observed, except for a slight difference in Gala at 60 °C. Dihydrochalcone losses (not shown here because of the small quantities detected in all cultivars) followed the same trend, with average losses of 37% at 45 °C and 62% at 60 °C.

Because Guillevic naturally contained no monomeric catechins, panels **c** and **d** of **Figure 3** show only the evolution of monomeric catechins in Gala and Marie Menard. The loss versus time curves were similar to those described for hydroxycinnamic acids, with total losses of around 27% at 45 °C and around 70% at 60 °C. However, when plotted versus water content, these losses were also linear, with a real difference between the two operating temperatures.

Panels **e** and **f** of **Figure 3** show the procyanidin losses observed. Because of the low procyanidin concentration in cv. Gala, the uncertainty regarding percentage variations was considerable and only the final values are presented. Procyanidins were the most preserved group of polyphenols, with only 15% lost at 45 °C and 40% at 60 °C. This may partly have been due to the polymerization of these molecules with a high molecular weight of up to 11−15 kDa (*46*), which hampers their migration. Another reason is that procyanidins are retained by weak interactions with cell wall polysaccharides (*36*). An increase in temperature from 45 to 60 °C exerted a different impact as a function of cultivar. In Marie Menard, the difference was measurable only at the end of the process and was mainly due to the difference in the final water content, whereas in Guillevic, a difference was clearly observed from the beginning of the process and was actually due to the increase in temperature, regardless of the water content. Procyanidins are polymers of monomeric catechins, and the difference

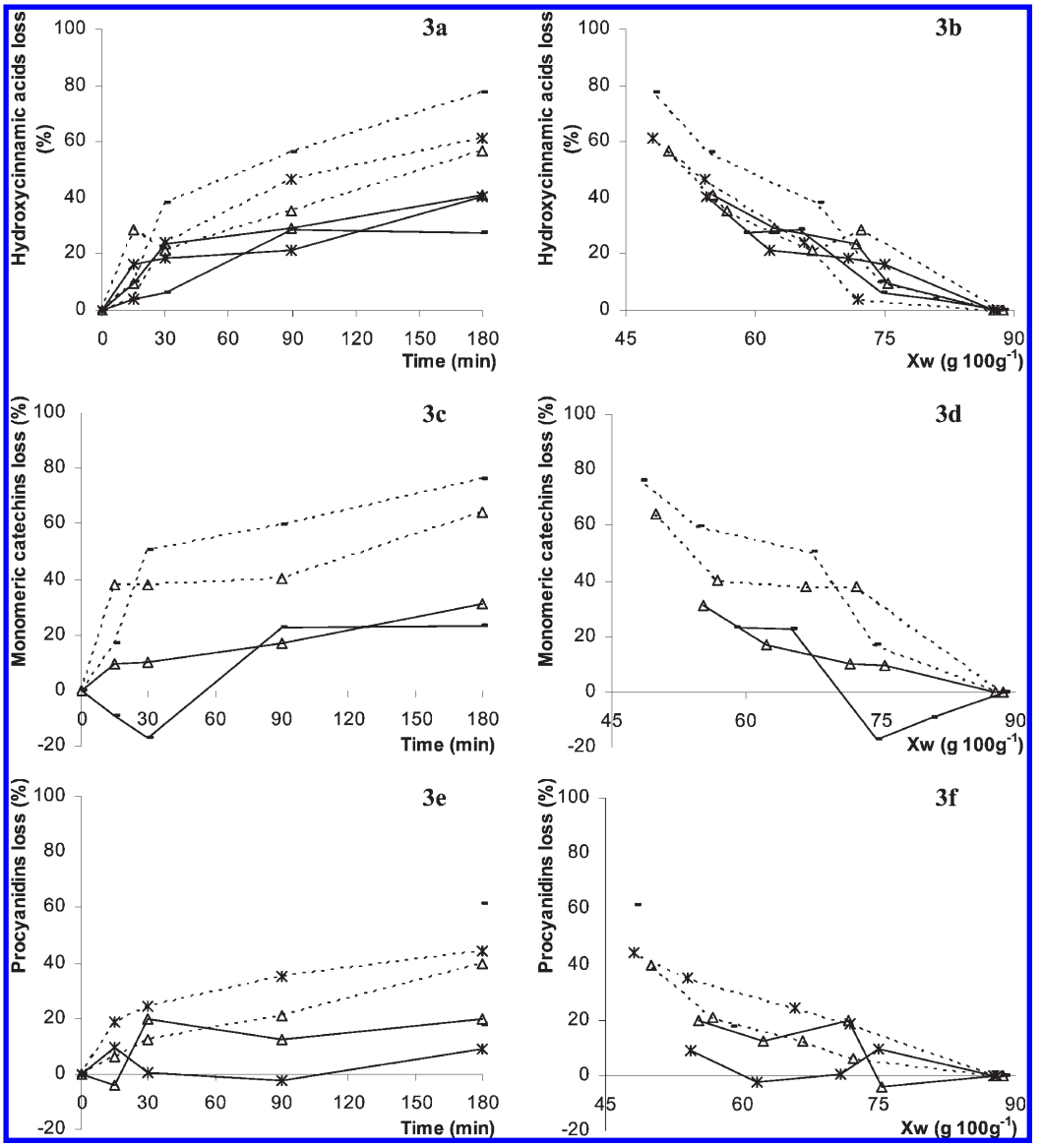


**Figure 3.** Losses of hydroxycinnamic acids, monomeric catechins, and procyanidins during osmotic dehydration at 45 °C (full line) or 60 °C (dotted line) in Marie Menard (△), Guillevic (∗), and Gala (—): (**a**, **c**, **e**) versus time; (**b**, **d**, **f**) versus mean moisture content. Standard deviation = 18, 5, and 8% for hydroxycinnamic acids, monomeric catechins, and procyanidins, respectively.

between cultivars was essentially due to the number of constitutive units. **Table 4** shows the time changes of the average degree of polymerization (DP*n*). Gala and Marie Menard had an initial DP*n* of 5, whereas Guillevic had a very high DP*n* of 63. The evolution of DP*n* with soaking time also differed. It remained constant, with a slight increase at 60 °C for long soaking times, in cultivars with a small DP*n* (Gala and Marie Menard), but increased similarly and significantly at both temperatures in cv. Guillevic. Oszmianski et al. (*34*) also observed an increase in DP*n* during the preparation of apple puree.

To our knowledge, no results concerning the loss of phenolic compounds during osmotic dehydration have been published to date, although similar trends have been observed during other processes: traditional sun-drying (*31*), conventional boiling (*32*), or vacuum impregnation (*32*). Whatever the process, the main losses concerned monomeric flavan-3-ols, as observed in **Figure 3c**,**d**, followed by hydroxycinnamic acids. When procyanidins were fully quantified (*30*, *31*), their losses were reduced, as during the present study (**Figure 3e**,**f**). The effect of processing therefore differed for procyanidins (which are polymerized molecules) and monomeric catechins (which reacted in the same way as hydroxycinnamic acids). In the latter group, two types of mechanisms could be considered. First, because they are small phenolic molecules devoid of tanning properties, they may diffuse into the osmotic solution. By contrast, oligomers and polymers of procyanidins are tannins that are well-known for their ability to associate with cell wall components through hydrophobic interactions and hydrogen bonding (*48*). As a consequence, they weakly diffuse in the osmotic solution. This hypothesis was also mentioned in another recent study, in which increasing proportions of hydroxycinnamic acids and small flavan-3-ols were measured in the liquid phase during the cooking of pears (*30*). The second mechanism may be enzymatic oxidation. Polyphenols, polyphenol oxidase (PPO), and oxygen may be placed in contact during peeling and cutting or when cell integrity is injured by thermal or hydrodynamic mechanisms (*31*). Moreover, both chlorogenic acid and catechins are involved in enzymatic browning. PPO has a stronger affinity for chlorogenic acid (*49*), but the latter can be regenerated by coupled oxidation involving catechins. Renard (*30*) emphasized that oxidation required enzymatic activity and was therefore relevant only during the first few minutes of heating. Quiles et al. (*53*) studied the effects of osmotic

**Table 4.** Average Degrees of Polymerization (DP*n*) Measured during Osmotic Dehydration at 45 or 60 °C for Gala, Guillevic, and Marie Menard Apples[a]

| | Gala | | Guillevic | | Marie Menard | |
|---|---|---|---|---|---|---|
| time (min) | 45 °C | 60 °C | 45 °C | 60 °C | 45 °C | 60 °C |
| 0 | 5 | 5 | 63. | − | 5 | 4 |
| 15 | 7 | 4 | 62 | 58 | 5 | 4 |
| 30 | 5 | 6 | 66 | 55 | 6 | 4 |
| 90 | 6 | 6 | 66 | 60 | 6 | 4 |
| 180 | 5 | 6 | 73 | 73 | 6 | 5 |

[a] Data expressed as mean, standard deviation = 10%. −, no data obtained for this point due to experimental problem.

dehydration (sucrose 65 °Brix, 25 °C, apple/solution ratio = 50:1) on PPO and concluded that PPO activity decreased in line with soaking duration because of shrinkage of the parenchyma flooded with osmotic solutes and a reduction in $O_2$ availability in the microstructure surrounding the enzyme. Enzymatic oxidation was certainly reduced under our osmotic dehydration conditions because no significant changes affected chlorogenic acid between experiments at 45 and 60 °C (**Figure 3b**). Akyildiz and Ocal (*54*) also showed that an increase in drying temperature from 60 to 80 °C did not affect the activity of apple PPO, but only 20% of initial activity remained after 1 h and only 2% after 2 h. They also proved that enzymatic activity differed markedly as a function of cultivar. Degradation by enzymatic oxidation was certainly negligible under our conditions, and hydroxycinnamic acid and monomeric catechin losses were certainly mainly due to leaching and water diffusion into the osmotic solution.

Procyanidins could not diffuse into the liquid phase because of their high molecular weight and also because they were probably linked by weak interactions with cell wall polysaccharides (*34*,*36*,*47*,*48*). Nevertheless, their content slowly diminished with processing time, and this was certainly due to a loss of cell membrane integrity after a certain period of processing. Other hypotheses could also be put forward: involvement in coupled oxidative reactions (*31*) or thermal degradation by acidolysis (*33*) splitting the terminal units of procyanidins in (+)-catechin and (−)-epicatechin.

From our study, the behavior of natural compounds in apples during osmotic dehydration appeared to differ, and their evolutions throughout the process were not all linked to the temperature applied. Water loss was temperature-dependent and positively correlated with time. Temperature had no impact on solute impregnation, which was mainly affected by the water content. By contrast, glucose, fructose, and ascorbic acid levels were mostly influenced by temperature, and losses were thus due to diffusion. Other phenomena seemed to affect ascorbic acid losses, but were of less importance. Diffusion was also the reason for losses of hydroxycinnamic acids and monomeric catechins and increased in line with soaking temperatures. Procyanidin losses could be induced by many factors but were less than those of other polyphenols because of their binding with cell wall polysaccharides.

Finally, from a technical point of view, and even if water losses were slightly lower, a moderate temperature such as 45 °C may be nutritionally beneficial because it reduces fructose, glucose, or ascorbic acid losses and limits sucrose impregnation. Furthermore, because soaked apples are unstable, further drying is necessary to stabilize the product. The duration of osmotic dehydration should between 15 and 60 min so that the losses of natural compounds will be reduced.

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