JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

pubs.acs.org/JAFC

Phytochemical Stability in Dried Tomato Pulp and Peel As Affected by Moisture Properties

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ABSTRACT: Phytochemical stability was studied in dried tomato pulp and dried tomato peel stored at 30 °C with various water activity (a_w) levels and related to glass transition temperature (T_g) and water mobility. At a_w < 0.32, the values for T_g were >30 °C for both the pulp and peel, indicating that they were in the glassy state, with little molecular mobility. At a_w = 0.56, T_g was <30 °C, indicating the samples were in the rubbery state, with decreased viscosity and increased molecular mobility. The hydrophilic antioxidants (hydroxycinnamic acids and naringenin) were stable for samples in the glassy state, but were unstable for samples in the rubbery state. In contrast, the lipophilic antioxidants lycopene and α-tocopherol were mostly unstable for samples in the glassy state. These results could be used to optimize phytochemical contents in tomato products that must be dried prior to further processing.

KEYWORDS: *tomato, drying, phytochemical, glass transition, water mobility*

INTRODUCTION

Tomato (*Lycopersicon esculentum*) is the second most important vegetable crop next to potato, with >80 million metric tonnes produced annually.[1] Globally, China is the largest producer of tomatoes, followed by the United States, India, Turkey, and Egypt. The demand for a wide range of processed tomato products has increased remarkably. It is worth noting that many developing countries face substantial postharvest losses of tomatoes due to inadequate processing and storage facilities. Fresh-market tomatoes are either consumed directly or sold at relatively cheap prices or become waste.[2] Furthermore, the tomato canning industry generates a huge amount of wet pomace (~95% moisture) that is a challenge to dispose of without affecting the environment. Thus, it would be of great benefit to produce dried functional ingredients from these product waste streams.

Drying is particularly important for tomato ingredients both to prevent microbial spoilage and to considerably reduce product weight and volume, thus providing important savings in transport and storage costs.[3] Drying has also been suggested to stabilize tomato pomace prior to further processing for nutrient recovery.[4] Hence, various studies on tomato drying have been conducted such as microwave-assisted air drying,[5] microwave-vacuum drying,[2] and rotating tray drying.[3]

The role that moisture levels or properties play in the stability of dried tomato products has not been extensively studied. A crucial optimization criterion for tomato drying is to minimize phytochemical loss. In fact, tomato is a good source of antioxidants including ascorbic acid, tocopherols, phenolic compounds, carotenoids, and especially lycopene.[6,7] A variety of epidemiological studies have suggested that the intake of tomato-based foods is inversely related to the incidence of cardiovascular disease and cancer of different types,[7,8] mainly due to tomatoes' relatively high lycopene content. Lycopene can be degraded by heat, but in some cases it is stable, and its extractability may increase during processing. For instance, moderate-intensity pulsed electric fields and combined pressure–heat treatments have been found to increase lycopene extractability from the fruit.[9,10] During air-drying at 110 °C, the lycopene content showed a 10% decrease, and it was stable during air-drying at 80 °C.[11] However, lycopene is sensitive to oxidation during storage in dried conditions.[7] Therefore, there is a need to minimize oxidation that occurs in dried tomatoes during storage.

Many studies have related water activity (a_w) to the chemical and microbial stability of foods. Whereas a_w has been a useful marker for constructing general rules regarding food stability, it does have some limitations.[12] For example, there is often a critical a_w level below which microorganisms do not grow. In contrast, whereas chemical reactions such as nonenzymatic browning may increase at intermediate moisture levels, the exact a_w at which the reaction is maximal may depend upon the solute, which depresses the a_w. The glass transition temperature (T_g) is another parameter that has been used to predict food stability. T_g is the temperature above which a hard amorphous solid will transform into a soft, rubbery material. This can be attributed to a marked decrease in viscosity and an increase in molecular mobility.[12] Foods are often considered very stable in the glassy state, as compounds involved in deterioration reactions take many months or even years to diffuse over molecular distances and approach close enough to each other to react.[12] Another approach has been to use proton NMR to monitor the environments in which water resides. Water with restricted mobility is better able to exchange nuclear spins with other molecules, resulting in a more rapid decay of the NMR

Received: September 15, 2012
Revised: November 28, 2012
Accepted: December 20, 2012
Published: December 21, 2012

signal.[13] As a_w, T_g, and proton relaxation are distinct methods of assessing water binding and molecular mobility, it may be useful to combine the approaches to study chemical reactions that occur in foods.[12]

Little is known about the effect of moisture on phytochemical stability in dried tomato products and whether phytochemicals are differently affected. In this study, dried powders were prepared from tomato pulp and peels and held at a range of relative humidity (a_w) levels. Both key hydrophilic and lipophilic compounds were determined, along with color changes, over time to monitor phytochemical degradation kinetics. The T_g and ^{1}H relaxation times were also measured as a function of moisture content and related to the chemical changes.

MATERIALS AND METHODS

Materials. Standards of *all-trans*-lycopene, rutin (quercetin 3-*O*-rutinoside), chlorogenic acid, and naringenin were purchased from Extrasynthese (Lyon, France). All other chemicals were purchased from Sigma-Aldrich (Milan, Italy). Tomatoes (var. Ikram) were purchased from a fruit market (Milan, Italy).

Preparation of Tomato Pulp and Peel. A homogeneous batch of tomatoes (about 30 kg) was washed with tap water and heated for 60 min at 100 °C to imitate the intense heating conditions that occur in a tomato processing plant. Fruits were then pureed with a Braun Multisystem K 3000 homogenizer, for 2 min at maximum speed. The puree was refined using a screw extractor (model 9008 Reber, Luzzara, Italy), which separated the pulp from the pomace (peels, seeds, and residual pulp). The seeds were separated from the peel by flotation in water. Pulp and peel samples were freeze-dried (Lyoflex Edwards, Crawley, UK), ground into powders, and sieved (800 μm).

Storage Study. The powders were weighed into Petri dishes (6 cm diameter, 5.5 g of product in each dish). The dishes were placed inside airtight plastic chambers on wire-mesh racks situated above saturated salt solutions. The chambers were stored for 6 months 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 ± 0.002), CH_3COOK (a_w = 0.216 ± 0.005), $MgCl_2$ (a_w = 0.324 ± 0.002), NaBr (a_w = 0.560 ± 0.004), and NaCl (a_w = 0.7509 ± 0.0011). Duplicate chambers were incubated for each a_w level.

Moisture Content and a_w. Moisture content of the tomato powders after equilibration at the various relative humidity conditions was determined using a vacuum oven at 70 °C and 50 Torr for 18 h. The a_w of tomato powders and saturated salt solutions was checked using a dew point hygrometer (Aqualab, Decagon Devices, Pullman, WA, USA). Duplicate determinations were made for each sample. The samples stored at relative humidity levels ≥22% reached equilibrium in a few days. The samples stored at 11% relative humidity reached an a_w level of 0.17 within 6 days, as previously observed,[14] and then remained unchanged after prolonged incubation for up to 6 months.

pH and Acidity. Freeze-dried tomato powders were diluted with water (0.5 g of powder in 20 mL, in duplicate). The pH was determined with a model 62 pH-meter (Radiometer, Copenhagen, Denmark). Titratable acidity was determined by titration with 0.1 M NaOH to pH 8.1. Results were expressed as grams of citric acid per 100 g of dry product.

Soluble and Insoluble Fiber, Protein, Fat, and Ash. Fiber, protein, fat, and ash values of tomato peel and pulp were measured in triplicate 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 according to 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).

Color. Color was measured in quadruplicate with a Chroma meter II (Konica Minolta, Osaka, Japan), which provides the 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 samples were covered with a glass, and the head of the colorimeter was put directly on top of the glass to take color measurements. Chroma was calculated as $(a^{*2} + b^{*2})^{1/2}$ and hue angle as $\tan^{-1}(b^*/a^*)$.

HPLC Equipment. The HPLC equipment consisted of a model 600 HPLC pump coupled with a Waters model 2996 photodiode array detector and a Shimadzu model RF-20AHS fluorometric detector, operated by Empower software (Waters, Vimodrone, Italy).

Lycopene and α-Tocopherol. Tomato powders were extracted in two steps using tetrahydrofuran (THF) stabilized by the addition of 0.1% butylated hydroxytoluene (2,6-di-*tert*-butyl-*p*-cresol, BHT).[14] Aliquots of tomato powders (0.125 g dw) were added to 10 mL of stabilized THF. The mixture was vortexed for 1 min and centrifuged (12000*g* at 5 °C for 10 min). The supernatant was recovered into a 25 mL flask. Ten milliliters of stabilized THF was added to the residual solids. The mixture was vortexed for 1 min, stirred for 30 min with a magnetic stirrer, and then centrifuged (12000*g* at 5 °C for 10 min). The extracts were pooled and brought up to 25 mL with stabilized THF.

Extractions were carried out in triplicate on initial samples and in duplicate on samples stored in different relative humidity environments for 39, 67, 101, and 179 days. Lycopene content was analyzed by HPLC as described previously.[16] In brief, a Vydac 201TP54 C18 column (250 × 4.6 mm i.d., 5 μm particle size), equipped with a C18 precolumn, was used (Labservice Analytica, Anzola dell'Emilia, Italy). Chromatographic separation was performed with methanol/stabilized THF (95:5) as an eluent under isocratic conditions, 1.0 mL/min flow rate, at room temperature. Peaks were detected at 454 nm. Lycopene was quantified from a calibration curve using a pure standard and expressed as milligrams per kilogram of dry product. α-Tocopherol was analyzed by HPLC as described previously with slight modifications.[17] Here, a Kromasil Phenomenex silica column equipped with a silica precolumn (250 × 4.6 mm i.d., 5 μm particle size) was used (Phenomenex, Castel Maggiore, Italy). Chromatographic separation was performed with *n*-hexane/ethyl acetate/acetic acid (97.3:1.8:0.9 v/v/v) as an eluent under isocratic conditions, with a flow rate of 1.6 mL/min. Fluorometric detection was performed at an excitation wavelength of 290 nm and an emission wavelength of 330 nm. α-Tocopherol was quantified from a calibration curve using a pure standard and expressed as milligrams per kilogram of dry product.

Hydroxycinnamic Acids, Naringenin, and Rutin. Key polyphenolic compounds were also determined including hydroxycinnamic acids, naringenin, and rutin. Aliquots of tomato powders (0.25 g dw) were first extracted with 10 mL of methanol. The mixture was vortexed for 1 min, mixed continuously for 30 min with a magnetic stirrer, and then centrifuged at 12000*g* and 5 °C for 10 min. Extractions were carried out in triplicate on initial samples and in duplicate for samples stored at different relative humidities for 53, 106, and 179 days. The phenolics content of methanolic extracts were analyzed by HPLC as described previously.[18] A 250 × 4.6 mm i.d., 5 μm particle size, Symmetry reverse phase C-18 column (Waters) equipped with a Symmetry C-18 precolumn was used. Formic acid (5%) was added to both methanol and water before the following mobile phases were prepared: water/methanol (95:5, v/v) (A); water/methanol (88:12, v/v) (B); water/methanol (20:80, v/v) (C); and methanol (D). 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 flow rate was 1 mL/min. Chlorogenic acid, rutin, and naringenin were quantified at 330, 350, and 288 nm, respectively, from calibration curves using pure standards. Phenolic concentrations were expressed as milligrams per kilogram of dry product.

Ascorbic Acid. Ascorbic acid was determined as described previously.[18] Extraction of samples was performed in duplicate, in 10 mL centrifuge tubes using 0.5 g of sample in 5 mL of 60 g/L metaphosphoric acid (containing 1 g/L of sodium metabisulfite). Samples were stirred for 15 min and then centrifuged at 12000*g* and 5

°C for 10 min. Supernatants were analyzed by HPLC, using a 300 × 7.8 mm i.d. Bio-Rad Aminex Ion Exclusion HPX-87H. An isocratic mobile phase of 1 mmol/L sulfuric acid at a 1 mL/min flow rate was used. Analyses were conducted at 22 °C, and ascorbic acid was detected at 245 nm. A calibration curve of ascorbic acid was made with pure standard. Results were expressed as milligrams per kilogram of dry product.

^{1}H Nuclear Magnetic Resonance. Dried tomato products were equilibrated to a specific a_w as described for producing moisture isotherms. Materials were immediately placed in 5 mm diameter NMR tubes, sealed, and placed in a Mercury 300 MHz NMR (Varian Inc., Palo Alto, CA, USA) held at 20 °C. For several samples, relaxation rates were too rapid to perform a CPMG sequence to recover true T_2 relaxation. Thus, samples were analyzed in triplicate using a single 90° pulse and a recycle delay of 2 s and averaged over 32 scans. Thus, spin−spin relaxation times are expressed as T_2* and do not strictly account for field inhomogeneity. Spin−spin relaxation times were determined from the line width (T_2* = $1/\omega_{1/2}$). Spectra were analyzed using Mnova NMR processing software (Mestrelab Research, Escondido, CA, USA), which allows the spectra to be deconvolved into one or more components.

Glass Transitions. T_g values were determined for dried samples equilibrated to the specified a_w levels. Approximately 10−15 mg of each sample was weighed and hermetically sealed in an aluminum crucible. Samples were analyzed in a DSC 1 differential scanning calorimeter (Mettler-Toledo, Inc., Columbus, OH, USA) from −60 to 200 °C at a rate of 10 °C/min. Nitrogen gas was used to flush the area during scans, and all analyses were performed in triplicate.

Statistical Analysis. Data were processed using Statgraphics 5.1 (STCC Inc., Rockville, MD, USA). ANOVA followed by Fisher's least significant difference test (LSD $p \leq 0.05$) was used.

RESULTS AND DISCUSSION

Color Values. Table 1 shows color values of the dried tomato products prior to storage. The pulp and the peel had L* values of 56.5 and 57.1, respectively, and were not significantly different. Hue angle (H*) values were 60.6° for pulp and 53.8° for the peel. This puts these samples in the red−yellow hue region. The lower H* for the peel indicates that it was slightly redder than the pulp.[19] The chroma (C*) measures the color purity. The peel had a higher C* (30.1) than the pulp (25.0), indicating that the dried peel also had more color saturation than the pulp. The color differences were also observed visually (Figure 1). The color of tomatoes derives from a variety of carotenoid pigments. In the ripe fruit, lycopene is the predominant carotenoid and is responsible for the red color. In fact, colorimeter measurements have been correlated with levels of lycopene as developed during ripening.[19] The outer pericarp of the skins contains the highest levels of lycopene. For example, Shi and Le Maguer[7] reported that the concentration of lycopene in tomato peel is about 3 times higher than in whole mature fruit.

Table 1. Colorimetric Parameters (Mean ± SD) of Dried Tomato Pulp and Peel[a]

colorimetric parameter	pulp	peel
hue angle* (deg)	60.6b ± 0.9	53.8a ± 0.8
chroma*	25.0a ± 1.1	30.1b ± 2.2
L*	56.5a ± 0.8	57.1a ± 1.5

[a]Values in the same row with the different letters are significantly different (LSD, $p \leq 0.05$).

Major Macronutrients, Titratable Acidity, and pH. Table 2 shows the major macronutrients, titratable acidity, and pH in the dried peel and pulp. As expected, the major component of the peel was dietary fiber, with IDF of 42.0 ± 0.6 g/100 g dw and SDF of 8.7 ± 0.2 g/100 g dw. In contrast, the pulp contained 18.6 ± 1 g/100 g dw of IDF and 2.9 ± 1 g/100 g dw of SDF. The protein (9.7 and 10.5%) and fat (2.0 and 1.9%) contents were similar in the pulp and peel.

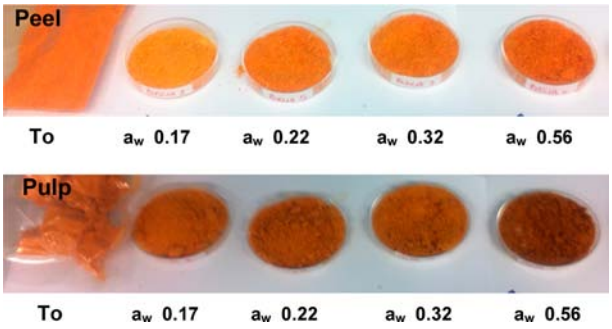

Figure 1. Pictures of tomato pulp and tomato peel at the beginning of incubation (T_0) and after 3 months of storage at different a_w levels, at 30 °C.

Table 2. Major Components, Acidity, and pH (Mean ± SD) of Dried Tomato Pulp and Peel

	pulp	peel
protein (g/100 g dw)	9.7 ± 0.7	10.5 ± 0.4
fat (g/100 g dw)	2.0 ± 0.2	1.9 ± 0.1
insoluble dietary fiber (g/100 g dw)	18.6 ± 1.0	42.0 ± 0.6
soluble dietary fiber (g/100 g dw)	2.9 ± 1	8.7 ± 0.2
ash (g/100 g dw)	4.98 ± 0.25	6.21 ± 0.14
titratable acidity (g/100 g dw)	3.64 ± 0.01	3.00 ± 0.01
pH	4.6 ± 0.1	4.7 ± 0.1

Hygroscopicity and Moisture Properties. Moisture sorption isotherms were developed in the a_w range between 0.11 and 0.75, at 30 °C. After freeze-drying and sieving, the powders had an a_w of 0.22. The samples stored at relative humidity levels ≥32% reached the equilibrium a_w through adsorption within 6 days of incubation. The samples stored at 11% relative humidity did not reach the equilibrium a_w level of 0.11, most likely due to their high hygroscopicity. These samples reached an a_w level of 0.17, which remained unchanged after prolonged incubation for up to 6 months. The pulp powder produced an isotherm more closely described as a Brunauer type II, whereas the peel was closer to a type III isotherm. The former is associated with adsorption on macroporous materials with stronger interactions between adsorbent and adsorbate and is typical for materials that form monolayer adsorption.[20] Type II isotherms are most commonly found for food systems. As shown in Figure 2, the pulp was more hygroscopic than the peel. That is, at a given a_w, the dried pulp powder had more adsorbed water than the dried peel. This results from the higher levels of sugars and organic acids in the pulp. In contrast, the peel has higher levels of fiber and a waxy cuticle that limit moisture adsorption.

T_g and Water Mobility. T_g values for the tomato powders as a function of a_w are shown in Figure 3. As expected, T_g decreased with increasing a_w/moisture content, as water plasticizes the molecules of the powder matrix. At the lowest studied a_w, T_g values were 52 °C for the dried peel and 57 °C for the pulp. At the highest studied moisture, T_g was −12 °C for the peel and −24 °C for the pulp. In general, T_g values for the pulp were lower than that of the peel at all a_w levels, except for the lowest a_w, at which the difference was not significant.

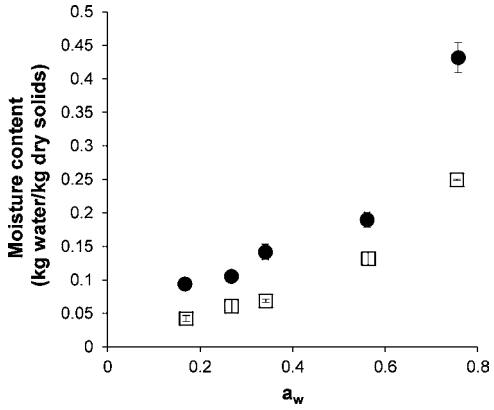

Figure 2. Moisture content (kg water/kg dry solids) of tomato pulp (●) and peel (□) as a function of a_w. Error bars indicate standard deviation.

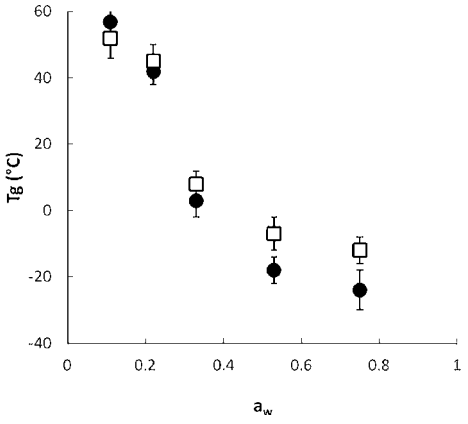

Figure 3. Glass transition temperatures (T_g) of dried tomato pulp (●) and peel (□) as a function of a_w. Error bars indicate standard deviation.

This is expected, in that materials with a greater amount of low molecular weight solutes decrease T_g more than materials composed of high molecular weight compounds. Researchers have reported various glass transition temperatures for dried tomato products. Telis and Sobal[21] found low-temperature T_g values that ranged between 11.8 and −43.4 °C for freeze-dried whole tomato held at a_w between 0.11 and 0.65. For samples air-dried at 40 °C, T_g values ranged from 4.8 to −44.1 °C in the same a_w range. They noted, however, that tomato often has two glass transitions attributed to separated phases formed by sugars and water and other natural macromolecules present in the vegetable. Goula et al.[22] studied spray-dried pulp and reported T_g values ranging from 36 °C at a_w = 0.02 to −43 °C at a_w = 0.53. They suggested their values were lower than those of Telis and Sobal[21] as their samples had higher levels of NaCl and citric acid. Jaya and Das[23] found that the T_g of vacuum-dried tomato powders varied from 62 to 22 °C over an a_w range of 0.08−0.49. The T_g values of the samples were intentionally designed to be higher, however, as they incorporated maltodextrin and tricalcium phosphate in the formula.

In this study, samples at a_w < 0.32 had T_g values >30 °C, indicating that they exist as amorphous solids with little internal mobility. This suggests that these powders would have little problem with stickiness and caking. In addition, it has been suggested that in glassy states various chemical reactions may become diffusion limited. In such cases, changes are triggered when the process temperature exceeds T_g and proceed in the rubbery state at a rate dependent on $T - T_g$.[24]

^{1}H NMR Relaxometry. In general, the ^{1}H NMR relaxation data were best described by a two-component model, one with relatively short relaxation times (T_{2S}* of 6−14 μs for pulp and 9−44 μs for peel) and one with relatively long relaxation times (T_{2L}* of 73−130 μs for pulp and 100−630 μs for peel). The relative proportions of protons associated with each fraction varied with a_w. Proton populations with short T_{2S}* are those associated with tightly bound water molecules or protons on macromolecular side chains with some mobility.[13] Proton populations with long T_{2L}* are associated with water molecules with greater mobility. In particular, these molecules are free to rotate and exchange molecular spins. It should be noted that such water does not have the unrestricted mobility found in bulk water, which typically has T_2* on the order of 1−2 s. Rather, the water molecules have some mobility and can diffuse to and from macromolecular surfaces in a relatively short time. Thus, the relaxation time is decreased by this interaction of water with macromolecules as they exchange molecular spins. One interpretation is that the short T_{2S}* is dominated by macromolecular protons, and additional water serves to plasticize these molecules. The long T_{2L}* is associated with hydration layers, which gain increasing mobility as more water is added to the system.

Figure 4 shows the fraction of protons associated with the slower relaxing component described by T_{2L}*. At $a_w \leq 0.22$ there was no T_{2L}* component for any samples. At this a_w, there was only a minimal amount of water closely associated with product solids, and it served to increase the free volume of motions. At $a_w \geq 0.32$, there was an increase in the long T_{2L}* component. At $a_w \geq 0.56$, the pulp had predominantly only a long component. For the peel, 100% of the relaxation was explained by the T_{2L}* component only at $a_w \geq 0.75$. This suggests that dried samples from pulp had more water in a relatively mobile phase. This is expected as these samples contain more low molecular weight compounds, including sugars, organic acids, and other hydrophilic components, which are hydrated by water. Although not as mobile as bulk water, it has some mobility and in turn helps provide freedom of motion to adjacent molecules. In contrast, the peel contains lesser amounts of sugars and organic acids. Rather, it has greater amounts of structural polysaccharides, including pectins,

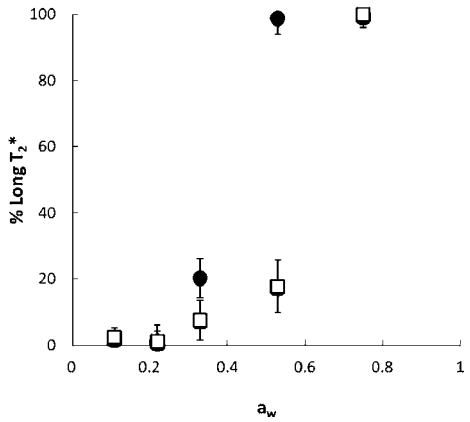

Figure 4. Percent of ^{1}H NMR relaxation attributed to the long T_2* component for dried tomato pulp (●) and peel (□) as a function of a_w. Error bars indicate standard deviation.

dx.doi.org/10.1021/jf303987v | J. Agric. Food Chem. 2013, 61, 700−707

cellulose, xyloglucans, and lignins, which are fairly rigid. In addition, the peel contains a waxy cuticle that increases the hydrophobic environment. Thus, at a given a_w, more water is adsorbed in the pulp (Figure 2), and this contributes to on overall enhanced mobility as compared to peel.

Results of the proton relaxometry are also consistent with the T_g values (Figure 3). At $a_w < 0.32$, T_g values were well above the ambient temperature, indicating the samples were in a glassy state. Also at $a_w < 0.32$, the proton relaxation results showed only one very short relaxation times indicative of a solid-state material. At higher a_w, T_g values were lower in the pulp than in the peel. This again shows the influence of sorbed water in the pulp, which increases the free volume of motions.

Phytochemical Stability. The initial ascorbic acid contents were 58 ± 3 mg/kg dw in the peel and 24 ± 3 mg/kg dw in the pulp. These values are low with respect to those reported in fresh tomato,[6] most likely due to ascorbic acid degradation during processing. Therefore, ascorbic acid was not well-balanced with respect to lipophilic antioxidants (as shown later), and possible synergistic effects were not hypothesized here. The initial contents of phenolics were higher than that of ascorbic acid. During storage, phenolics displayed different stabilities as a function of a_w and whether the powder was made from pulp or peel. At long storage times mold growth was observed in samples at $a_w = 0.75$ (data not shown).

The initial contents of total hydroxycinnamic acids were 171 ± 3 mg/kg dw in the pulp and 104 ± 2 mg/kg dw in the peel, with chlorogenic acid being the main component. In the pulp, hydroxycinnamic acids were stable up to $a_w = 0.32$ (not shown), but their levels diminished with time at $a_w = 0.56$ (Table 3). Phenolic degradation may occur via a radical-mediated oxidation pathway, resulting in the formation of quinones, which in turn condense to form brown pigments.[25] As these reactions are autocatalytic, this may explain the reason for a rapid drop of phenolic content in the pulp between 53 and 106 days of storage (Table 3), after which the compounds were no longer detectable. As shown in Figure 1, samples stored at $a_w = 0.56$ became much darker during storage. Phenolic oxidation may be responsible for browning of the samples. In addition, nonenzymatic browning cannot be ruled out, as it has been observed in several tomato products. Ghavidel and Davoodi[26] measured products of nonenzymatic browning in tomato powders and found that it could be reduced by adding $CaCl_2$ and potassium metabisulfite. In fact, the rate of nonenzymatic browning in foods is often maximum at intermediate a_w levels.[18] In the peel, hydroxycinnamic acids were stable up to $a_w = 0.56$. The flavonoids rutin and naringenin were present only in the peel, at levels of 42 ± 6 and 440 ± 58 mg/kg dw, respectively. Naringenin was stable up to $a_w = 0.32$ (not shown), but its level diminished slowly at $a_w = 0.56$, with 84% of retention after 179 days of incubation. In contrast, rutin was stable up to $a_w = 0.56$.

The initial lycopene contents were 2465 ± 20 and 6412 ± 41 mg/kg dw in the pulp and peel, respectively. In a previous study, it was hypothesized that lycopene, which is mostly present in tomato as the *all-trans* form, reversibly isomerizes to more oxidizable *cis* isomers; both *cis* and *trans* isomers autoxidize, forming volatile fragments.[27] In this study, the formation of *cis* isomers was not observed, probably due to their rapid loss.

In contrast to changes in the hydrophilic antioxidants (Table 3), lycopene was particularly unstable at the lowest a_w (Table 4). This was particularly true in dried peel, which is a less hydrophilic matrix than the pulp. For instance, after 39 days of storage at $a_w = 0.17$ the retention of lycopene was 35 and 72% in the peel and pulp, respectively. With increasing a_w level, the stability of lycopene increased progressively in the peel, and at $a_w = 0.56$ its retention was similar to that found in the pulp. The α-tocopherol content showed a dependence on a_w similar to that of lycopene. For instance, after 39 days of storage at $a_w = 0.17$ the retention of α-tocopherol was 26 and 60% in the peel and pulp, respectively. However, the stability of α-tocopherol increased with increasing a_w (Table 4). The α-tocopherol concentration has been reported to decrease slowly during extra virgin olive oil storage in the a_w interval 0.4−0.6.[28] In powdered paprika stored in a wider a_w interval (0.01−0.75), α-tocopherol was found to be unstable at low a_w, but very stable at high a_w.[29]

Moisture properties played a major role in antioxidant stability, as antioxidant degradation was strongly affected by the a_w level. Exposure of samples to increasing relative humidity environments (a_w from 0.11 to 0.56) resulted in a destabilizing effect on the hydrophilic antioxidants such as hydroxycinnamic acids and naringenin, whereas the hydrophobic antioxidants such as lycopene and α-tocopherols degraded less slowly. The role of water in phenolic degradation is similar to that of other chemical reactions involving water-soluble reagents. It is well-known that increasing the amount of water above a specific

Table 3. Changes in the Contents of Chlorogenic Acid, Total Hydroxycinnamic Acids, Naringenin, and Rutin (Mean ± SD) in Dried Tomato Pulp and Peel during Storage at a_w = 0.56 and 30 °C for up to 179 Days

compound	time (days)	concentration[a] (mg/kg dw)
chlorogenic acid		
pulp	0	123c ± 18
	53	92b ± 4 (25)
	106	nda (100)
	179	nda (100)
peel	0	82a ± 9
	53	82a ± 4
	106	77a ± 4
	179	81a ± 4
total hydroxycinnamic acids		
pulp	0	171c ± 3
	53	135b ± 6 (22)
	106	nda
	179	nda
peel	0	104a ± 2
	53	112a ± 6
	106	104a ± 6
	179	104a ± 6
naringenin		
peel	0	440b ± 58
	53	466b ± 7
	106	395a ± 6 (18)
	179	404a ± 6 (16)
rutin		
peel	0	42a ± 6
	53	40a ± 3
	106	38a ± 2
	179	40a ± 2

[a]Percent of loss is shown in parentheses. Data in the same column with different letters are significantly different (LSD, $p \leq 0.05$). nd, not detectable.

Table 4. Changes in Lycopene and α-Tocopherol Contents (Mean ± SD) in Dried Tomato Pulp and Peel during Storage at a_w between 0.17 and 0.56 for up to 139 Days at 30 °C

		concentration[a] (mg/kg dw)			
compound	time (days)	a_w = 0.17	a_w = 0.22	a_w = 0.32	a_w = 0.56
			pulp		
lycopene	0	2465e ± 20	2465e ± 20	2465d ± 20	2465e ± 20
	39	1783d ± 73 (28)	2149d ± 15 (13)	2249c ± 30 (9)	1872d ± 13 (24)
	67	1460c ± 18 (41)	1486c ± 20 (40)	1970b ± 22 (20)	1701c ± 43 (31)
	101	1080b ± 27 (56)	1143b ± 37 (54)	1190a ± 40 (52)	1462b ± 32 (41)
	136	822a ± 19 (67)	818a ± 15 (67)	1097a ± 26 (55)	977a ± 14 (60)
			peel		
	0	6412d ± 41	6412e ± 41	6412e ± 41	6412d ± 41
	39	2276c ± 32 (65)	4543d ± 17 (29)	4695d ± 50 (27)	5114c ± 41 (20)
	67	1251b ± 15 (80)	2981c ± 23 (54)	3638c ± 28 (43)	4311b ± 25 (33)
	101	662a ± 35 (90)	2138b ± 34 (67)	2734b ± 23 (57)	4249b ± 22 (43)
	136	613a ± 31 (90)	1555a ± 20 (76)	2015a ± 30 (69)	2420a ± 18 (62)
			pulp		
α-tocopherol	0	163e ± 4	163e ± 4	163e ± 4	163e ± 4
	39	97d ± 2 (40)	107d ± 2 (34)	108d ± 1 (34)	121d ± 1 (26)
	67	63c ± 1 (61)	78c ± 3 (52)	75c ± 3 (54)	85c ± 2 (48)
	101	48b ± 1 (70)	54b ± 1 (67)	74b ± 1 (55)	99b ± 1 (39)
	136	22a ± 1 (86)	36a ± 2 (78)	41a ± 1 (75)	50a ± 1 (69)
			peel		
	0	73c ± 1	73e ± 1	73e ± 1	73d ± 1
	39	19b ± 1 (74)	57d ± 1 (21)	57d ± 1 (21)	76d ± 1
	67	15a ± 1 (79)	44c ± 1 (40)	52c ± 1 (28)	62b ± 1 (15)
	101	15a ± 1 (80)	48b ± 1 (34)	54b ± 1 (26)	57c ± 1 (22)
	136	14a ± 1 (80)	37a ± 1 (50)	48a ± 1 (35)	51a ± 1 (31)

[a]Percent of loss is shown in parentheses. Data in the same column with different letters are significantly different (LSD, $p \leq 0.05$).

level increases the rate of reactions in aqueous solvents. Water acts as a plasticizing agent, enhancing the mobility of reactants and allowing catalysts to function in solution. As the solid matrix swells, new surfaces for catalysts are exposed.[18] The increase of moisture also decreases T_g.[12] Zhou et al.[30] found that the stability of the water-soluble vitamins, namely, thiamin hydrochloride and ascorbic acid, which are very sensitive to oxygen, depends on the T_g of the solid matrix in which they are incorporated. It decreases above T_g, which decreases viscosity and increases the level of dissolved oxygen. In this study, it was found that at $a_w < 0.32$, T_g values for all tomato samples were above the storage temperature of 30 °C, indicating that the samples were in the glassy state and phenolic degradation could have been inhibited by diffusional limits. This was confirmed by the proton relaxometry results, indicating limited mobility of the water phase, which could explain the stability of these compounds. At $a_w \geq 0.32$ for all tomato samples, T_g values were below the storage temperature of 30 °C. Whereas at a_w = 0.32 phenolics were still stable, at a_w = 0.56 these compounds were degraded over time. For diffusion-limited reactions, changes are triggered when the process temperature exceeds T_g and proceed with a rate dependent on $T - T_g$. Compared to the pulp, this temperature difference was lower in the peel, which also showed higher phenolic stability.

The water mobility as measured by ^{1}H NMR also helps to explain the degradation of phenolics as moisture increased. At a_w of 0.22 and lower, there was evidence for only a single primarily solid phase. As moisture level was increased, overall mobility increased. In the a_w range of 0.32−0.56, a new proton population became apparent and associated with a more mobile aqueous phase, and greater levels of water increased the fraction of protons in this phase. At a_w = 0.56, phenolic stability was lowest in the pulp, which showed a large fraction of the T_{2L}* component, indicating enhanced mobility. In contrast, phenolic stability was highest in the peel, which had a relatively small fraction of the T_{2L}* component and, therefore, less water that could move freely and serve as a solvent. Therefore, storage of tomato powders at intermediate humidity conditions can result in loss of some nutrients and phytochemicals. It should be noted that tomato products at even higher a_w may be less susceptible to degradation. For example, storage of tomato juices and ketchups results in only a slight decrease in their polyphenolics content, and a beneficial effect from the consumption of these products can be expected throughout storage.[31] Lower phenolic losses may be expected as the phenolics are "diluted" in ketchup and tomato juice by a large amount of water. Whereas in very dry tomato products phenolic degradation is limited by the low molecular mobility, in intermediate moisture tomato products (a_w = 0.56) molecular mobility and reactant concentrations are sufficient to allow phenolic degradation. This accounts for the very low storage stability of phenolics at a_w = 0.56.

Lycopene and α-tocopherol degradation was also sensitive to moisture levels, but in a much different way from that of the phenolics. The degradation of these hydrophobic antioxidants as a function of the a_w level was more akin to that of oxidation of unsaturated lipids. For unsaturated lipids, increasing water from the dry state may slow oxidation by hydrating or diluting heavy metal catalysts or precipitating them as hydroxides. Indeed, Boon et al.[32] found that transition metal induced oxidation of lycopene may be the predominant mechanism of degradation at low pH values. Water may also counteract peroxide decomposition by hydrogen bonding with hydroperoxides and encourage radical recombination, which could

dx.doi.org/10.1021/jf303987v | J. Agric. Food Chem. 2013, 61, 700−707

interrupt the oxidation reaction chain.[18] At a_w = 0.17 both lycopene and α-tocopherol were particularly unstable. However, all samples stored at a_w = 0.17 were in the glassy state (30 °C < T_g). Thus, the presence of a mobile phase of water is not required for their degradation.

Microstructural factors may also contribute to increased stability of lipophilic compounds at higher a_w. In a related study on encapsulated β-carotene stability, Prado et al.[33] found that β-carotene degradation was also greatest at low a_w (0.11). However, they noted that degradation was minimal in systems that were fully plasticized, that is, where $T > T_g$. This suggested that more than just molecular mobility is important to reactions involving lipophilic compounds. They believed that the glassy systems were more porous and thus allowed easier diffusion of oxygen. At $T > T_g$, the material could undergo structural collapse, which collapsed the micropores and limited oxygen access to β-carotene. Mono- and disaccharides were shown to increase β-carotene stability at a_w levels of 0.11 and 0.33.[34] In related work, Harnkarnsujarit et al.[35] studied the microstructural formations of maltodextrin and sugar matrices in freeze-dried systems by scanning electron microscopy and demonstrated that the presence of sugars (glucose, fructose, and sucrose) results in smaller pore sizes in the freeze-dried solids. As sugars cause a decrease in freezing temperature, melting of ice crystals can occur during freeze-drying; this leads to structural collapse and causes the formation of small pores in the dried matrices.[35] In this study, the higher stability of lycopene and α-tocopherol in the pulp than in the peel at low a_w levels (where T_g was >30 °C) could be due to smaller pore size in the dry pulp than in the peel, thus allowing less penetration by oxygen.

In conclusion, the least hygroscopic matrix, namely, the dried peel, provided better retention of phenolics in the rubbery state, whereas the most hygroscopic matrix, namely, the pulp, provided better stability for lycopene and α-tocopherol in the glassy state. This is evident from the pictures of the samples shown in Figure 1. The peel showed a higher loss of red color than the pulp at the lowest a_w, which is indicative of higher lycopene loss. In contrast, the pulp became darker than the peel, particularly at the highest a_w, which is indicative of phenolic oxidation. As a general rule, T_g was a meaningful parameter to predict the oxidative stability of samples, as it represented a borderline between two degradation trends.

It should be noted that the peel had greater levels of lycopene than the pulp, and thus storage at a_w > 0.22 may be warranted for such products. In some cases, a compromise may be needed. For example, storage at a_w = 0.32 would result in relatively stable phenolic compounds and losses of 55−70% of lycopene after 136 days storage. In addition, vacuum or nitrogen-flushed packaging in oxygen-impermeable bags would help reduce losses of lycopene and α-tocopherol.

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Notes

The authors declare no competing financial interest.

REFERENCES

(1) FAOSTAT, 2008 FAO statistics database, *Food and Agriculture Organization*; http://faostat.fao.org (accessed Nov 2011).

(2) Abano, E. E.; Ma, H.; Qu, W. Influence of combined microwave-vacuum drying on drying kinetics and quality of tomato slices. *J. Food Qual.* **2012**, *35*, 159−168.

(3) Santos-Sanchez, N. F.; Valadez-Blanco, R.; Gomez-Gomez, M. S.; Perez-Herrera, A.; Salas-Coronado, R. Effect of rotating tray drying on antioxidant components, color and rehydration ratio of tomato saladette slices. *LWT−Food Sci. Technol.* **2012**, *46*, 298−304.

(4) Al-Muhtaseb, A. H.; Al-Harahsheh, M.; Hararah, M.; Magee, T. R. A. Drying characteristics and quality change of unutilized-protein rich-tomato pomace with and without osmotic pre-treatment. *Ind. Crops Prod.* **2010**, *31*, 171−177.

(5) Heredia, A.; Peinado, I.; Rosa, E.; Andrés, A. Effect of osmotic pre-treatment and microwave heating on lycopene degradation and isomerization in cherry tomato. *Food Chem.* **2010**, *123*, 92−98.

(6) Wilcox, J. K.; Catignani, G. L.; Lazarus, S. Tomatoes and cardiovascular health. *Crit. Rev. Food Sci. Nutr.* **2003**, *43*, 1−18.

(7) Shi, J.; Le Maguer, M. L. Lycopene in tomatoes: chemical and physical properties affected by food processing. *Crit. Rev. Food Sci. Nutr.* **2000**, *40*, 1−42.

(8) Erdman, J. W.; Ford, N. A.; Lindshield, B. L. Are the health attributes of lycopene related to its antioxidant function? *Arch. Biochem. Biophys.* **2009**, *483*, 229−235.

(9) Gupta, R.; Kopec, R. E.; Schwartz, S. J.; Balasubramaniam, V. M. Combined pressure-temperature effects on carotenoid retention and bioaccessibility in tomato juice. *J. Agric. Food Chem.* **2011**, *59*, 7808−7827.

(10) Vallverdu-Queralt, A.; Oms-Oliu, G.; Odriozola-Serrano, I.; Lamuela-Raventos, R. M.; Martín-Belloso, O.; Elez-Martínez, P. Effects of pulsed electric fields on the bioactive compound content and antioxidant capacity of tomato fruit. *J. Agric. Food Chem.* **2012**, *60*, 3126−3134.

(11) Zanoni, B.; Peri, C.; Nani, R.; Lavelli, V. Oxidative heat damage of tomato halves as affected by drying. *Food Res. Int.* **1998**, *31*, 395−401.

(12) Venturi, L.; Rocculi, P.; Cavani, C.; Placucci, G.; Dalla Rosa, M.; Cremonini, M. A. Water absorption of freeze-dried meat at different water activities: a multianalytical approach using sorption isotherm, differential scanning calorimetry, and nuclear magnetic resonance. *J. Agric. Food Chem.* **2007**, *55*, 10572−10578.

(13) Wang, X.; Choi, S. G.; Kerr, W. L. Water dynamics in white bread and starch gels as affected by water and gluten content. *Lebensm. Wiss. Technol.* **2004**, *37*, 377−384.

(14) Lavelli, V.; Torresani, M. C. Modelling the stability of lycopene-rich by-products of tomato processing. *Food Chem.* **2011**, *125*, 529−535.

(15) AOAC. *Official Methods of Analysis*, 15th ed.; Association of Official Analytical Chemists: Washington, DC, 1990.

(16) Riso, P.; Porrini, M. Determination of carotenoids in vegetable foods and plasma. *Int. J. Vitam. Nutr. Res.* **1997**, *67*, 47−54.

(17) Panfili, G.; Fratianni, A.; Irano, M. Normal phase high-performance liquid chromatography method for the determination of tocopherols and tocotrienols in cereals. *J. Agric. Food Chem.* **2003**, *51*, 3940−3944.

(18) Corey, M.; Kerr, W.; Mulligan, J.; Lavelli, V. Phytochemical stability in dried apple and green tea functional products as related to moisture properties. *LWT−Food Sci. Technol.* **2011**, *44*, 67−74.

(19) Arias, R.; Lee, T. C.; Logendra, L.; Janes, H. Correlation of lycopene measured by HPLC with the *L*,*a*,*b** color readings of a hydroponic tomato and the relationship of maturity with color and lycopene. *J. Agric. Food Chem.* **2000**, *48*, 1697−1702.

(20) Andrade P., R. D.; Lemus M., R.; Pérez C., C. E. Models of sorption isotherms for food: uses and limitations. *Vitae* **2011**, *18*, 325−334.

(21) Telis, V. R. N.; Sobal, P. J. A. Glass transitions for freeze-dried and air-dried tomato. *Food Res. Int.* **2002**, *35*, 435−443.

(22) Goula, A. M.; Karapantsios, T. D.; Achilias, D. S.; Adamopoulos, K. G. Water sorption isotherms and glass transition temperature of spray dried tomato pulp. *J. Food Eng.* **2008**, *85*, 73−83.

(23) Jaya, S.; Das, H. Glass transition and sticky point temperatures and stability/mobility diagram of fruit powders. *Food Bioprocess. Technol.* **2009**, *2*, 89−95.
(24) Kerr, W. L.; Lim, M. H.; Reid, D. S.; Chen, H. Chemical reaction kinetics in relation to glass transition temperatures in frozen food polymer solutions. *J. Sci. Food Agric.* **1993**, *61*, 51−56.
(25) Laine, P.; Kylli, P.; Heinonen, M.; Jouppila, K. Storage stability of microencapsulated cloudberry (*Rubus chamaemorus*) phenolics. *J. Agric. Food Chem.* **2008**, *56*, 11251−11261.
(26) Ghavidel, R. A.; Davoodi, M. G. Studies on physicochemical properties of tomato powder as affected by different dehydration methods and pretreatments. *World Acad. Sci., Eng. Technol.* **2010**, *70*, 596−605.
(27) Anguelova, T.; Warthesen, J. Lycopene stability in tomato powders. *J. Food Sci.* **2000**, *65*, 67−70.
(28) Fregapane, G.; Lavelli, V.; León, S.; Kapuralin, J.; Salvador, M. D. Effect of filtration on virgin olive oil stability during storage. *Eur. J. Lipid Sci. Technol.* **2006**, *108*, 134−142.
(29) Kanner, J.; Harel, S.; Mendel, H. Content and stability of α-tocopherol in fresh and dehydrated pepper fruits (*Capsicum annuum* L.). *J. Agric. Food Chem.* **1979**, *27*, 1316−1318.
(30) Zhou, Y.; Roos, Y. H. Stability and plasticizing and crystallization effects of vitamins in amorphous sugar systems. *J. Agric. Food Chem.* **2012**, *60*, 1075−1083.
(31) Anna Vallverdu-Queralt, A.; Arranz, S.; Medina-Remon, A.; Casals-Ribes, I.; Lamuela-Raventos, R. M. Changes in phenolic content of tomato products during storage. *J. Agric. Food Chem.* **2011**, *59*, 9358−9365.
(32) Boon, C. S.; McClements, D. J.; Weiss, J.; Decker, E. A. Role of iron and hydroperoxides in the degradation of lycopene in oil-in-water emulsions. *J. Agric. Food Chem.* **2009**, *57*, 2993−2998.
(33) Prado, S. M.; Buera, M. P.; Elizalde, B. E. Structural collapse prevents β-carotene loss in a supercooled polymer matrix. *J. Agric. Food Chem.* **2006**, *54*, 79−85.
(34) Desorby, S. A.; Netto, F. M.; Labuza, T. P. Comparison of spray-drying, drum-drying and freeze-drying for β-carotene encapsulation and preservation. *J. Food Sci.* **1997**, *62*, 1158−1162.
(35) Harnkarnsujarit, N.; Charoenrein, S.; Roos, Y. H. Microstructure formation of maltodextrin and sugar matrices in freeze-dried systems. *Carbohydr. Polym.* **2012**, *88*, 734−742.