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Apple Pomace Is a Good Matrix for Phytochemical Retention

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ABSTRACT: Phytochemical content and color changes in dried apple pomace and pulp (mixture of Red Delicious and Golden Delicious varieties) were studied during 9 months storage in the water activity (a_w) range 0.11−0.75 at 30 °C. Water mobility was measured at various a_w levels by ^{1}H NMR. During storage, antioxidant degradation (including flavonols, flavanols, dihydrochalcones, anthocyanins, and hydroxycinnamic acids) followed first-order kinetics, whereas color changes followed zero-order kinetics. These changes were accelerated by increasing a_w. Phytochemical and color were more stable in the pomace than in the pulp over the entire a_w range, having 2−6 times smaller degradation rates. These results were related to the lower water mobility found in apple pomace as compared to the pulp. The overall results show that apple pomace can be exploited as a food ingredient with good phytochemical retention, and may help in the development of new matrices with maximum phytochemical retention.

KEYWORDS: *apple pomace, water mobility, water activity, antioxidant, color*

INTRODUCTION

Consumption of apples has been linked to the prevention of coronary disease, cerebrovascular disease, lung cancer, and obstructive pulmonary disease.[1] These health-promoting properties have been attributed to fiber and phenolic compounds present in apples, which may act synergistically.[2,3] Apple fiber is composed of cellulose (43.6%), hemicellulose (24.4%), lignin (20.4%), and pectin (11.7%).[4]

Dietary fiber decreases postconsumption blood glucose and insulin levels.[3] The products of microbiological fiber fermentation enhance intestinal health and lower total cholesterol and LDL levels.[3]

The primary structural classes of apple phenolics include monomeric (epicatechin and catechin), dimeric, trimeric, and oligomeric flavanols; hydroxycinnamates (chlorogenic acid and *p*-coumaric acid derivatives); dihydrochalcones (phloridzin, i.e. phloretin 2′-*O*-glucoside, and phloretin 2′-*O*-xyloglucoside); flavonols (quercetin glycosides); and anthocyanins (cyanidin glycosides).[1]

Polyphenol-rich extracts from apple were found to effectively diminish DNA oxidation damage by reduction of the cellular level of reactive oxygen species. This preventive effect is attributable to induction of cellular defenses rather than to the radical scavenging activity of these compounds.[5]

It has been estimated that about 70% of apples are consumed fresh, whereas 30% of apples are consumed after processing into juice, cider, purees, jams, and dried products. A huge amount of apple pomace results from the worldwide processing of apples and consists of skin, seeds, stems, and residual flesh.[6] The pomace actually contains much of the phytochemicals and fiber found in whole apples. As such, sustainable procedures for extracting apple pomace phenolics have been proposed.[7,8] Alternatively, whole apple pomace has been considered as a potential value-added food ingredient.[9]

The enrichment of food with apple pomace could be an effective way both to enhance its nutritional value and to modulate food rheological and thermal properties. Soukoulis et al.[10] studied the effect of enrichment of ice cream with apple fiber to control crystallization and recrystallization phenomena. Sun-Waterhouse et al.[11] developed a functional snack bar which included apple dietary fiber and apple phenolic extract. Ibraim et al.[12] found that apple pomace can be used as a clouding agent and radical scavenger in cloudy apple juice.

Most apple pomace is accumulated during the fruit ripening season, typically from July to October. To be used as a stable commercial ingredient, the pomace needs to be dried to limit microbial growth. The stability and physical properties of the dried product, however, depend on the final water activity (a_w) attained after drying. In addition, moisture migration may occur during storage depending on the environmental relative humidity, resulting in changes in the a_w of the product. The a_w level in turn affects the rate of degradation reactions.[13] While a_w has proven to be an adequate marker for food stability, the exact role that water plays in the chemical reactions that occur at low moisture is complex and not well understood. Many theories posit that water mobility is the limiting factor that controls reaction rates at low moisture. Various approaches have been used to assess moisture mobility including nuclear magnetic resonance (NMR), dielectric spectroscopy, electron spin resonance, and differential scanning calorimetry.[14]

The aim of this study was to investigate the fiber and phytochemical contents of dried apple pomace as compared to apple flesh, and to measure the kinetics of antioxidant degradation and color changes as a function of a_w. In addition, ^{1}H NMR was used to assess water mobility in dried samples and results were related to the observed reaction kinetics.

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MATERIALS AND METHODS

Materials. Standards of epicatechin, procyanidin B2, quercetin 3-*O*-galactoside, and cyanidin 3-*O*-galactoside were purchased from Extrasynthese (Lyon, France). The integrated total dietary fiber assay procedure kit was purchased from Megazyme International Ireland Ltd. (Bray, Ireland). All other chemicals were purchased from Sigma Aldrich (Milan, Italy).

Apple Pomace and Pulp. A batch of apple pomace (30% Red Delicious and 70% Golden Delicious varieties) was recovered from an industrial plant (Conserve Italia, San Lazzaro di Savena, Italy). At the plant, fruits were washed, sorted, and fed into a continuous puree processing line. The first step consisted of pitting and crushing in the presence of ascorbic acid (0.5 g/kg). The pulp was heated to 100 °C by steam injection and passed hot through a 0.5 mm screen pulper/finisher to produce a puree. The pomace, consisting of mainly peels with some seeds and stalks, was collected from the screen and immediately frozen at −20 °C. The pomace was then transported frozen to the lab.

A pulp sample was produced at the lab to compare with the industrial pomace, using the same apple varieties processed at the industrial plant. To this end, fruits were sorted, peeled, decored, and cut into eight slices. Apple pieces were blanched for 4 min in 100 °C deionized water, then immersed in ice water, drained over paper towels, and pureed in a K 3000 Braun Multisystem food processor (Braun, Kronberg, Germany) for 3 min. Both apple pomace and pulp were freeze-dried. The temperature profile of the freeze-drying shelves was set to −45 °C for 8 h, −20 °C for 24 h, 0 °C for 24 h, and 10 °C for 10 h. The chamber pressure was maintained at 30 Pa throughout the drying process.

Soluble and Insoluble Fiber, Protein, Fat, and Ash. Fiber, protein, fat, and ash values of apple pomace and pulp were measured according to AOAC official methods of analysis.[15] Soluble (SDF) and insoluble (IDF) fiber contents were determined by the Megazyme total dietary fiber assay procedure (based on AOAC 991.43). Protein content was measured by the Kjehdahl method (AOAC 22.052), fat content by extraction in diethyl ether (AOAC 14.126), and ash content by ashing at 500 °C (AOAC 22.027).

Soluble Solids. Freeze-dried apple pomace and apple pulp were separately mixed with water (0.5 g of powder in 20 mL). The mixtures were equilibrated at 20 °C and filtered through Whatman No. 4 filter paper. Soluble solids were measured at 20 °C using a RFM 340 refractometer (Bellingham & Stanley Ltd., Tunbridge Wells, U.K.), and expressed as °Brix (grams of sucrose per 100 g of dry product).

Storage Study. Freeze-dried samples of pomace and pulp were ground into powders and sieved (800 μm). The powders were weighed into Petri dishes (6 cm diameter, 5.5 g of product in each dish). The open dishes were then placed into airtight plastic chambers on wire-mesh racks situated above saturated salt solutions. The solutions created different relative humidity environments in the air inside the chambers. The chambers were stored for up to 9 months in the dark at 30 °C in a thermostated cabinet. To create different relative humidity environments, the following saturated salt solutions were used: LiCl (a_w = 0.113), CH_3COOK (a_w = 0.216), $MgCl_2$ (a_w = 0.324), NaBr (a_w = 0.560), NaCl (a_w = 0.7509). Duplicate chambers were held at 30 °C for each a_w level studied.

Moisture Content and a_w. Moisture contents of the apple products were calculated by drying in a vacuum oven at 70 °C and 50 Torr for 18 h. The a_w of saturated salt solutions was measured at the beginning of storage; the a_w of apple products was measured at regular time intervals during storage, using a dew-point hygrometer (Aqualab, Decagon Devices, WA). Triplicate determinations were made for each sample.

Moisture isotherms were developed for the apple samples by plotting the equilibrium moisture content (m) versus the storage a_w. The Guggenheim−Anderson−de Boer (GAB) equation was used to fit the experimental data:

$$m = \frac{m_0 C k a_w}{(1 - k a_w)(1 - k a_w + C k a_w)} \quad (1)$$

where m is the equilibrium moisture content on a dry basis (g of water/g of dry solids); m_0 is the monolayer moisture content on a dry basis; C and k are constants related to the interaction energies of the first and subsequently adsorbed water molecules.[13]

Nuclear Magnetic Resonance Studies. Apple powders equilibrated at each relative humidity were analyzed in a 20 MHz ^{1}H NMR spectrometer (Resonance Instruments, Whitney, U.K.). Samples from the controlled humidity chambers were rapidly transferred to 18 mm diameter glass NMR tubes to a height of approximately 20 mm. The tubes were then sealed to prevent moisture pickup from the environment. Samples were analyzed using free induction decay to determine T_2* times. A single 90° pulse was used at 4.1 μs with a recycle delay of 2 s. All analyses were conducted at 22 °C.

Ascorbic Acid. Ascorbic acid content was determined as described previously.[16] Pomace samples were analyzed in duplicate at the beginning of storage. In brief, aliquots of 0.8 g of dehydrated apple pomace or apple pulp samples were extracted with 5 mL of 6% metaphosphoric acid containing 1 g/L of sodium metabisulfite. The mixture was vortexed for 2 min, stirred for 30 min, and then centrifuged at 9000*g* for 10 min at 15 °C. The supernatant fraction was filtered through Whatman No. 4 filter paper.

To determine ascorbic acid concentration, extract samples were applied to a Bio-Rad Fruit Quality Analysis column (300 × 7.8 mm i.d). Chromatographic separation was performed with 1 mM H_2SO_4 as an eluent under isocratic conditions, 1 mL/min flow rate, and at room temperature (∼23 °C). Ascorbic acid was detected at 245 nm and quantified using a calibration curve built with a pure standard. Concentrations were expressed as milligrams per kilogram of dry product.

Phenolic Compounds. Phenolic compounds were analyzed as described previously.[16] Pomace samples stored at various a_w levels were analyzed in triplicate at the beginning of storage and in duplicate after 13, 63, 134, and 275 d of storage at 30 °C. Aliquots of 0.8 g of apple pomace or apple pulp samples were extracted with 10 mL of acetone/water at a ratio of 70:30 by volume. The mixture was vortexed for 2 min, stirred for 30 min, and then centrifuged at 9000*g* for 10 min at 15 °C. The supernatant fraction was filtered through Whatman No. 4 filter paper. To determine phenolic concentration, extract samples were applied to a 250 × 4.6 mm i.d., 5 μm, Symmetry reverse phase C-18 column (Waters, Vimodrone, Italy) equipped with a Symmetry C-18 precolumn. Formic acid (5%) was added to both methanol and water before preparing the following mobile phase: (A) water/methanol (95:5, v/v); (B) water/methanol (88:12, v/v); (C) water/methanol (20:80, v/v); and (D) methanol. The following gradient elution was used: 0−5 min, 100% A; 5−10 min linear gradient to reach 100% B; 10−13 min 100% B; 13−35 min linear gradient to reach 75% B and 25% C; 35−50 min linear gradient to reach 50% B and 50% C; 50−52 min linear gradient to reach 100% C; 52−57 min 100% C; 57−60 min 100% D. The injection volume was 20 μL and flow rate was 1 mL/min.

Standards of chlorogenic acid, *p*-coumaric acid, epicatechin, procyanidin B2, phloridzin, cyanidin 3-*O*-galactoside, and quercetin 3-*O*-galactoside were used to identify peaks by retention times and UV−vis spectra, and to build calibration curves for quantification. A peak was tentatively assigned to phloretin 2′-*O*-xyloglucoside based on its UV−vis spectrum and literature data, and quantified at 280 nm using the calibration curve built with phloridzin. The presence of a *p*-coumaric acid ester was revealed by alkaline hydrolysis.[16] Phloridzin and the other dihydrochalcone, epicatechin, procyanidin B2, and unidentified procyanidins were quantified at 280 nm; chlorogenic acid at 330 nm; *p*-coumaric acid ester at 311 nm; cyanidin 3-*O*-galactoside at 520 nm; quercetin 3-*O*-galactoside and other quercetin glycosides at 360 nm. Concentrations of phenolic compounds were expressed as milligrams per kilogram of dry product. For each compound, the initial concentration (C_o) and the concentrations during storage at each a_w (C) were analyzed over time (t) and fitted to a first-order kinetic model:

$$\ln C = \ln C_0 - kt \quad (2)$$

The reaction rate constant (k) was then calculated at each storage a_w.

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Color. Color evaluation of pomace samples stored at various a_w levels was performed in triplicate at 0, 7, 13, 36, 79, 134, and 275 d of storage. Color was measured with a Chroma meter II (Konica Minolta, Osaka, Japan), which provides the Hunter L^*, a^*, and b^* coordinates representing lightness and darkness (L^*), red ($+a^*$) to green ($-a^*$), and yellow ($+b^*$) to blue ($-b^*$). The chromameter was calibrated with a white standard tile. Petri dishes containing the pomace samples were covered with a glass cover, and the head of the colorimeter was put directly on top of the glass to take color measurements. For sample lightness, the initial value (L^*_0) and the values during storage at each a_w (L^*) were analyzed over time (t) and fitted to a zero-order kinetic model:

$$L^* = L^*_0 - kt \quad (3)$$

The reaction rate constant (k) was then calculated at each storage a_w.

Statistical Analysis of Data. Experimental data were analyzed by one-way ANOVA using the least significant difference (LSD) as a multiple range test, and by linear and nonlinear regression analyses using Statgraphics 5.1 (STCC Inc.; Rockville, MD).

RESULTS AND DISCUSSION

Chemical Composition. The chemical composition of apple pomace obtained from a mixture of Red Delicious and Golden Delicious varieties is shown in Table 1. Total dietary fiber content was 59.2 g/100 g dw, of which IDF was 46.1 g/100 g dw and SDF was 13.1 g/100 g dw. These values are in agreement with others found for apple pomace[6,17] and commercial apple fiber.[10] Apple varieties, however, differ in their total fiber content and the ratio of insoluble and soluble fiber. The factors of variation are genetic. In fact, in a previous study it has been shown that the IDF/SDF ratio varies between 12.9:1 in Granny Smith and 4.5:1 in Royal Gala apples. Total dietary fiber ranges from 60.7 g/100 g for Granny Smith to 89.8 g/100 g for Liberty apples.[17] Apple pulp had relatively lower fiber, with 6.8 g/100 g dw IDF and 4.4 g/100 g dw SDF. The fat and protein contents of apple pomace were 6.5 and 6.7 g/100 g dw, respectively, while those for pulp were 0.46 and 1.2 g/100 g dw. Fat content in pomace was higher than that found previously.[6,17] As apples had not been waxed, this difference probably depends on the different proportions of seeds remaining in the pomace. Similarly, protein content was higher than that found previously.[6,17] Indeed in our study the seeds were collected together with the skins and stems, whereas in a previous study the pomace was recovered from processing of cored apples.[17] The ash content of apple pomace was 1.8 g/100 g dw. The ash contents also shows a wide variability among pomace samples, ranging from 0.5 to 6 g/100 g dw.[6] Soluble solids in apple pomace were 24 g/100 g dw, and for pulp 70 g/100 g dw. This fraction consists of a mixture of simple sugars (fructose, glucose, and sucrose) and organic acids (mainly malic acid).[18]

Table 1. Major Components, Antioxidants and Colorimetric Parameters (mean ± SD) of the Pomace and Pulp of a Mixture of Golden Delicious and Red Delicious Apple Varieties

quality index	pomace	pulp
major components (g/100 g dw)		
soluble fiber	13.1 ± 0.9	4.4 ± 0.4
insoluble fiber	46.1 ± 0.6	6.8 ± 0.4
protein	6.7 ± 0.3	1.2 ± 0.1
fat	6.50 ± 0.10	0.46 ± 0.01
ash	1.8 ± 0.1	1.3 ± 0.1
soluble solids (sucrose equiv)	24 ± 2	70 ± 6
antioxidants (mg/kg dw)		
monomeric and dimeric flavanols	1064 ± 60	850 ± 50
hydroxycinnamic acids	714 ± 40	885 ± 30
dihydrochalcones	1709 ± 80	120 ± 10
flavonols	2032 ± 80	
anthocyanins	130 ± 7	
ascorbic acid	55 ± 5	130 ± 10
colorimetric parameters		
L^*	54.0 ± 3.0	78.0 ± 1.0
a^*	3.5 ± 0.2	−1.3 ± 0.1
b^*	11.1 ± 1.3	21.9 ± 0.8

Hygroscopicity and Water Mobility. The moisture sorption isotherms for apple pomace and pulp are shown in Figure 1A. Apple pomace was less hygroscopic than the pulp, especially at $a_w \geq 0.32$. In fact, when apple pomace was equilibrated at relative humidity ≥ 32%, it adsorbed much lower water than the pulp stored under the same conditions. In a previous study, Aguilera et al.[19] characterized the cell wall material of apple for its sorption properties. The cell wall material primarily contains the water-insoluble structural carbohydrate fraction. In this study, the sorption isotherm of apple pomace was most similar to that developed by Aguilera et al.[19] for isolated apple cell wall material, and similar to that of microcrystalline cellulose, which was also reported in the above paper. For apple pomace, fitting to the GAB model gave constants of C = 8.2, K = 1.0, and monomolecular moisture content m_0 = 3.87 g of moisture/100 g of dry solids, corresponding to an a_w level of 0.26. Similarly, Aguilera et al.[19] found an m_0 value of 3.40 g of moisture/100 g of dry solids for the apple cell wall material. On the other hand, the sorption isotherm of apple pulp is similar to that found for amorphous fructose and sucrose, the main sugars in apple pulp.[19] Also, the higher lipid content of apple pomace should be considered, as it contributes to lower equilibrium moisture content in the corresponding isotherm at a_w values between 0.4 and 0.8.[20] Thus, the isotherms were recalculated using moisture content based on "dry solids" and not including the lipid fraction. After this recalculation, the isotherms of apple pulp and pomace were still different, suggesting that the higher hygroscopicity of apple pulp was attributable to amorphous sugars (Figure 1B).

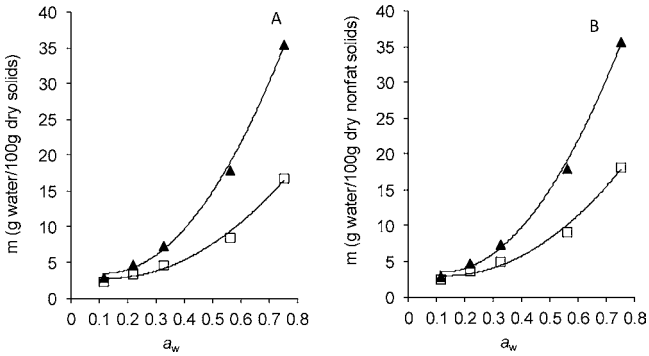

Figure 1. Absorption isotherms for freeze-dried apple pulp (▲) and apple pomace (□) at 30 °C. Curves were fitted by the GAB equation. (A) % of moisture with respect to dry solids as a function of a_w. (B) % of moisture with respect to dry solids not including the lipid fraction as a function of a_w.

Several theories ascribing the role of a_w in chemical reaction rates in low moisture foods suggest that both concentration of

reactants and their relative mobility are critical factors.[13,21] The mobility of water, both as a participant in reactions and as a medium in which other molecules move, is therefore critical. In this study ^{1}H NMR free induction decay was used to study water mobility in dried apple samples as a function of a_w. As shown in Figure 2, the NMR data were indicative of increasing

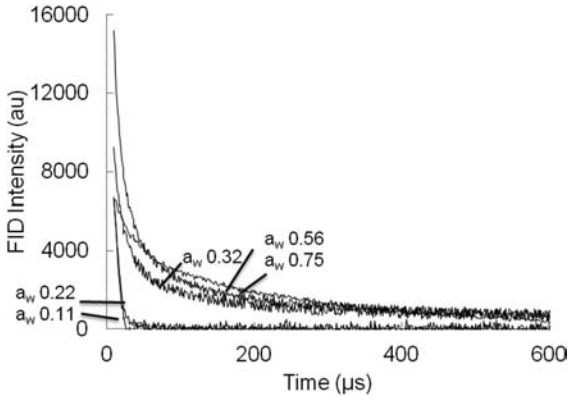

Figure 2. ^{1}H NMR free induction decay of dried apple as a function of a_w.

water mobility with increasing a_w. Samples at a_w of 0.11 or 0.22 had signals that decayed within 40 μs, indicative of solid-like behavior. That is, protons in these systems have limited mobility and more time in which they can interact and exchange spins. At a_w of 0.32 and above, the signal decayed over several hundred microseconds. While this is not the highly mobile domain associated with bulk water, it does show enhanced mobility within a viscous domain. This suggests that, at $a_w \geq 0.32$, there may be an adsorbed water layer with an additional aqueous phase with enhanced mobility, and increasing mobility of polymers. Unfortunately, the method is not sensitive enough to distinguish which protons have increased mobility and which do not. Indeed, at a given a_w value, some molecules can be mobile, while other are not.

Interestingly, even at $a_w \geq 0.32$ water mobility in apple pomace was much lower than that found in apple pulp.[22] In fact, for apple pulp held at $a_w \geq 0.32$, the ^{1}H NMR free induction decay curves show decay over thousands of microseconds, which were better fitted by a 2-component model. The fast decaying component (T_{2a}) was 44.2 and 60.4 μs at a_w of 0.56 and 0.75, respectively, and can be attributed to relaxation processes in the solid component with enhanced mobility due to the plasticization of water. The slower decaying component (T_{2b}) was 305.6 and 526.1 μs at a_w of 0.56 and 0.75, respectively, and can be attributed to more mobile water not closely associated with larger molecules. Changes in moisture content or mobility in apple pulp greatly affected the rate of color variations and phytochemical degradation, with maximum stability being in the region were water is strongly bound to solids, as suggested by both ^{1}H NMR data and isotherm modeling.[22]

Phytochemical Content and Kinetics of Degradation. The antioxidant contents of apple pomace obtained from a mixture of Red Delicious and Golden Delicious varieties are shown in Table 1. The pomace contained 2032 mg/kg dw flavonols (quercetin glycosides), among which quercetin 3-*O*-galactoside (32%) was the main component. No flavonols were measured in the pulp. The pomace contained 1709 mg/kg dw of dihydrochalcones, with phloridzin being the main component (74%), while the pulp contained only 120 mg/kg dw. Dihydrochalcone content has been found to be quite high in apple seeds.[23] The sum of monomeric and dimeric flavanols was 1064 mg/kg dw in the pomace, and 850 mg/kg dw in the pulp. Among these compounds we identified epicatechin (56%) and procyanidin B2 (23%). The pomace contained 714 mg/kg dw of hydroxycinnamic acids, the main being chlorogenic acid (96%), while the pulp contained 885 mg/kg dw. The anthocyanin cyanidin 3-*O*-galactoside was present at 130 mg/kg dw in the pomace. In previous papers on apple pomace composition ascorbic acid content has not been considered.[6] We measured the amount of ascorbic acid in apple pomace as this compound was added during puree processing (as described in Material and Methods). Indeed, ascorbic acid is generally added during apple puree processing to control browning.[12,24] The residual amount of ascorbic acid was very low (55 mg/kg dw), most likely due to its thermal degradation and oxidation during processing, as observed previously.[25]

Van der Sluis et al.[26] showed that phenolics of whole fresh apples have high storage stability under controlled atmosphere conditions at 1.5 °C; they found that most of the identified phenolic compounds do not vary significantly in concentration up to 50 weeks. However, phenolic stability decreases upon processing. Rossle et al.[27] have reported that, for minimally processed skin-on apple wedges, storage has a great effect on phenolic content, which decreases significantly within 5 days at 4 °C, due to polyphenol oxidase activity. As found by Oszmianzky et al.,[24] during apple puree processing, polyphenol oxidase is deactivated; however phenolic degradation occurs in bottled apple puree during storage at 30 °C. After 6 months of storage of apple puree, cyanidin 3-*O*-galactoside is not detectable, and the losses of other phenolics are in the range 30−70% for flavanols, 20−30% for chlorogenic acid, and 5−10% for phloridzin.[24] In fresh apple and apple puree, phenolics are "diluted" in a large amount of water. In intermediate moisture apple (a_w 0.75) phenolics are concentrated, and this accounts for their lower stability during storage in air at 30 °C.[28] However, when water content is decreased close to the dry state (a_w 0.11) phenolic stability greatly increases.[29] Decreasing water decreases chemical reaction rates as water may act as reactant and solvent. Furthermore, water reduces the viscosity of the matrix due to plasticization and increases the mobility of reactants.[13]

In this study, phenolic stability was investigated in dehydrated apple pomace, and it was related to water mobility. Changes in phenolic contents during storage were well-fitted to a first-order kinetic model, as also observed for apple pulp.[22] An example of this degradation is shown in Figure 3. The first-order reaction constants for antioxidant loss are reported in Table 2. In the a_w range 0.11−0.22, only cyanidin 3-*O*-galactoside showed measurable changes. This is also the range over which NMR results showed there is limited water mobility. At a_w 0.32, epicatechin and procyanidin B2 were also degraded, whereas above this value the contents of all phenolics decreased. The exception was phloridzin, which had measurable changes only at a_w 0.75.

Therefore, for all antioxidants the stability decreased with increasing a_w. Phenolic degradation occurring in apple pomace was then compared to that occurring in apple pulp.[28,29] The various apple phenolics showed similar "stability ranking" in both the pulp and pomace of apple, but their degradation occurred on a very different time scale (Table 2). In general, phenolic degradation was much slower in the pomace than in

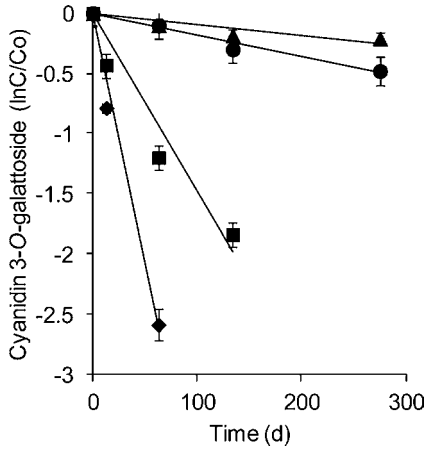

Figure 3. Changes in cyanidin 3-*O*-galactoside content during storage of apple pomace at the a_w levels of 0.11 (▲), 0.32 (●), 0.56 (■), and 0.75 (◆), at 30 °C. Variations were fitted to a first-order kinetics.

the pulp. In apple pomace, epicatechin degradation was significant above a_w 0.32, and the half-life decreased from 384 to 40 d when the a_w was increased from 0.32 to 0.75. In comparison, in apple pulp the half-life of epicatechin decreased from 65 to 20 d when the storage a_w increased from 0.11 to 0.75. For procyanidin B2, the half-life decreased from 414 to 26 d in apple pomace and from 43 to 13 d in apple pulp, when a_w was increased from 0.32 to 0.75. For chlorogenic acid, the half-life decreased from 713 to 319 d in apple pomace, and from 345 to 138 d in apple pulp in the a_w range 0.56−0.75. Phloridzin, which was relatively more stable, had a half-life of 698 d in apple pomace and of 138 d in apple pulp at the a_w level of 0.75.

From the rate constants reported in Table 2, the percent of degradation of individual phenolic compounds was calculated after 6 months of storage at 30 °C. This calculation allowed a direct comparison to be made with the stability of phenolics in apple puree that was reported previously.[24] This showed that dehydration of apple pomace to $a_w \leq 0.32$ increased the stability of all phenolics with respect to their stability in apple puree. However, this effect was not observed with dehydration of apple pulp at $a_w \leq 0.32$. For instance, after 6 months of storage at 30 °C, phloretin content did not vary in apple pomace at $a_w \leq 0.32$; it decreased by about 10% in apple puree,[24] and it decreased by 63% in dehydrated apple pulp at $a_w \leq 0.32$.[29]

Color. As seen in Table 1, the apple pomace was darker (lower L^* value), more red (higher a^* value), and less yellow (lower b^* value) than the apple pulp. During storage of dehydrated pomace the lightness index, L^*, decreased, especially at $a_w \geq 0.56$, according to zero-order kinetics (Figure 4). The zero-order rate constants are reported in Table 3. The redness index a^* initially decreased, as expected from anthocyanin degradation, then it increased slightly, most likely due to the formation of brown compounds from phenolic oxidation and/or Maillard reaction. The yellowness index, b^*, first increased then decreased (Figure 4). Similar behavior was observed in anthocyanin-rich peach puree[25] but not in apple pulp, which does not contain anthocyanins.[28,29]

Changes in L^* were far slower in the dehydrated apple pomace than in the dehydrated apple pulp. In fact, the zero-order rate constants for decreasing L^* in the pomace were 0.026 and 0.032 CU d^{-1} for samples stored at a_w 0.56 and 0.75, respectively. In apple pulp stored at the same a_w levels, the zero-order rate constants for decreasing L^* were 0.139 and 0.180 CU d^{-1}. In parallel, a^* increased sharply in the pulp, indicating the occurrence of browning.[29]

Overall Picture of Apple Pomace Stability as Compared to Apple Pulp. In general, the antioxidants and color were more stable in apple pomace than in the pulp. This result could be related to the relatively lower water mobility in apple pomace than in the pulp. As mentioned previously, there are structural and compositional differences between the two dried materials. As it encompasses more peel, pomace contains a greater fraction of compact plant cells and cell wall polysaccharides that give rigidity to the epidermal layer. The pulp contains more loosely associated parenchymal cells that

Table 2. First-Order Rate Constant (k_{pomace}, Mean ± SE), Correlation Coefficient (R), Predicted Half-Life ($t_{1/2}$), and First-Order Rate Constant Observed in the Pulp versus the First-Order Rate Constant Observed in the Pomace (k_{pulp}/k_{pomace}) for the Degradation of Major Antioxidants in Apple Pomace during Storage at Different a_w Levels at 30 °C

antioxidant	a_w [a]	k_{pomace} (d^{-1})	R	$t_{1/2}$ (d)	k_{pulp}/k_{pomace} [b]
cyanidin 3-*O*-galactoside	0.11	0.00092 ± 0.00039	−0.83	748	
	0.22	0.0018 ± 0.0006	−0.81	384	
	0.32	0.0019 ± 0.0007	−0.82	350	
	0.56	0.014 ± 0.002	−0.95	50	
	0.75	0.041 ± 0.003	−0.97	17	
quercetin 3-*O*-galactoside	0.56	0.00065 ± 0.00023	−0.69	1058	
	0.75	0.0067 ± 0.0008	−0.94	103	
epicatechin	0.32	0.0018 ± 0.0007	−0.69	384	5.9
	0.56	0.0066 ± 0.0024	−0.75	104	3.2
	0.75	0.017 ± 0.003	−0.91	40	2.0
procyanidin B2	0.32	0.0017 ± 0.0008	−0.80	414	9.5
	0.56	0.021 ± 0.004	−0.97	33	1.8
	0.75	0.026 ± 0.004	−0.93	26	2.1
chlorogenic acid	0.56	0.00097 ± 0.00023	−0.95	713	2.1
	0.75	0.0022 ± 0.0002	−0.80	319	2.3
phloridzin	0.75	0.00099 ± 0.00050	−0.71	698	5.1

[a] All compounds were studied in the a_w range 0.11−0.75; when kinetic parameters are not reported, degradation was not significant ($p \geq 0.05$). [b] Rate constants are compared to those reported elsewhere for antioxidant degradation in apple pulp under the same storage conditions.[27,28]

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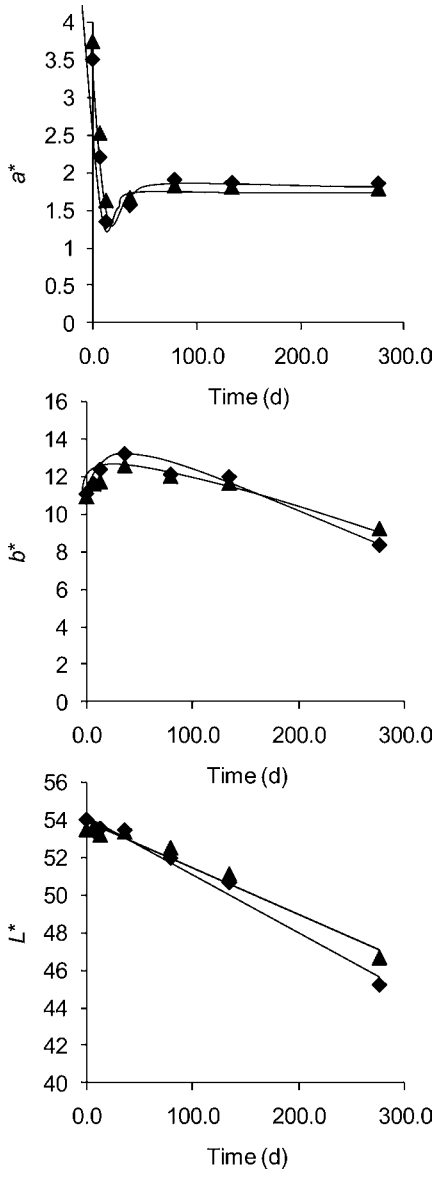

Figure 4. Changes in the Hunter's colorimetric parameters during storage of apple pomace at the a_w level of 0.56 (▲) and 0.75 (◆), at 30 °C. L^* variation was fitted to a zero-order kinetics.

incorporate vacuoles and contains much of the sugars and organic acids that give apples a characteristic taste. During drying and subsequent grinding, some of the compartmentalization may have been lost, but the dried pomace still has substantial cell wall polysaccharides, while the pulp has a greater fraction of low molecular weight sugars. Thus, the pulp has a greater tendency to bind water, promoting a higher molecular mobility environment. Relatively low molecular weight sugars can also act as plasticizers, and this also contributes to greater mobility. Differing levels of compartmentalization of phytochemicals in the pomace and pulp powders also cannot be discounted as a reason for the different rates of degradation.

Table 3. Zero-Order Rate Constant (k_{pomace}, Mean ± SE), Correlation Coefficient (R), and Zero-Order Rate Constant Observed in the Pulp versus the Zero-Order Rate Constant Observed in the Pomace (k_{pulp}/k_{pomace}) for the Decrease in the Lightness Index (L^*) in Apple Pomace during Storage at Different a_w Levels at 30 °C

a_w[a]	k_{pomace} (CU d^{-1})[b]	R	k_{pulp}/k_{pomace}[c]
0.56	0.026 ± 0.004	−0.911	5.3
0.75	0.032 ± 0.002	−0.977	5.6

[a]In the a_w range 0.11−0.32 changes in L^* were not significant ($p \geq 0.05$). [b]CU = colorimetric units. [c]Rate constants are compared to those reported for apple pulp (k_{pulp}) under the same storage conditions.[28]

It has been shown that polysaccharides may be used to improve stability of both color and oxidation-sensitive substances by creating specially designed food mixtures[30] or food microstructures.[31] Polysaccharides are often used to increase the glass transition temperature of a food mixture, thus decreasing the rate of chemical reactions.[13] For example, Telis et al.[30] found that the addition of carbohydrate polymers to grapefruit juice powder increased color stability and glass transition temperature of the mixture. To help stabilize oxygen sensitive substance, one effective method is to encapsulate the materials into a protective solid carbohydrate matrix, which creates a physical barrier to oxygen permeation.[31] In the present work, amorphous sucrose and other small solutes found in the equilibrated apple pulp matrices determined the water sorption behavior of this material (Figure 1). This coincided with the higher water mobility observed in dried apple pulp than in pomace at the same value of a_w. On the other hand, polysaccharides that constitute apple pomace matrix were able to better immobilize water.

To our knowledge, no previous studies have investigated phenolic stability in a fiber-rich matrix such as apple pomace. A few investigations have been carried out on the effect of fiber on ascorbic acid stability. Leon and Rojas[32] found that, in gellan matrices stored at a_w values of 0.33, 0.55, and 0.75 at 25 °C, the rate constant for ascorbic acid degradation is correlated to water mobility. They hypothesized that ascorbic acid degradation can be controlled by adequate selection of the hydrophilic polymer used as the carrier, with the aim of reducing water mobility. That hypothesis was validated by Perez et al.,[33] who selected high-methoxyl pectin as an ascorbic acid carrier. The high-methoxyl pectin network was demonstrated to provide a better immobilization of the water molecules when compared to the gellan matrix at a_w in the range 0.33−0.55, and thus higher retention of ascorbic acid. At a_w 0.75, where the high-methoxyl pectin has less effect on water immobilization, this result was reversed. As for antioxidant degradation, reduced browning has also been demonstrated in fiber matrices that limit water mobility.[32,33]

In conclusion, apple pomace is an excellent source of antioxidants, especially flavonols and dihydrochalcones, whose contents largely surpass those of apple pulp and apple derivatives. The novelty of this work is that it demonstrated that phytochemical compounds were remarkably more stable in dehydrated apple pomace than in dehydrated apple pulp, having 2−6 times smaller degradation rate constants. This effect most likely was due to better water immobilization in the pomace than in the pulp. In other words, the pomace was shown to be an optimal natural carrier for phytochemicals. This result endorses the exploitation of apple pomace as a food ingredient. At the same time, this work may lead to further avenues for developing new matrices with maximum phytochemical retention.

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Notes

The authors declare no competing financial interest.

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