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# Stability of the Phenolic and Carotenoid Profile of Gazpachos during Storage

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**ABSTRACT:** Gazpacho is a ready-to-use vegetable soup containing tomato, cucumber, pepper, olive oil, and other minor constituents such as onion, garlic, wine vinegar, sea salt, and water. In this work, changes in individual phenolic and carotenoid compounds of commercial gazpachos, as well as in their hydrophilic and lipophilic antioxidant capacities (measured through $ABTS^+$ and DPPH radicals), were assessed for 3 months at 4 °C. The storage of gazpachos at 4 °C for 3 months results in a slight decrease in their polyphenol and carotenoid content and also in the hydrophilic and lipophilic antioxidant capacities, but the levels achieved could not be construed as a nutritional drawback. The main degradation was quercetin oxidation because the hydroxy function at the C-ring of the flavonoid is not blocked by a sugar moiety as it is in the case of rutin and kaempferol-3-*O*-rutinoside and glycosylated caffeic and ferulic acids. Lycopene underwent significant losses throughout storage as 11 conjugated double bonds are present in its structure and should be more reactive than *trans*-lutein and *trans*-*β*-carotene. *cis*-Lycopene isomers slightly decreased. However, 5-*cis*-lycopene underwent a slight increase. This phenomenon could be explained by *cis*-isomerization increasing the proportion of *cis*-isomers.

**KEYWORDS:** *gazpachos, stability, carotenoids, polyphenols, antioxidant capacity, storage*

## INTRODUCTION

The popularity of gazpachos, a ready-to-use vegetable soup, is rapidly becoming more widespread partly due to the fact that a high consumption of fruits and vegetables has been associated with the prevention of cancer, cardiovascular illnesses, and several degenerative chronic diseases.[1,2] These beneficial properties of fruits and vegetables have been attributed partially to their content of functional compounds, such as carotenoids and phenolic compounds.[3] Tomatoes and tomato-based products such as gazpachos are of great interest because of their high content of carotenoids. Some of these compounds, such as *β*-carotene and *trans*-*α*-carotene, may exhibit provitamin A activity.[4] Studies have proven that the consumption of lycopene decreases the risk of degenerative diseases, such as certain kinds of cancers and cardiovascular diseases.[5]

In addition, tomato-based products are a good source of phenolic compounds, which contribute substantially to their antioxidant potential.[6] Several studies have demonstrated that a diet rich in phenolic compounds correlates with a reduced risk of coronary heart disease. Tomatoes possess antioxidative, anti-inflammatory, antimutagenic, and anticarcinogenic properties and the capacity to modulate some key cellular enzyme functions, thus being ascribed to many phenolic compounds.[7,8]

Tomato-based products may potentially contain the same range of phenolic compounds and carotenoids as the tomatoes from which they are derived; however, due to differences among varieties of tomatoes and their origin,[9,10] polyphenol and carotenoid contents could vary considerably.

Storage conditions and thermal treatments affect the quality of tomato products. In particular, thermal treatments are known to be the main cause of the depletion of natural antioxidants. Browning and oxidation reactions are the main causes of degradation of naturally occurring antioxidants during the storage of tomato products.[11,12]

Because of the important health-protecting role of polyphenols and carotenoids, the consumption of tomatoes and tomato-based products could be seen as a nutritional indicator of good dietary habits and a healthy lifestyle. As gazpachos typically have a commercial shelf life of 3 months, as provided by commercial labels, studies are necessary to determine their nutritional quality during storage. However, as far as we know, no information is currently available on how the phenolic and carotenoid compounds of gazpachos are influenced by storage time. Moreover, there is no information available concerning changes in flavonols, flavanones, hydroxycinnamic acids, and individual carotenoids of gazpachos during storage.

We carried out a pilot study to evaluate the stability of antioxidant compounds present in commercially available gazpachos during 3 months of storage. Therefore, hydrophilic and lipophilic antioxidant capacities and the content of

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flavonols, flavanones, hydroxycinnamic acids, and carotenoids were analyzed.

## MATERIALS AND METHODS

**Standards and Reagents.** All samples and standards were handled without exposure to light. Caffeic and chlorogenic acids, rutin and quercetin, *trans*-$\beta$-carotene, $\beta$-apo-8′-caortenal, *trans*-$\alpha$-carotene, *trans*-lycopene, and *trans*-lutein, methyl *tert*-butyl ether (MTBE), 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid (ABTS), (±)-6-hydroxy-2,5,7,8-tetramethylchromane-2-carboxylic acid (Trolox, 97%), manganese dioxide, and 2,2-diphenyl-1-picrylhydrazyl (DPPH) were purchased from Sigma (Madrid, Spain); naringenin, naringenin-7-*O*-glucoside, kaempferol-3-*O*-rutinoside, and hexane were from Extrasynthèse (Genay, France). Ethanol, methanol, *p*-phenylenediamine, hydrogen peroxidase, monobasic and dibasic sodium phosphate, and formic acid of HPLC grade were obtained from Scharlau (Barcelona, Spain), and ultrapure water (Milli-Q) was from Millipore (Bedford, MA).

**Commercial Samples.** In this study, a 3 month storage trial was designed to investigate the stability of the main antioxidant compounds of six commercially available gazpachos. All of the studied brands contained the same ingredients (tomato, cucumber, pepper, olive oil, and other minor constituents such as onion, garlic, wine vinegar, sea salt, and water), but in some cases the amount of each ingredient was not known. The processing date was March 2010. Each brand of gazpacho was analyzed immediately after purchase (month 0). Three cartons of each brand of gazpacho were stored for 4, 8, and 12 weeks. Gazpachos were kept in Tetra Paks at a storage temperature of 4.0 ± 0.1 °C. All products analyzed were available in Barcelona markets.

**Extraction of Phenolic Compounds from Gazpachos.** Samples were treated in triplicate in a darkened room with a red safety light to avoid oxidation of the analytes, following a procedure found in the literature[13] with some modifications.

Lyophilized gazpachos (0.5 g) were weighed and homogenized with 80% ethanol in Milli-Q water (4 mL); they were then sonicated for 5 min and centrifuged (4000 rpm at 4 °C) for 20 min. The supernatant was transferred into a flask, and extraction was repeated. The supernatants were combined and evaporated under nitrogen flow; finally, the residue was reconstituted with Milli-Q water (0.1% of formic acid) up to 1.5 mL and filtered through a 13 mm, 0.45 $\mu$m PTFE filter (Waters).

**Extraction of Carotenoid Compounds from Gazpachos.** There is a wide range of carotenoids present in vegetables and fruits. Therefore, the identification of these compounds in the food matrix is a difficult task. To avoid exposure to light, oxygen, and high temperatures and to pro-oxidant metals such as iron or copper, the extractions of carotenoids were carried out quickly in darkness and using dry ice to minimize autoxidation and *cis*–*trans* isomerization.

Lyophilized gazpachos (0.5 g) were weighed and homogenized with 5 mL of EtOH/hexane (4:3, v/v) following a procedure described in the literature;[14] they were then sonicated for 5 min and centrifuged (4000 rpm at 4 °C) for 15 min. The supernatant was transferred into a flask, and extraction was repeated. The supernatants were combined and evaporated under nitrogen flow; finally, the residue was reconstituted with MTBE to 1 mL and filtered through a 25 mm, 0.45 $\mu$m PTFE filter (Waters).

**Antioxidant Capacity.** The hydrophilic and lipophilic antioxidant capacities in gazpachos were measured by $ABTS^+$ and DPPH assays following the procedures described in the literature.[15,16]

**Peroxidase (POD) Activity Measurement.** POD activity of gazpachos was measured using the method described by Aguiló-Aguayo et al.[12] Enzyme extracts were obtained by homogenization of 10 mL of gazpacho with 20 mL of 0.2 mol $L^{-1}$ sodium phosphate buffer (pH 6.5). Then, the homogenate was centrifuged (4000 rpm, 15 min) at 4 °C. The supernatant was filtered through a Whatman no. 1 paper and the resulting liquid constituted the enzymatic extract, which was immediately used for the POD activity determination. POD activity was assayed spectrophotometrically by placing 260 $\mu$L of 0.050 mol $L^{-1}$ sodium phosphate buffer (pH 6.5), 20 $\mu$L of *p*-phenylenediamine (10 g $kg^{-1}$) as H-donor, 10 $\mu$L of hydrogen peroxidase (15 g $kg^{-1}$) as oxidant, and 10 $\mu$L of enzymatic extract in a 96-well plate. The oxidation of *p*-phenylenediamine was measured at 509 nm and 25 °C using a UV–vis Thermo Multiskan Spectrum spectrophotometer (Vantaa, Finland). POD activity was determined by measuring the initial rate of the reaction, which was computed from the linear portion of the plotted curve. One unit of POD activity was defined as a change in absorbance at 509 nm $min^{-1}$ $mL^{-1}$ of enzymatic extract. The percentage of residual POD activity (RA) was defined as indicated by eq 1

$$\mathrm{RA} = 100 \times \frac{A_t}{A_0} \quad (1)$$

where $A_t$ is the enzyme activity of gazpachos from week 0, 4, 8, or 12 and $A_0$ is the enzyme activity of gazpachos from week 0.

**Analysis of Polyphenols in Gazpachos.** HPLC-ESI-MS/MS was used to evaluate the effect of time on the content of flavonols, flavanones, and hydroxycinnamic acids.[13] An API 3000 (PE Sciex, Concord, ON, Canada) triple-quadrupole mass spectrometer equipped with a Turbo Ionspray source in negative-ion mode was used to obtain MS/MS data. Turbo Ionspray source settings were as follows: capillary voltage, −3500 V; nebulizer gas ($N_2$), 10 au (arbitrary units); curtain gas ($N_2$), 12 au; collision gas ($N_2$), 4 au; focusing potential, −200 V; entrance potential, −10 V; drying gas ($N_2$), heated to 400 °C and introduced at a flow rate of 8000 $cm^3$ $min^{-1}$. The declustering potential and collision energy were optimized for each compound in infusion experiments: individual standard solutions (10 $\mu$g $mL^{-1}$) dissolved in 50:50 (v/v) mobile phase were infused at a constant flow rate of 5 $\mu$L $min^{-1}$ using a model syringe pump (Harvard Apparatus, Holliston, MA). Full-scan data acquisition was performed scanning from $m/z$ 100 to 800 using a cycle time of 2 s with a step size of 0.1 unit and a pause between each scan of 2 ms. To confirm the identity of some compounds, neutral loss scan and precursor ion scan experiments were carried out.[17]

For quantification purposes, data were collected in the multiple reaction monitoring (MRM) mode, tracking the transition of parent and product ions specific to each compound. Quantification of polyphenols was performed by the internal standard method. Polyphenols were quantified with respect to their corresponding standard. When standards were not available, as in the case of caffeic-*O*-hexoside and ferulic-*O*-hexoside acids, they were quantified with respect to the corresponding hydroxycinnamic acid (caffeic and ferulic acids).

The liquid chromatograph was an Agilent series 1100 HPLC instrument (Agilent, Waldbronn, Germany) equipped with a quaternary pump, an autosampler, and a column oven set to 30 °C. Mobile phases consisted of 0.1% formic acid in Milli-Q water (A) and 0.1% formic acid in acetonitrile (B). The injection volume was 20 $\mu$L, and the flow rate was 0.4 mL $min^{-1}$. Separation was carried out in 20 min under the following conditions: 0 min, 5% B; 16 min, 40% B; 17 min, 95% B; 19 min, 95% B; 19.5 min, 5% B. The column was equilibrated for 5 min prior to each analysis.

**Analysis of Carotenoids in Gazpachos.** Chromatographic analysis was performed using the HPLC system described for polyphenol analysis. The analytes were separated on a $C_{30}$ column, 250 × 4.6 mm i.d., 5 $\mu$m (YMC, Waters Co., Milford, MA), and kept at 20 °C. The injection volume was 20 $\mu$L and the flow rate, 1 mL $min^{-1}$. The mobile phase consisted of two different solvent mixtures: A, water/methanol/MTBE (4:26:70, v/v), and B, the same solvents but in the range 4:90:6 (v/v). The linear gradient was from 26 to 90% B in 23 min. The column was equilibrated for 10 min prior to each analysis. The modification procedure followed the protocol previously published.[18] MTBE was used as a modifier to facilitate the elution of lycopene, which is strongly retained in a methanol environment.

*Diode Array Detector.* Commercially available carotenoid standards (*trans*-lutein, *trans*-$\alpha$-carotene, *trans*-$\beta$-carotene, and *trans*-lycopene) were used to identify analytes by retention times and UV–vis spectra. The LC-DAD chromatograms were acquired by selecting the 450 nm

Table 1. Changes in the Hydrophilic and Lipophilic Antioxidant Capacities and Relative Residual POD Activity in Gazpachos ($n$ = 3) during 12 Weeks of Storage[a]

| weeks of storage | mmol TE 100 $g^{-1}$ FW | | | | relative residual POD activity (%) |
|---|---|---|---|---|---|
| | $ABTS^+$ hydrophilic | DPPH hydrophilic | $ABTS^+$ lipophilic | DPPH lipophilic | |
| | | | **Gazpacho 1** | | |
| 0 | 3.38 ± 0.04 a | 4.68 ± 0.11 a | 1.01 ± 0.01 a | 1.19 ± 0.10 a | 100 a |
| 4 | 3.27 ± 0.07 b | 4.55 ± 0.26 b | 0.97 ± 0.08 b | 1.12 ± 0.04 b | 90.25 ± 4.08 b |
| 8 | 3.13 ± 0.04 c | 4.36 ± 0.23 c | 0.93 ± 0.05 c | 1.08 ± 0.02 c | 85.11 ± 4.05 c |
| 12 | 3.09 ± 0.02 d | 4.29 ± 0.28 d | 0.92 ± 0.03 c | 1.05 ± 0.04 d | 82.15 ± 3.97 d |
| | | | **Gazpacho 2** | | |
| 0 | 3.20 ± 0.05 a | 4.23 ± 0.14 a | 1.29 ± 0.03 a | 1.36 ± 0.04 a | 100 a |
| 4 | 3.13 ± 0.05 b | 4.12 ± 0.32 b | 1.23 ± 0.06 b | 1.32 ± 0.05 b | 90.51 ± 3.18 b |
| 8 | 3.05 ± 0.08 c | 4.02 ± 0.28 c | 1.19 ± 0.03 c | 1.28 ± 0.05 c | 88.16 ± 4.07 c |
| 12 | 3.02 ± 0.03 d | 3.93 ± 0.16 d | 1.17 ± 0.09 c | 1.26 ± 0.09 c | 84.46 ± 4.12 d |
| | | | **Gazpacho 3** | | |
| 0 | 3.95 ± 0.05 a | 4.82 ± 0.11 a | 1.07 ± 0.02 a | 1.30 ± 0.07 a | 100 a |
| 4 | 3.84 ± 0.05 b | 4.69 ± 0.22 b | 1.02 ± 0.02 b | 1.27 ± 0.08 b | 93.51 ± 3.11 b |
| 8 | 3.70 ± 0.04 c | 4.50 ± 0.28 c | 0.99 ± 0.05 c | 1.25 ± 0.06 c | 86.10 ± 4.18 c |
| 12 | 3.63 ± 0.06 d | 4.41 ± 0.10 d | 0.97 ± 0.09 c | 1.24 ± 0.03 c | 83.00 ± 4.03 d |
| | | | **Gazpacho 4** | | |
| 0 | 3.41 ± 0.04 a | 4.69 ± 0.07 a | 1.16 ± 0.05 a | 1.22 ± 0.06 a | 100 a |
| 4 | 3.30 ± 0.05 b | 4.54 ± 0.18 b | 1.12 ± 0.03 b | 1.20 ± 0.05 b | 91.10 ± 4.09 b |
| 8 | 3.15 ± 0.07 c | 4.41 ± 0.20 c | 1.09 ± 0.02 c | 1.16 ± 0.04 c | 87.43 ± 3.91 c |
| 12 | 3.09 ± 0.03 d | 4.36 ± 0.25 d | 1.08 ± 0.03 c | 1.14 ± 0.06 c | 83.00 ± 3.87 d |
| | | | **Gazpacho 5** | | |
| 0 | 4.11 ± 0.05 a | 5.00 ± 0.05 a | 1.02 ± 0.09 a | 1.24 ± 0.05 a | 100 a |
| 4 | 4.03 ± 0.06 b | 4.85 ± 0.25 b | 0.99 ± 0.08 b | 1.22 ± 0.08 b | 90.10 ± 4.15 b |
| 8 | 3.95 ± 0.07 c | 4.76 ± 0.30 c | 0,97 ± 0.07 c | 1.15 ± 0.07 c | 83.56 ± 4.02 c |
| 12 | 3.91 ± 0.09 d | 4.65 ± 0.19 d | 0.95 ± 0.05 c | 1.14 ± 0.03 c | 80.01 ± 4.06 d |
| | | | **Gazpacho 6** | | |
| 0 | 3.07 ± 0.05 a | 4.29 ± 0.08 a | 1.25 ± 0.02 a | 1.34 ± 0.06 a | 100 a |
| 4 | 2.98 ± 0.08 b | 4.16 ± 0.18 b | 1.21 ± 0.05 b | 1.30 ± 0.04 b | 91.70 ± 4.09 b |
| 8 | 2.89 ± 0.05 c | 4.09 ± 0.20 c | 1.18 ± 0.04 c | 1.25 ± 0.07 c | 87.50 ± 3.89 c |
| 12 | 2.84 ± 0.09 d | 4.01 ± 0.06 d | 1.17 ± 0.03 c | 1.23 ± 0.02 c | 84.18 ± 3.73 d |

[a]Letters in the columns represent statistically significant differences ($P < 0.05$).

wavelength; afterward, the UV−vis spectra were recorded in the range of 350−550 nm for the tentative identification of carotenoids and their geometrical isomers (*cis*-lycopene isomers), on the basis of the retention times and absorption spectrum characteristics described in the literature.[18,19]

*Mass Spectrometry.* The API 3000 (PE Sciex) triple-quadrupole mass spectrometer in positive-ion mode was used to obtain MS/MS data for carotenoid analysis. Turbo Ionspray source settings were the same as previously described for polyphenol analysis. A solvent delivery system connected postcolumn (Applied Biosystems, Foster City, CA) was used for the delivery of 100 $\mu$L $min^{-1}$ of a LiCl solution at a concentration of 500 mg $L^{-1}$.

**Statistical Analysis.** The significance of the results was analyzed using the Statgraphics Plus v.5.1 Windows Package (Statistical Graphics Co., Rockville, MD). Analysis of variance (ANOVA) was used to compare the means of groups of measurement data. Relationships between variables were examined using Pearson correlation coefficients. $P$ values of <0.05 were considered to be statistically significant.

## RESULTS AND DISCUSSION

**Effect of Time of Storage on Hydrophilic and Lipophilic Antioxidants in Gazpachos.** The contribution of carotenoids to total antioxidant capacity is considered to be small in comparison with hydrophilic antioxidant capacity. In tomatoes, the hydrophilic fraction displays greater antioxidant capacity than the lipophilic fraction. Wu et al.[20] reported that hydrophilic antioxidant capacity represents >90% of the total antioxidant capacity of fruits and vegetables. These results concur with our study. Although hydrophilic antioxidant capacity does not account for >90% of the total antioxidant capacity, hydrophilic antioxidant content is greater than lipophilic content (Table 1).

The $ABTS^+$ and DPPH values decreased over the 12 weeks of storage for both lipophilic and hydrophilic antioxidants. Although there was a slight variation between different brands of gazpachos in the content of antioxidants, the trends reflecting the effects of storage were similar. The content of hydrophilic antioxidants decreased by about 7.34% for the $ABTS^+$ assay and by 7.42% for the DPPH assay. For lipophilic antioxidant capacity, the contents decreased by 7.95 and 7.76% for the $ABTS^+$ and DPPH assays, respectively. The most significant decrease was observed after 4 weeks of storage. Del Caro et al.[21] described a decrease of about 5% in the TEAC value for orange juice stored for 12 days at 4 °C. Controversially, Piga et al.[22] reported an increase in the DPPH content over 15 days of storage of mandarin juices at 4 °C. They attributed this increase in the antioxidant capacity to the formation of Maillard reaction products.

**Effect of Time of Storage on Individual Phenolic Compounds in Gazpachos.** POD is involved in the oxidative degradation of phenolic compounds.[23] Therefore, the residual

Table 2. Changes in the Content of Hydroxycinnamic Acids in Gazpachos ($n$ = 3) during 12 Weeks of Storage[a]

| weeks of storage | $\mu$g g$^{-1}$ FW | | | | |
|---|---|---|---|---|---|
| | caffeic acid | caffeic acid-*O*-hexoside | ferulic acid | ferulic acid-*O*-hexoside | chlorogenic acid |
| | | | **Gazpacho 1** | | |
| 0 | 4.23 ± 0.04 a | 10.69 ± 0.11 a | 31.10 ± 1.21 a | 34.47 ± 0.72 a | 10.93 ± 0.14 a |
| 4 | 4.09 ± 0.09 b | 10.49 ± 0.27 b | 30.51 ± 1.15 b | 33.48 ± 1.44 b | 10.63 ± 0.25 b |
| 8 | 3.99 ± 0.07 c | 10.20 ± 0.15 c | 29.43 ± 1.54 c | 32.91 ± 1.29 c | 10.31 ± 0.29 c |
| 12 | 3.84 ± 0.08 d | 10.00 ± 0.26 c | 29.00 ± 1,45 c | 32.31 ± 1.14 c | 10.02 ± 0.40 c |
| | | | **Gazpacho 2** | | |
| 0 | 3.33 ± 0.05 a | 13.44 ± 0.14 a | 24.11 ± 1.50 a | 39.62 ± 0.40 a | 9.32 ± 0.09 a |
| 4 | 3.27 ± 0.10 b | 13.09 ± 0.29 b | 23.54 ± 0.92 b | 38.29 ± 1.43 b | 8.99 ± 0.43 b |
| 8 | 2.98 ± 0.12 c | 12.67 ± 0.18 c | 22.87 ± 1.30 c | 37.80 ± 1.31 c | 8.52 ± 0.40 c |
| 12 | 2.91 ± 0.09 d | 12.31 ± 0.22 c | 22.09 ± 1.20 d | 36.60 ± 1.29 d | 8,43 ± 0,41 d |
| | | | **Gazpacho 3** | | |
| 0 | 3.67 ± 0.05 a | 9.68 ± 0.11 a | 26.51 ± 1.02 a | 35.12 ± 0.87 a | 12.11 ± 0.15 a |
| 4 | 3.51 ± 0.03 b | 9.41 ± 0.27 b | 25.60 ± 0.95 b | 34.07 ± 0.89 b | 11.91 ± 0.21 b |
| 8 | 3.42 ± 0.09 c | 9.05 ± 0.22 c | 23.99 ± 1.10 c | 33.31 ± 1.15 c | 11.22 ± 0.35 c |
| 12 | 3.30 ± 0.08 d | 8.82 ± 0.15 d | 23.02 ± 1.22 d | 32.97 ± 1.32 d | 11.08 ± 0.26 c |
| | | | **Gazpacho 4** | | |
| 0 | 4.05 ± 0.04 a | 15.35 ± 0.07 a | 21.46 ± 1.15 a | 28.98 ± 0.36 a | 11.19 ± 0.10 a |
| 4 | 3.97 ± 0.07 b | 15.09 ± 0.15 b | 20.87 ± 1.53 b | 27.50 ± 0.55 b | 11.01 ± 0.29 b |
| 8 | 3.78 ± 0.08 c | 14.55 ± 0.19 c | 20.09 ± 1.13 c | 26.78 ± 0.59 c | 10.79 ± 0.34 c |
| 12 | 3.72 ± 0.08 d | 14.38 ± 0.21 c | 19.70 ± 1.32 c | 26.68 ± 0.65 c | 10.54 ± 0.27 d |
| | | | **Gazpacho 5** | | |
| 0 | 4.47 ± 0.05 a | 17.34 ± 0.05 a | 30.41 ± 1.09 a | 25.70 ± 0.58 a | 9.55 ± 0.12 a |
| 4 | 4.29 ± 0.10 b | 16.98 ± 0.22 b | 28.60 ± 1.15 b | 25.01 ± 1.25 b | 9.21 ± 0.25 b |
| 8 | 4.17 ± 0.13 c | 16.51 ± 0.25 c | 28.01 ± 1.11 c | 24.86 ± 1.23 c | 9.10 ± 0.29 c |
| 12 | 4.13 ± 0.05 d | 16.39 ± 0.16 c | 27.94 ± 1.33 c | 24.23 ± 1.30 c | 8.92 ± 0.31 d |
| | | | **Gazpacho 6** | | |
| 0 | 3.85 ± 0.05 a | 11.87 ± 0.08 a | 20.57 ± 1.22 a | 33.64 ± 0.64 a | 10.09 ± 0.12 a |
| 4 | 3.71 ± 0.10 b | 11.61 ± 0.18 b | 20.21 ± 1.19 b | 33.01 ± 0.89 b | 9.59 ± 0.15 b |
| 8 | 3.53 ± 0.04 c | 11.44 ± 0.20 c | 19.82 ± 1.40 c | 32.28 ± 1.21 c | 9.34 ± 0.43 c |
| 12 | 3.45 ± 0.09 d | 11.31 ± 0.15 d | 19.47 ± 1.23 d | 32.12 ± 1.38 c | 9.20 ± 0.29 c |

[a]Letters in the columns represent statistically significant differences ($P < 0.05$).

activity of POD might be associated with the degradation of phenolic compounds during storage. Table 1 shows the relative POD activity after 4, 8, and 12 weeks of storage. Ferulic, caffeic, and chlorogenic acid, ferulic acid-*O*-hexoside, and caffeic acid-*O*-hexoside were identified in gazpachos (Table 2). Levels of caffeic acid in gazpachos were in line with those reported by Martínez-Valverde et al.[24] for tomato products, which ranged between 1.39 and 13 $\mu$g g$^{-1}$ FW. The content of ferulic acid was higher than that found by Luthria et al.[25] for tomato products, who reported values between 9 and 15 $\mu$g g$^{-1}$ FW, whereas in our study the results were between 20.57 and 31.10 $\mu$g g$^{-1}$ for ferulic acid and between 25.70 and 39.62 $\mu$g g$^{-1}$ for its glycosidic form. The trends reflecting the effects of storage were similar for all of the gazpachos analyzed.

The content of hydroxycinnamic acids decreased after 12 weeks of storage at 4 °C. The greatest decrease ($P < 0.05$) occurred for ferulic (8.33%) and caffeic (9.68%) acids during the 12 weeks of storage, whereas their glycosidic forms decreased by 6.37 and 6.71%, respectively. The higher stability of the glycosidic forms toward their aglycones could be attributed to the blockage of the 3-hydroxy function at the C-ring by a sugar moiety.[26] Similarly, chlorogenic acid decreased by 7.94%.

As described by Gliszczynska-Swiglo and Tyrakowska,[27] caffeic and chlorogenic acids decreased during the storage of apple juices. They found that the initial concentrations of caffeic acid were 3.31−8.66 mg L$^{-1}$ and underwent losses reaching values of 1.51 to 3.49 mg L$^{-1}$. The same pattern was observed for chlorogenic acids. Hydroxycinnamic acids are formed in plant products via the action of phenylalanine ammonia-lyase activity (PAL) due to the phenylpropanoid metabolism.

Biosynthesis of flavonols consists of the sequential addition of three molecules of malonyl-CoA to hydroxycinnamic acid CoA esters to form chalcones. These chalcones are then isomerized into (2*S*)-flavanones, which, through hydroxylation and desaturation, are converted into flavonols.[28] In our study, it could not be hypothesized that the disappearance of hydroxycinnamic acids is due to their conversion to flavonols, as quercetin, rutin, and kaempferol-3-*O*-rutinoside did not increase during storage and other flavonols were not detected. Therefore, decreases may be due to the oxidation of chlorogenic to reactive *O*-quinones through the catalytic oxidation process.[29]

A slight decrease in naringenin and naringenin-7-*O*-glucoside was observed (Table 3). The naringenin content found in gazpachos was in the range reported by other authors in tomato products.[24,30] The initial concentrations of naringenin in the studied gazpachos were 44.08−46.83 $\mu$g g$^{-1}$ FW, whereas naringenin-7-*O*-glucoside was found at concentrations of 2.16−2.54 $\mu$g g$^{-1}$ FW. The naringenin content in gazpachos

Table 3. Changes in the Content of Flavonols and Flavanones in Gazpachos ($n$ = 3) during 12 Weeks of Storage[a]

| weeks of storage | $\mu$g g$^{-1}$ FW | | | | |
|---|---|---|---|---|---|
| | rutin | quercetin | kaempferol-3-*O*-rutinoside | naringenin | naringenin-7-*O*-glucoside |
| | | | **Gazpacho 1** | | |
| 0 | 59.98 ± 1.04 a | 2.79 ± 0.02 a | 20.47 ± 0.82 a | 44.08 ± 1.10 a | 2.48 ± 0.08 a |
| 4 | 57.93 ± 3.30 b | 2.63 ± 0.07 b | 19.80 ± 1.79 b | 42.90 ± 2.60 b | 2.39 ± 0.18 b |
| 8 | 55.81 ± 2.66 c | 2.48 ± 0.05 c | 19.19 ± 1.44 c | 41.49 ± 2.30 c | 2.32 ± 0.16 c |
| 12 | 54.00 ± 2.90 d | 2.29 ± 0.03 d | 18.53 ± 1.53 d | 41.00 ± 2.35 c | 2.28 ± 0.11 d |
| | | | **Gazpacho 2** | | |
| 0 | 56.99 ± 1.59 a | 2.47 ± 0.01 a | 20.77 ± 1.28 a | 46.83 ± 1.24 a | 2.26 ± 0.13 a |
| 4 | 54.91 ± 3.31 b | 2.32 ± 0.03 b | 22.35 ± 1.12 b | 45.21 ± 1.87 b | 2.22 ± 0.12 b |
| 8 | 52.81 ± 2.54 c | 2.15 ± 0.04 c | 19.81 ± 1.33 c | 44.29 ± 2.25 c | 2.19 ± 0.05 c |
| 12 | 51.93 ± 2.98 c | 2.00 ± 0.05 d | 19.50 ± 1.21 c | 43.02 ± 2.13 d | 2.17 ± 0.18 c |
| | | | **Gazpacho 3** | | |
| 0 | 54.40 ± 1.33 a | 2.61 ± 0.02 a | 19.57 ± 0.76 a | 44.46 ± 1.25 a | 2.19 ± 0.13 a |
| 4 | 52.67 ± 1.50 b | 2.44 ± 0.06 b | 18.90 ± 1.59 b | 42.21 ± 1.76 b | 2.14 ± 0.19 b |
| 8 | 50.54 ± 2.85 c | 2.33 ± 0.05 c | 18.31 ± 1.13 c | 41.51 ± 2.09 c | 2.10 ± 0.26 c |
| 12 | 49.31 ± 2.60 d | 2.16 ± 0.03 d | 17.92 ± 1.56 d | 41.33 ± 2.15 c | 2.07 ± 0.15 d |
| | | | **Gazpacho 4** | | |
| 0 | 60.68 ± 1.24 a | 2.48 ± 0.01 a | 20.59 ± 0.52 a | 46.50 ± 1.43 a | 2.53 ± 0.07 a |
| 4 | 58.03 ± 2.31 b | 2.32 ± 0.05 b | 20.01 ± 0.23 b | 45.65 ± 1.87 b | 2.49 ± 0.13 b |
| 8 | 57.37 ± 2.23 c | 2.21 ± 0.02 c | 19.70 ± 0.34 c | 44.80 ± 1.75 c | 2.45 ± 0.15 c |
| 12 | 57.00 ± 1.25 c | 2.15 ± 0.04 d | 19.25 ± 0.40 c | 44.01 ± 1.99 c | 2.41 ± 0.24 d |
| | | | **Gazpacho 5** | | |
| 0 | 51.04 ± 1.03 a | 2.08 ± 0.01 a | 19.05 ± 0.99 a | 44.90 ± 1.48 a | 2.16 ± 0.09 a |
| 4 | 50.00 ± 1.95 b | 2.00 ± 0.05 b | 18.70 ± 1.43 b | 43.01 ± 1.87 b | 2.10 ± 0.22 b |
| 8 | 48.77 ± 2.25 c | 1.83 ± 0.06 c | 18.00 ± 1.22 c | 42.90 ± 1.75 c | 2.09 ± 0.05 c |
| 12 | 48.00 ± 2.89 c | 1.75 ± 0.05 d | 17.88 ± 1.12 d | 42.50 ± 1.98 c | 2.01 ± 0.06 d |
| | | | **Gazpacho 6** | | |
| 0 | 61.83 ± 1.21 a | 2.74 ± 0.02 a | 20.41 ± 0.78 a | 45.20 ± 3.23 a | 2.54 ± 0.08 a |
| 4 | 58.00 ± 1.79 b | 2.55 ± 0.06 b | 19.87 ± 1.01 b | 43.18 ± 2.43 b | 2.41 ± 0.14 b |
| 8 | 57.43 ± 2.31 c | 2.49 ± 0.04 c | 19.37 ± 1.91 c | 42.61 ± 2.50 c | 2.35 ± 0.15 c |
| 12 | 57.03 ± 2.77 c | 2.25 ± 0.05 d | 19.05 ± 1.82 c | 42.40 ± 2.30 c | 2.30 ± 0.18 d |

[a]Letters in the columns represent statistically significant differences ($P < 0.05$).

decreased by 6.53% and that of naringenin-7-*O*-glucoside by about 6.44%.

Gazpachos have been found to be a rich source of flavonols such as quercetin, kaempferol, and rutin. Naringenin (45%) is reported to be the main flavonoid, followed by quercetin (39%), myricetin (10%), and kaempferol (5%).[9] Other studies report rutin to be the major flavonoid in several tomato cultivars.[17] In this study, rutin was the dominant flavonol in all of the gazpachos, followed by kaempferol-3-*O*-rutinoside and quercetin.

The initial concentrations of quercetin in the studied gazpachos were 2.08−2.79 $\mu$g g$^{-1}$ FW, whereas kaempferol-3-*O*-rutinoside was found at concentrations of 19.05−20.77 $\mu$g g$^{-1}$ FW. Quercetin underwent significant losses throughout the gazpacho storage period, reaching values of 1.75−2.29 $\mu$g g$^{-1}$ FW. Our results were in line with those found by Vallverdú-Queralt et al.[31] during the storage of ketchups and tomato juices.

Changes in rutin content are also shown in Table 3; rutin decreased by 8.00%. It could be hypothesized that the oxidative degradation of phenolic compounds is due to the residual peroxidase activity and the autocatalytic oxidative reactions. Flavonols may capture reactive oxygen species and, during the thermal processing, flavonols could form quinonoid structures, which leads to the formation of quinones. In the case of rutin and kaempferol-3-*O*-rutinoside, in comparison with quercetin, the 3-hydroxy function at the C-ring of the flavonoid is blocked by a sugar moiety. Thus, the blockage of the 3-hydroxyl group might explain the higher stability of rutin and kaempferol toward oxidation.

**Effect of Time of Storage on Individual Carotenoids in Gazpachos.** Table 4 shows the evolution of the carotenoid content in gazpachos over 12 weeks of storage at 4 °C. The initial concentrations of *all-trans*-lycopene in the studied gazpachos were 2.99−4.31 $\mu$g g$^{-1}$ FW. *all-trans*-Lycopene underwent significant losses throughout the storage of gazpachos, reaching values of 2.45−3.51 $\mu$g g$^{-1}$ FW. *trans*-Lycopene decreased by 16.91% in comparison to *trans*-$\beta$-carotene, *trans*-$\alpha$-carotene, and *trans*-lutein, which decreased by 8.54, 10.24, and 5.44%, respectively.

Our results are in line with those reported by Lin and Chen,[32] who attributed the higher stability of *trans*-lutein and *trans*-$\beta$-carotene to the coplanar structure of *trans*-lycopene, in which 11 conjugated double bonds are present and which should be more reactive than *trans*-lutein and *trans*-$\beta$-carotene.

In another study, Zanoni et al.[33] reported that *trans*-lycopene underwent a high loss of 50% in dried tomatoes after a 30 day storage period and a loss of 70% after 90 days. Similarly, Odriozola-Serrano et al.[11] reported final *trans*-lycopene losses of approximately 70% in tomato juice stored at 4 °C for 3 months. Moreover, similar lycopene degradation patterns (35−75%) have been described by Giovanelli and Paradiso[34] during

Table 4. Changes in the Content of Carotenoids in Gazpachos ($n$ = 3) during 12 Weeks of Storage[a]

| | μg g$^{-1}$ FW | | | | | | |
|---|---|---|---|---|---|---|---|
| weeks of storage | *trans*-α-carotene | *trans*-β-carotene | *trans*-lutein | *trans*-lycopene | 5-*cis*-lycopene | 9-*cis*-lycopene | 13-*cis*-lycopene |
| **Gazpacho 1** | | | | | | | |
| 0 | 0.25 ± 0.01 a | 9.10 ± 0.04 a | 2.04 ± 0.02 a | 3.24 ± 0.16 a | 2.37 ± 0.05 a | 1.18 ± 0.02 a | 1.64 ± 0.16 a |
| 4 | 0.21 ± 0.01 b | 8.75 ± 0.12 b | 2.00 ± 0.09 b | 3.10 ± 0.13 b | 2.35 ± 0.10 a | 1.15 ± 0.04 b | 1.55 ± 0.15 b |
| 8 | 0.20 ± 0.01 c | 8.45 ± 0.11 c | 1.98 ± 0.08 c | 2.85 ± 0.15 c | 2.40 ± 0.07 b | 1.15 ± 0.06 b | 1.54 ± 0.12 b |
| 12 | 0.19 ± 0.01 c | 8.34 ± 0.03 c | 1.95 ± 0.06 d | 2.74 ± 0.17 d | 2.45 ± 0.09 c | 1.14 ± 0.05 b | 1.52 ± 0.10 c |
| **Gazpacho 2** | | | | | | | |
| 0 | 0.32 ± 0.03 a | 15.69 ± 0.05 a | 1.98 ± 0.08 a | 4.31 ± 0.19 a | 3.42 ± 0.04 a | 0.74 ± 0.01 a | 1.42 ± 0.12 a |
| 4 | 0.30 ± 0.02 b | 15.35 ± 0.02 b | 1.92 ± 0.09 b | 4.06 ± 0.15 b | 3.45 ± 0.08 b | 0.71 ± 0.02 b | 1.36 ± 0.011 b |
| 8 | 0.30 ± 0.01 b | 14.75 ± 0.09 c | 1.89 ± 0.07 c | 3.78 ± 0.17 c | 3.46 ± 0.03 c | 0.70 ± 0.03 b | 1.35 ± 0.10 b |
| 12 | 0.29 ± 0.01 b | 14.50 ± 0.07 c | 1.85 ± 0.06 d | 3.51 ± 0.14 d | 3.50 ± 0.02 d | 0.70 ± 0.01 b | 1.32 ± 0.09 c |
| **Gazpacho 3** | | | | | | | |
| 0 | 0.27 ± 0.02 a | 11.43 ± 0.01 a | 1.90 ± 0.04 a | 3.25 ± 0.16 a | 2.96 ± 0.07 a | 1.04 ± 0.04 a | 1.38 ± 0.11 a |
| 4 | 0.26 ± 0.02 b | 11.13 ± 0.05 b | 1.84 ± 0.05 b | 3.05 ± 0.19 b | 2.98 ± 0.06 b | 1.02 ± 0.05 b | 1.32 ± 0.10 b |
| 8 | 0.25 ± 0.01 b | 10.69 ± 0.04 c | 1.80 ± 0.04 c | 2.82 ± 0.10 c | 3.00 ± 0.05 b | 1.00 ± 0.03 c | 1.30 ± 0.09 c |
| 12 | 0.25 ± 0.01 b | 10.42 ± 0.08 c | 1.79 ± 0.03 c | 2.71 ± 0.15 d | 3.05 ± 0.07 c | 0.98 ± 0.01 c | 1.29 ± 0.08 c |
| **Gazpacho 4** | | | | | | | |
| 0 | 0.37 ± 0.03 a | 14.56 ± 0.04 a | 1.88 ± 0.04 a | 3.18 ± 0.12 a | 2.83 ± 0.11 a | 0.86 ± 0.02 a | 1.35 ± 0.11 a |
| 4 | 0.35 ± 0.02 b | 14.20 ± 0.05 b | 1.81 ± 0.05 b | 2.99 ± 0.19 b | 2.86 ± 0.15 b | 0.85 ± 0.06 a | 1.28 ± 0.06 b |
| 8 | 0.35 ± 0.03 b | 13.65 ± 0.09 c | 1.76 ± 0.07 c | 2.71 ± 0.11 c | 2.90 ± 0.12 c | 0.83 ± 0.07 b | 1.27 ± 0.05 b |
| 12 | 0.34 ± 0.03 b | 13.34 ± 0.08 c | 1.73 ± 0.08 d | 2.67 ± 0.15 d | 2.89 ± 0.06 d | 0.82 ± 0.05 b | 1.25 ± 0.07 b |
| **Gazpacho 5** | | | | | | | |
| 0 | 0.31 ± 0.03 a | 10.72 ± 0.03 a | 1.85 ± 0.05 a | 2.99 ± 0.14 a | 2.71 ± 0.06 a | 1.36 ± 0.09 a | 1.36 ± 0.11 a |
| 4 | 0.30 ± 0.02 b | 10.33 ± 0.06 b | 1.81 ± 0.07 b | 2.80 ± 0.15 b | 2.73 ± 0.06 b | 1.32 ± 0.12 b | 1.30 ± 0.07 b |
| 8 | 0.29 ± 0.02 b | 9.95 ± 0.04 c | 1.80 ± 0.06 c | 2.61 ± 0.13 c | 2.76 ± 0.03 c | 1.30 ± 0.10 c | 1.27 ± 0.05 c |
| 12 | 0.28 ± 0.02 b | 9.75 ± 0.03 d | 1.78 ± 0.09 d | 2.45 ± 0.19 d | 2.79 ± 0.08 d | 1.25 ± 0.08 d | 1.25 ± 0.09 c |
| **Gazpacho 6** | | | | | | | |
| 0 | 0.53 ± 0.05 a | 15.78 ± 0.04 a | 1.95 ± 0.06 a | 3.86 ± 0.15 a | 3.36 ± 0.08 a | 1.71 ± 0.15 a | 1.65 ± 0.15 a |
| 4 | 0.51 ± 0.05 b | 15.40 ± 0.05 b | 1.90 ± 0.06 b | 3.61 ± 0.16 b | 3.39 ± 0.10 b | 1.69 ± 0.16 b | 1.57 ± 0.13 b |
| 8 | 0.50 ± 0.04 b | 14.73 ± 0.06 c | 1.88 ± 0.05 c | 3.30 ± 0.14 c | 3.41 ± 0.15 c | 1.65 ± 0.14 c | 1.55 ± 0.12 c |
| 12 | 0.49 ± 0.03 b | 14.33 ± 0.08 c | 1.87 ± 0.07 c | 3.21 ± 0.15 d | 3.45 ± 0.19 d | 1.62 ± 0.13 d | 1.53 ± 0.14 c |

[a]Letters in the columns represent statistically significant differences ($P$ < 0.05).

the storage of tomato paste. Controversially, García Alonso et al.[35] found that the total lycopene content remained fairly stable throughout the storage trial and varied from 99 to 120 mg kg$^{-1}$ in tomato juice packaged in Tetra Paks and from 96 to 115 mg kg$^{-1}$ in samples stored in glass bottles. For both types of samples, no clear temperature dependency was revealed regarding the rate of total lycopene loss, which was affected only by storage time. At the end of the storage trial, the final losses in the total lycopene content varied from 7 to 17%. The differences in lycopene stability between these studies could be attributed to the presence and stability of other antioxidants such as polyphenols or to the thermal inactivation of oxidizing enzymes during tomato processing.[36]

We also looked at *cis*-isomers of lycopene. Human health studies have demonstrated the nutritional benefits of *cis*-isomers in tomato products, because these compounds seem to be better absorbed in the intestine.[36] We tentatively identified three isomers in gazpachos: 5-, 9-, and 13-*cis*-lycopene (Table 4). This lycopene isomer profile is in line with that described by other authors in different tomato products, in which *trans*-lycopene represents the most abundant lycopene isomer, varying from 35 to 96% of total lycopene, with 5-, 9-, 13-, and 15-*cis*-lycopene being the main *cis*-isomers detected.[19,37] It was shown that during meal preparation, lycopene undergoes *trans*/*cis*-isomerization, increasing the proportion of *cis*-isomers.[32] As mentioned above, *all-trans*-lycopene underwent a 16.91% loss in gazpachos in comparison to *cis*-lycopene isomers, which slightly decreased, 5.52 and 7.27% for 9-*cis*-lycopene and 13-*cis*-lycopene, respectively. An increase of 2.72% for the 5-*cis*-lycopene isomer was observed in gazpacho products. These results are in line with those reported by Lin and Chen.[32] They observed the formation of *cis*-lycopene isomers during the 3 month storage period of tomato juice. This could be explained by the isomerization phenomenon. *all-trans*-Lycopene can be converted to 13-*cis*-lycopene, which can then be converted into other *cis*-isomers.

To our knowledge, this is the first time a study has been carried out to evaluate the stability of flavonols, flavanones, hydroxycinnamic acids, and individual carotenoids in gazpachos during storage.

The storage of gazpachos at 4 °C results in a slight decrease in their polyphenol and carotenoid contents and also in the hydrophilic and lipophilic antioxidant capacities, but the levels achieved do not signify a nutritional drawback. Therefore, we can expect a beneficial effect from the consumption of gazpachos at any point during their shelf life.

The main degradation was observed for quercetin oxidation because the hydroxy function at the C-ring of the flavonoid is not blocked by a sugar moiety as it is in the case of rutin, kaempferol-3-*O*-rutinoside, and glycosylated caffeic and ferulic acids.

Lycopene underwent significant losses throughout storage, due mainly to the 11 conjugated double bonds that are present in its structure, and should be more reactive than *trans*-lutein and *trans*-β-carotene. *cis*-Lycopene isomers slightly decreased. However, 5-*cis*-lycopene underwent a slight increase; this phenomenon could be explained by *cis*-isomerization increasing the portion of *cis*-isomers.

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