

Stability of Dried and Intermediate Moisture Tomato Pulp during Storage

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Commercial tomato pulp was air-dried to two final moisture contents in order to obtain intermediate moisture pulp (IMP, 23% moisture) and dried pulp (DP, 9% moisture). IMP and DP were stored at 4, 20, and 37 °C for approximately 5 months; periodically samples were analyzed to evaluate heat and oxidative damage by measurement of color changes, total phenolics, rutin, lycopene and furosine concentrations, and antioxidant activity of the lipophilic extract. IMP and DP, despite different drying degree, had similar antioxidant activity; in fact, whereas lycopene was stable to drying treatments, ascorbic acid was totally degraded in both products. During storage, IMP and DP showed different behavior: IMP was more sensitive to degradation than DP, especially with regard to lycopene, rutin, and antioxidant activity degradation and to nonenzymatic browning. Effects of storage temperature varied with regard to different parameters: variations in rutin, furosine, and color indices were higher in products stored at higher temperatures, while lycopene and antioxidant activity of the lipophilic fraction were maximally degraded in products stored at 4 °C.

KEYWORDS: Dried tomato; antioxidant activity; oxidative heat damage; shelf life

INTRODUCTION

Tomato and tomato products are a primary source of vitamins and antioxidant components (ascorbic acid, carotenoids, and phenolic compounds). Drying is a critical technology in terms of oxidative damage, because the product is in most cases exposed to high temperature and high oxygen levels. In addition, solid concentration increases during drying, thus increasing the rate of oxidative and degradation reactions. Recent research concerning the effects of drying on tomato antioxidant components (1–4) has demonstrated that lycopene and carotenoids are substantially stable to industrial drying. Nguyen and Schwartz (4) detected maximum 6.25% *cis*-lycopene isomers in drum-dried tomato powder, while Shi et al. (3) found 16.6% *cis*-isomers in air-dried samples, with total lycopene loss of 3.9%. In contrast, ascorbic acid is lost to a great extent, and significant changes occur in phenolic content during tomato air-drying (2, 5). Dehydrated tomato products are sensitive to color fading and loss of acceptability; this is mainly due to lycopene isomerization and oxidation. Various studies showed that significant oxidative damage can occur during storage of dried tomatoes. Anguelova and Warthesen (6) detected 30–40% lycopene loss in spray-dried tomato powder stored for 6 weeks at 6 °C in air and in the dark and suggested that degradation proceeded through isomerization and autoxidation of *all-trans*-lycopene. Baloch et al. (7) found that carotenoid loss was above 50% in tomato powder after 20 days of storage at 40 °C in air and in the dark. Zanoni et al. (2) observed a marked lycopene

loss (more than 70%) after 90 days of storage of powdered air-dried tomato at 37 °C in the dark in the presence of air. Sharma and Le Maguer (8) studied the kinetics of lycopene degradation during storage of tomato pulp solids under various conditions. Lycopene loss was maximum (77.6%) after 60 days of storage at 25 °C in the presence of air and light. Freeze-drying and oven-drying of tomato pulp solids did not cause any loss in lycopene content; however, lycopene loss reached 97% and 79% in freeze-dried and oven-dried samples, respectively, after storage at room temperature in the dark for 4 months.

The general conclusion of shelf-life studies is that significant lycopene degradation can occur in dehydrated tomatoes; degradation reactions are made faster by high temperature, oxygen and light exposure, and very low moisture content and water activity (*aw*). Little information is available about the fate of antioxidant components other than carotenoids and about other physicochemical parameters, which are critical for nutritional and sensory characteristics of tomato products.

The aim of this study was to evaluate the stability of tomato antioxidant components and of quality parameters during storage of dried tomato pulp, with respect to storage conditions (storage temperature and oxygen exposure) and to residual moisture content. For this purpose, commercial tomato pulp was air-dried at two final moisture levels to obtain dried pulp (DP, moisture ≈ 9%, *aw* ≈ 0.35) and intermediate moisture pulp (IMP, moisture ≈ 23%, *aw* ≈ 0.7). Intermediate moisture foods are characterized by water activity values ranging from 0.6 to 0.8; at these values, foods maintain some of the original sensory

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characteristics (color, flavor, and texture) and show good microbial stability (9).

To evaluate the effects of drying degree and storage conditions on the stability of tomato pulp, the two products were stored for 5 months at 4, 20, and 37 °C in air and under CO₂. Products were periodically analyzed for the following parameters: ascorbic acid; total phenolics; rutin (quercetin-3-rutinoside), which represents a major constituent of tomato phenolics with high antioxidant activity; *all-trans*-lycopene and antioxidant activity of the lipophilic fraction, as oxidative damage indices (5, 13); furosine [ϵ -*N*-(2-furoyl-methyl-L-lysine)]; and color (a^* / b^* and ΔE) as heat damage indices (10).

MATERIALS AND METHODS

Production and Storage of Dried Tomato Pulp. Dried tomato pulp was obtained by air-drying of a homogeneous lot of Italian commercial pulp (diced tomato) in a pilot-plant cabinet air-dryer designed and built by Thermo Lab (Milan, Italy). Tomato pulp cubes were drained and placed onto a perforated stainless steel tray connected to a balance to measure tomato weight during drying. Drying was carried out at 70 °C by 1.5 m/s air flow rate in through-flow. Drying was stopped when the product had reached approximately 9% moisture (dried pulp, DP) and approximately 23% moisture (intermediate moisture pulp, IMP); these moisture levels were determined on the basis of tomato pulp sorption isotherm (1) and corresponded to water activity values of 0.35 and 0.71, respectively.

About 100-g aliquots of dehydrated samples were placed in 1-L, airtight, clear glass bottles. For storage under CO₂, air was removed from the bottles by a vacuum pump and was then replaced by CO₂. Dried and intermediate moisture samples, in air and in CO₂, were stored in temperature-controlled chambers at 4, 20, and 37 °C in the dark for approximately 5 months. Samples were analyzed for heat and oxidative damage at 3–4-week intervals.

Analytical Methods. Moisture content was determined gravimetrically after drying in a vacuum oven at 70 °C (1), and water activity was measured by a dew point hygrometer (Aqualab, Decagon Devices, Pullman, WA).

Ascorbic acid content was measured by HPLC as previously described (1); lycopene was determined by extraction with tetrahydrofuran and subsequent HPLC analysis (1). The method allowed us to identify and quantify *all-trans*-lycopene, whereas *cis* isomers could not be identified. Total phenolics were extracted and purified by separation on a C18 Sep Pak cartridge and determined by Folin Ciocalteu reagent (5); rutin (quercetin-3-rutinoside) was determined by HPLC analysis of the phenolic extract (5); the antioxidant activity of the lipophilic extract was measured by the linoleic acid/CuSO₄ model system as reported by Lavelli et al. (17); furosine was determined by HPLC after acid hydrolysis and expressed as milligrams of furosine per 100 g of protein, as reported by Hidalgo and Pompei (11); color indices (L^* , a^* , and b^*) were measured with a tristimulus chromameter (Minolta, Tokyo, Japan, model CR-210), calibrated with a red standard (No. 482, Bureau Communautaire de Reference), and red color index was expressed as a^*/b^* ; color change (ΔE) during storage was calculated according to the equation

$$\Delta E = [(a^* - a^*_0)^2 + (b^* - b^*_0)^2 + (L^* - L^*_0)^2]^{1/2}$$

where a^*_0 , b^*_0 , and L^*_0 are the color indices at the beginning of storage.

Before analysis, samples were rehydrated to 10% solid content. All analyses were performed at least in duplicate, and standard deviation values were calculated. Results are expressed on a dry weight basis in order to compare products with different solid content, while color values are referred to samples at 10% solid content.

RESULTS AND DISCUSSION

Table 1 shows analytical data of tomato pulp, DP, and IMP prior to the aging test. Furosine concentration, which was determined as an index of heat damage intensity (10, 11), was

Table 1. Initial Composition of Raw Tomato Pulp, IMP, and DP before the Storage Test (Mean Value \pm Standard Deviation)^a

	tomato pulp	IMP (aw = 0.71)	DP (aw = 0.35)
solid content (g/100 g)	7.02 \pm 0.03	77.3 \pm 1.16	91.3 \pm 0.95
furosine (mg/100 g of protein)	147 \pm 14	462 \pm 22	1000 \pm 62
L^*	22.12 \pm 0.24	21.6 \pm 0.04	21.25 \pm 0.02
a^*	28.14 \pm 0.21	24.62 \pm 0.03	25.18 \pm 0.02
b^*	15.44 \pm 0.10	13.85 \pm 0.04	13.39 \pm 0.02
a^*/b^*	1.82 \pm 0.031	1.78 \pm 0.07	1.88 \pm 0.04
ascorbic acid (mg/kg dw)	1165 \pm 10	n.d.	n.d.
total phenolics (mg/kg dw)	3383 \pm 82	5998 \pm 204	7621 \pm 339
rutin (mg/kg dw)	328 \pm 12	303 \pm 7	364 \pm 14
<i>all-trans</i> -lycopene (mg/kg dw)	1852 \pm 175	2270 \pm 260	2306 \pm 453
β -carotene (mg/kg dw)	148 \pm 9	142 \pm 5	130 \pm 26

^a nd, not detectable; dw, dry weight.

higher in dehydrated products than in raw material and was correlated to the intensity of the drying process: DP showed a furosine content more than double that of IMP. Air-drying caused complete loss of ascorbic acid, even in the intermediate moisture product. Literature data demonstrate that significant losses in ascorbic acid occur during tomato processing, and the extent of degradation is correlated to the severity of heat and oxidative stress (5, 11). Previous trials carried out in our department (2) demonstrated that air-drying at 80 °C of fresh tomato halves to 23% final moisture produced approximately 85% ascorbic acid loss. In our case, drying to a similar final moisture content produced a complete degradation of ascorbic acid. This difference can be due to the fact that fresh tomato halves had much higher ascorbic acid content than commercial tomato pulp and that the physical structure of tomato halves partly preserved ascorbic acid from oxidation.

Total phenolics content increased due to drying, and the increase was proportional to drying severity. This behavior had already been observed (2, 5) and was ascribed to the hydrolysis of glycosylated and complexed compounds, which is favored by high temperature, acidic pH, and high solid concentration. Conversely, air-drying did not cause significant changes in rutin concentration. With respect to carotenoids, *all-trans*-lycopene showed great stability (the increase in lycopene concentration in dehydrated products can be ascribed to increased extractability), and β -carotene was fairly stable as well. Small variations in color values (L^* , a^* , b^* , and a^*/b^*) confirm that minor changes occurred to pigmented carotenoids during drying.

Figures 1–3 show variations of the analytical parameters total phenolics, rutin, and *all-trans*-lycopene concentration, respectively, during storage of DP and IMP at various temperatures. We did not observe different behavior between samples stored in air and under CO₂ (mean standard error between the two series of data was 8% for *all-trans*-lycopene values, 5.2% for total phenolics, and 4% for rutin). We can conclude that the system we used did not allow effective air exclusion from the bottles, so the two series of data were considered as a duplicate, and mean values are presented.

Total phenolics were substantially stable in DP and IMP stored at 4 and 20 °C (**Figure 1**), while a progressive increase was observed in samples stored at 37 °C, especially in DP.

In contrast, rutin concentration showed minor changes in DP and IMP stored at 4 and 20 °C, and a dramatic degradation occurred in both products stored at 37 °C (**Figure 2**). At the

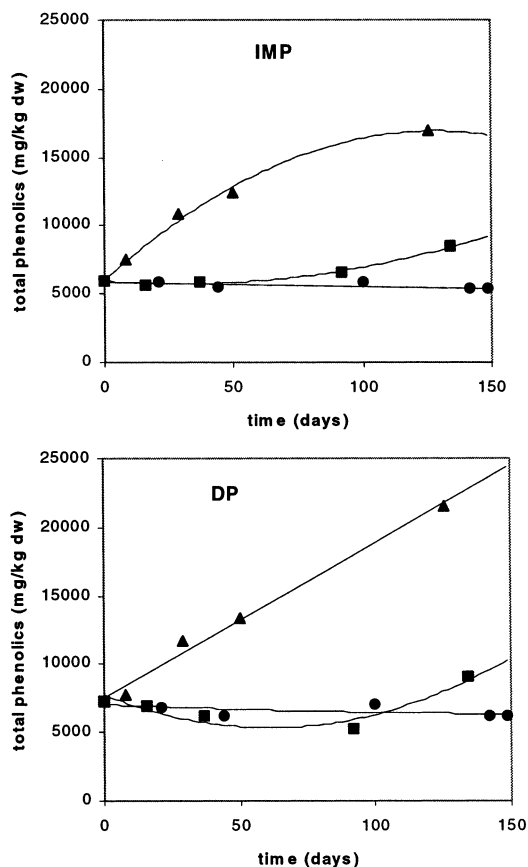


Figure 1. Variation in total phenolics concentration during storage of IMP and DP at 4 (●), 20 (■), and 37 °C (▲).

end of storage, rutin was completely degraded in IMP, and about 80% loss occurred in DP. Data referring to total phenolics and rutin are somewhat inconsistent. In our previous studies about the effects of processing and storage of tomato products (5, 14), we had already observed an increase in phenolic substances, as evaluated by Folin-Ciocalteu, in heat-treated products. This effect had been ascribed to an increase in free hydroxyl groups as a consequence of hydrolysis of glycosidic groups or other substituents. In the present study, we observe an increase in total phenolics in DP and IMP stored at 37 °C which is associated with a marked decrease in rutin concentration. It must be noticed that the decrease in rutin concentration was not associated with the formation of quercetin or other HPLC peaks, which would have been evident in the HPLC profile. We can thus conclude that rutin was destroyed via oxidative degradation. The increase in Folin-Ciocalteu reactive products can be explained by the formation of Maillard reaction products (MRPs) as a consequence of nonenzymatic browning. It is known that intermediate as well as final MRPs (melanoidins) exert antioxidant activity (15). Studies on the antioxidant activity of heat-treated tomato juice demonstrated that the antioxidant activity decreased at the beginning of heating because of the degradation of natural antioxidant components, and then increased because of the formation of MRP (16). This assumption is substantiated by the fact that, in our previous studies on processing and storage of tomato products, a marked increase in the antioxidant activity of the hydrophilic extract (as measured by xanthine/xanthine oxidase-mediated oxidation in model system) had been observed in tomato products subjected to heat damage (thermal processing or storage at high temperature) and was associated with an increase in total phenolics (5, 14). Even in the case of DP and IMP stored at 37

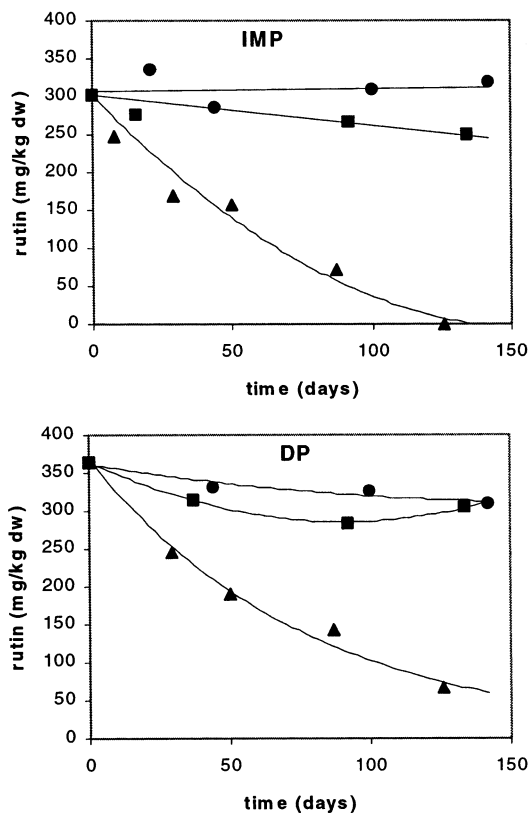


Figure 2. Variation in rutin concentration during storage of IMP and DP at 4 (●), 20 (■), and 37 °C (▲).

°C, furosine concentration and color changes (i.e., heat damage indices) are correlated with the increase in Folin-Ciocalteu reactive products (Table 3).

Variations in *all-trans*-lycopene content during storage are reported in Figure 3. Lycopene degradation was negligible in DP stored at 20 and 37 °C, while some decrease was observed in DP stored at 4 °C (about 18% loss after 5 months). Lycopene degradation was more significant in IMP and inversely related to storage temperature: about 28%, 38%, and 75% loss occurred after 5 months of storage at 37, 20, and 4 °C, respectively. The evaluation of the antioxidant activity of the lipophilic extract confirmed lycopene concentration values (Table 2). The antioxidant activity was measured on IMP and DP stored at 4 and 37 °C as the ability to inhibit lipid oxidation in a model system (17). The antioxidant activity value is expressed as I_{50} , i.e., milligrams of sample (dw) which exert 50% inhibition of the control reaction (17); therefore, the higher the I_{50} value, the lower the antioxidant activity. It can be observed that the antioxidant activity at the end of storage dramatically dropped in products stored at 4 °C, especially in IMP; smaller changes occurred in IMP stored at 37 °C, and no decrease was observed in DP stored at 37 °C.

These data are consistent with *all-trans*-lycopene concentration detected in the differently stored samples. Lycopene evolution with respect to storage temperature was quite unexpected, since maximum stability was observed at 37 °C and minimum stability was observed at 4 °C; this fact will be discussed in the Conclusions.

Variations in analytical parameters related to heat damage (furosine content and color indices) after storage of IMP and DP at the three temperatures are reported in Table 3. It can be clearly observed that furosine formation was related to storage temperature both in IMP and in DP. In a previous study (10), we had observed pseudo-first-order kinetics for furosine forma-

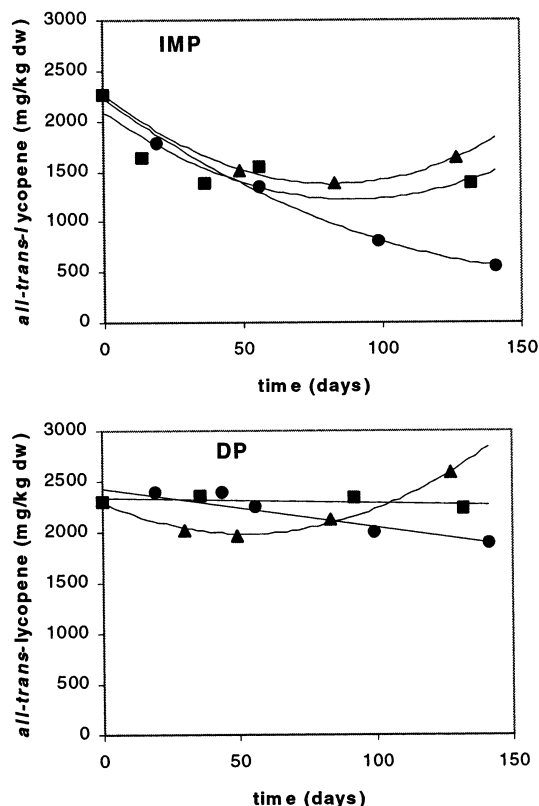


Figure 3. Variation in *all-trans*-lycopene concentration during storage of IMP and DP at 4 (●), 20 (■), and 37 °C (▲).

Table 2. Antioxidant Activity (I_{50} , mg dw) of the Lipophilic Extract of IMP and DP at the Beginning and at the End of Storage at 4 and 37 °C^a

	antioxidant activity (I_{50} , mg dw)			
	IMP		DP	
	4 °C	37 °C	4 °C	37 °C
t_0	1.24 ± 0.05	1.24 ± 0.05	1.14 ± 0.07	1.14 ± 0.07
t_{fin}	5.6 ± 0.2	1.85 ± 0.31	2.5 ± 0.07	0.9 ± 0.1

^a t_0 , beginning of storage; t_{fin} , end of storage.

tion in tomato pulp, tomato puree, and tomato paste stored between 30 and 50 °C. Hidalgo and Pompei (11) found a linear increase in furosine formation in tomato puree heated in the temperature range 80–120 °C. In both studies, it was observed that the higher the solid content in the product, the higher was the furosine formation rate, and this was ascribed to a higher concentration of the reaction substrates in more concentrated products. Furosine evolution in IMP and DP confirms the

dependence of furosine formation rate on storage temperature but does not evidence any dependence on solid concentration, probably because a saturation effect takes place at such a high solid content. Heat degradation of IMP and DP during storage was also associated with major color variations. The decrease in a^*/b^* values is usually considered as an index of red color fading, while the ΔE value represents overall color change. Data in Table 3 show that a^*/b^* values slightly increased in DP and IMP stored at 4 °C and decreased in samples stored at 20 °C and more markedly in samples stored at 37 °C. ΔE variations were maximum in samples stored at 37 °C and minimum in samples stored at 4 °C. As a matter of fact, color change was already evident after 30 days of storage at 37 °C, especially in IMP, and at the end of the aging test both DP and IMP stored at 37 and 20 °C were dark brown. We can observe that ΔE variations are related to furosine increase and can be considered as an effect of heat damage, since browning is mainly due to the formation of colored Maillard reaction products. Variations in red color index a^*/b^* were less significant and can be ascribed both to nonenzymatic browning and to *all-trans*-lycopene degradation.

CONCLUSIONS

This study shows that incomplete drying of tomato pulp was not effective in improving the total antioxidant activity of the product. In fact, while carotenoids were substantially stable to air-drying, ascorbic acid was completely degraded, even in the IMP. Consequently, the antioxidant potential of IMP was not higher than that of DP.

The shelf-life study gave the following results about the stability of IMP and DP. Since literature data evidence that very low moisture content or very low water activity seem to favor oxidative degradation in tomato products (8, 12), we expected that a higher moisture level would provide some protection against oxidation. This was not the case: IMP was more sensitive than DP toward degradation reactions involving lycopene, rutin, antioxidant activity of the lipophilic fraction, and browning. Lovric et al. (13) discussed the effect of very low moisture content on the oxidative stability of dried tomato and concluded that the protective activity of water can be ascribed to a number of factors: water can inactivate pro-oxidative metal ions which are present in traces; the hydrogen bonding between hydroperoxide molecules and water results in delayed chain propagation reactions in lipid autoxidation; finally, water can compete with oxygen for the active absorption sites. With regard to our data, we can conclude that moisture level in DP (approximately 9%) provides some of the protective effect, whereas at higher moisture levels (such as approximately 23% found in IMP) the solvent effect of water prevails and reactions are favored by enhanced mobility of reaction substrates and cosubstrates.

Table 3. Variations in Furosine Content and in Color Indices a^*/b^* (Red Color Index) and ΔE (Color Change) after Storage of IMP and DP at 4, 20, and 37 °C^a

		IMP			DP		
		4 °C	20 °C	37 °C	4 °C	20 °C	37 °C
		furosine (mg/100 g of protein)	t_0	462 ± 22	462 ± 22	462 ± 22	1000 ± 62
	t_{fin}	801 ± 6	1038 ± 9	1881 ± 46	1146 ± 6	1382 ± 61	2594 ± 124
a^*/b^*	t_0	1.78 ± 0.07	1.78 ± 0.07	1.78 ± 0.07	1.88 ± 0.04	1.88 ± 0.04	1.88 ± 0.04
	t_{fin}	1.95 ± 0.08	1.48 ± 0.04	1.11 ± 0.04	2.27 ± 0.02	1.74 ± 0.12	1.21 ± 0.03
ΔE	t_0	0	0	0	0	0	0
	t_{fin}	8.09 ± 1.35	10.37 ± 1.24	20.44 ± 0.70	9.36 ± 0.29	12.55 ± 0.43	19.24 ± 0.57

^a t_0 , beginning of storage; t_{fin} , end of storage.

When considering the effects of storage temperature on the degradation rates, we observed that total phenolics, rutin, and furosine, as well as color variations, were directly related to storage temperature, as expected. In contrast, lycopene and antioxidant activity losses were maximum in products stored at 4 °C. Literature data about the effects of storage temperature on the stability of lycopene in dehydrated tomato products do not give univocal conclusions. Anguelova and Warthesen (6) found that lycopene and color retention were higher in tomato powder stored at 6 °C compared to 45 °C, while Lovric et al. (13) concluded that color, total lycopene, and *all-trans*-lycopene in foam-mat-dried tomato powder were better retained at 20 °C compared to -10, 2, and 37 °C (in both cases products were stored in air and in the dark). This was ascribed to the facts that *all-trans*-lycopene is partly converted to *cis* isomers during drying and that re-isomerization from *cis* isomers to the *all-trans* form is favored at 20 °C (with respect to -10 and 2 °C). Since *cis* isomers are more readily oxidized than *all-trans* isomers, lycopene oxidation during storage occurred faster when a high *cis* isomer ratio was present (i.e., at -10 and 2 °C). Revising published data about lycopene stability in dehydrated tomato products, Boskovich (18) concluded that low storage temperatures as well as very low water activity and moisture levels have a pro-oxidative effect. Moreover, oxygen solubility increases at lower temperatures, and this could be of some importance in a particulate matter such as tomato pulp pieces. It must be considered that the formation of Maillard reaction products affects the antioxidant stability of tomato products, too. In our trials, nonenzymatic browning occurred to a great extent in IMP and DP stored at 37 °C, and Maillard reaction products could provide some protection against carotenoid oxidation. This fact cannot be considered as positive, since it is known that products deriving from the advanced steps of the Maillard reaction may be biologically toxic.

The antioxidant stability of dried tomato products during storage can be controlled by a number of factors: besides oxygen and light exposure, moisture content and storage temperature can play a major role, and their effect is not completely explained. A deeper investigation of lycopene isomerization and autoxidation mechanism and kinetics is needed to define optimal storage conditions for various tomato products.

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