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Changes in the contents of carotenoids, phenolic compounds and vitamin C during technical processing and lyophilisation of red and yellow tomatoes

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ABSTRACT

We present the results of the first study on the impact of thermal processing and lyophilisation on three major micronutrient families: carotenoids, total polyphenols and vitamin C in two different tomato cultivars: a red tomato (RT) and a yellow one (YT). Micronutrients were analysed in fresh tomatoes, tomato purée and lyophilised tomatoes. YT contained no lycopene, lower β-carotene, similar vitamin C and higher total polyphenol contents than RT. Processing did not affect the carotenoid content in RT, but significantly lowered β-carotene in YT and also the contents of total polyphenol and vitamin C in both cultivars. Lyophilisation lowered the carotenoid content in RT but not in YT; in contrast, the total polyphenol content was preserved in RT but lowered in YT, and the vitamin C content was not affected in both cultivars. These results provide new data on the effect of thermal processing and lyophilisation on the content of the three main families of micronutrients in red and yellow tomatoes.

1. Introduction

Tomato is the second most consumed vegetable in the world, after potato, (<http://faostat.fao.org>), and approximately 30% is consumed as transformed products. Among them, tomato powder is a common product widely used by food processors. Consumption of processed tomato products is rising in western countries. Between 1996 and 2001, the quantity of processed tomatoes increased from 7.88 to 8.45 million tons in the EU (<www.wptc.to>). Tomato, as a fresh or transformed product, possesses a high nutritional value, due to its content of different types of micronutrients: vitamins (C and E), folates, carotenoids and phenolic compounds (Beecher, 1998; Periago & Garcia-Alonso, 2009). Tomato is the main source of lycopene in the western diet. This carotenoid confers the characteristic red colour. Epidemiological studies have suggested that people with a high lycopene intake from tomato products have a lower risk of prostate cancer (Giovannucci, 2005), although controversy still remains among the scientific community.

Whereas numerous studies on the micronutrient content of fresh tomato have been conducted, very little is known about the effects of processing on its nutritional quality, and controversial results can be found in the literature. Most of these studies focused on the loss of one type of micronutrient, e.g., one carotenoid, mainly lycopene (Graziani et al., 2003; Sharma & LeMaguer, 1996) or two types of micronutrients, such as phenolic compounds and vitamin C (Gahler, Otto, & Böhm, 2003) or flavonoids and carotenoids (Re, Bramley, & Rice-Evans, 2002). However, only a few studies describe the impact of technological processes on various antioxidants in tomatoes, thus taking account of the different parameters implied in the nutritional value of tomato, such as lycopene, vitamin C and phenolic compounds (Capanoglu, Beekwilder, Boyacioglu, Hall, & De Vos, 2008; Dewanto, Wu, Adom, & Liu, 2002), or lycopene, vitamin C, phenolic compounds and folates (Perez-Conesa et al., 2009), or lycopene, vitamin C and vitamin E (Abushita, Daood, & Biacs, 2000).

Lyophilisation is often used at the laboratory level to dehydrate fresh biological material for storage because no enzymatic reactions can occur in the dry state. Freeze-dried botanical samples can also be found as commercial products in the public area. It is commonly assumed that the lyophilisation process itself does not

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affect the composition of the plant material. However, few analytical data are available to confirm this assumption (Abascal, Ganora, & Yarnell, 2005).

In this paper, we describe the effect of a classical thermal process to produce tomato purée and a freeze-drying treatment on the three main families of bioactive components of tomato: carotenoids, phenolic compounds and vitamin C. Two varieties of tomatoes were chosen for their different carotenoid content: a red cultivar and a yellow one. Their content of targeted micronutrients in the fresh state was compared to those after processing and lyophilisation.

2. Materials and methods

2.1. Tomato growth conditions and harvesting

Two genotypes of tomato plants, one producing red fruits (*Solanum lycopersicum* L. cv. Cheers, De Ruiter) and the other producing yellow fruits (*Solanum lycopersicum* L. cv. 6205, Séminis) were grown during spring 2006, on N–S oriented coco slabs in the same glasshouse at Bellegarde in Southern France (43.75°N, 4.5°E). Nutrient supply as well as chemical control of pests and diseases followed commercial practices. Water was supplied to the plants according to the potential evapotranspiration in order to maintain 20–30% drainage. Flowers were open-pollinated by bumble bees and all side shoots were removed as they appeared. Every fortnight, old leaves were removed up to the youngest turning truss. Mature red and yellow tomatoes were harvested at three different times between June 8th and July 20th 2006, in order to be representative of fruits grown during summertime. The maturity stage was harmonised according to the external colour of the fruit and its firmness (measured with a Durofel; COPA-Technologie SA, St Etienne du Grès, France). The maturity stage corresponded to the red-ripe stage for the red tomato and to a golden-yellow colour for the yellow tomato.

2.2. Sampling and colour measurement

At each harvest, samples of both red and yellow tomatoes were taken from three batches of 13 tomatoes, representative subsets of the harvested tomatoes. The external colour was measured near the pistil scar by a Minolta chromameter (CR 300; Minolta SA, Carrières-Sur-Seine, France) using the CIELAB ($L^*a^*b^*$) colour space (Hunter colour coordinates, where L^* represents lightness, a^* ranges from green to red, b^* ranges from blue to yellow). The values a^* and b^* were used to calculate the hue angle ($H = \arctan(b^*/a^*)$) and metric chroma value ($C = (a^{*2} + b^{*2})^{1/2}$).

Tomato fruit were cut into quarters; two opposite quarters of each tomato fruit were chopped to reduce their size to less than 1 square cubic centimetre, immediately frozen in a freezing tunnel at −30 °C and then stored at −80 °C until they were ground to a homogeneous powder in liquid nitrogen. Aliquots of powder were prepared and stored at −80 °C for a maximum of 3 months until they were analysed. Such samples are regarded as fresh tomato in this work.

2.3. Lyophilisation

Aliquots of tomato powder (prepared as described in Section 2.2) were submitted to a one-week lyophilisation (freezing at −20 °C, followed by two successive drying steps at 0.5 mbar and 0.1 mbar, respectively, at 10 °C). The samples were stored at −20 °C for a maximum of 3 months until they were analysed.

2.4. Tomato processing

Tomato purée was produced from three batches of red or yellow tomatoes that had been harvested at three different times. The tomatoes were processed in a pilot plant at the French Technical Centre for Food Industry (CTCPA, Avignon, France). For each batch, the tomatoes were washed for 5 min in three volumes of water under slight agitation, ground with a hammer mill (Fryma) before being heated for 10 min at 92 °C in a tubular heat exchanger. The mixture was then passed through a sieve (Robocoupe) equipped with a 1-mm grid, to remove seeds and residual skins. The mixture was concentrated under a pressure of −0.96 bar at 65 °C, until it reached 14 Brix. The purée was filled into 425-ml cans, pasteurised by immersion at 100 °C for 10 min, and then stored at 4 °C. The three resulting tomato purées were mixed, canned and subjected to a final thermal treatment at 100 °C for 50 min (Fig. 1). The dry matter contents of the red and yellow tomato purées were analysed by vacuum-drying the samples for at least 6 h at 60 °C to constant weight.

2.5. Chemicals

The standard chemicals (lycopene, β-carotene) were purchased from Sigma (St Quentin-Fallavier, France). Acetone (p.a.), acetonitrile (HPLC grade), ethanol (p.a.), *n*-hexane (p.a.), methanol (HPLC grade), petroleum ether 35–60° and L-ascorbic acid were purchased from Carlo Erba (Val de Reuil, France). Folin–Ciocalteu reagent, gallic acid and 1,2-*o*-phenylenediamine were purchased from Merck (Limonest, France). Ascorbate oxidase spatulas were purchased from Roche Diagnostics GmbH (Mannheim, Germany).

2.6. Analysis of carotenoids

2.6.1. Extraction methods

The efficiency of two different solvent mixtures on the extraction of carotenoids from red processed tomato (1–10 g of red tomato purée) was compared: a mixture of hexane/acetone/ethanol (50/25/25, v/v/v, HAE) inspired by Sadler and Davis (1990), and acetone/petroleum ether (Buret, 1991). The first procedure involved placing tomato material in a beaker with 100 ml HAE in the dark. The mixture was thoroughly agitated with a magnetic stirrer for 20 min. The extract was filtered and then transferred into a separating funnel. The organic phase was washed three times with 20 ml distilled water to remove acetone and ethanol. The aqueous phase was discarded, remaining water in the organic phase was removed with anhydrous sodium sulphate, and the volume was made up to 50 ml with hexane. The second procedure involved extracting with acetone as follows: tomato material was mixed with 50 ml acetone for 20 min in the dark, and the mixture was filtered through carded cotton. Carotenoids from the remaining material were subsequently extracted in the same way twice by mixing with 30 ml acetone for 5 min and combining the filtrates in a separating funnel. Petroleum ether (75 ml) was added, and the organic phase was washed three times with 50 ml water. Remaining water was removed with anhydrous sodium sulphate, and the volume was made up to 100 ml with petroleum ether.

Carotenoids from frozen and lyophilised tomato were obtained by solid/liquid extraction from an appropriate amount of material (i.e., 2–10 g frozen powder, or 0.1 g lyophilisate) using the acetone method described above.

2.6.2. Quantitative analysis

The concentrations of lycopene and β-carotene were determined spectrophotometrically (Perkin Elmer – Lambda 25) using the following equations (Lime, Griffiths, O'Connor, Heinzelman, & McCall, 1957):

$$C_{\beta-\text{carotene}} = 4.624 \times A_{450} - 3.091 \times A_{503} \quad (1)$$

$$C_{\text{lycopene}} = 3.956 \times A_{450} - 0.806 \times A_{503} \quad (2)$$

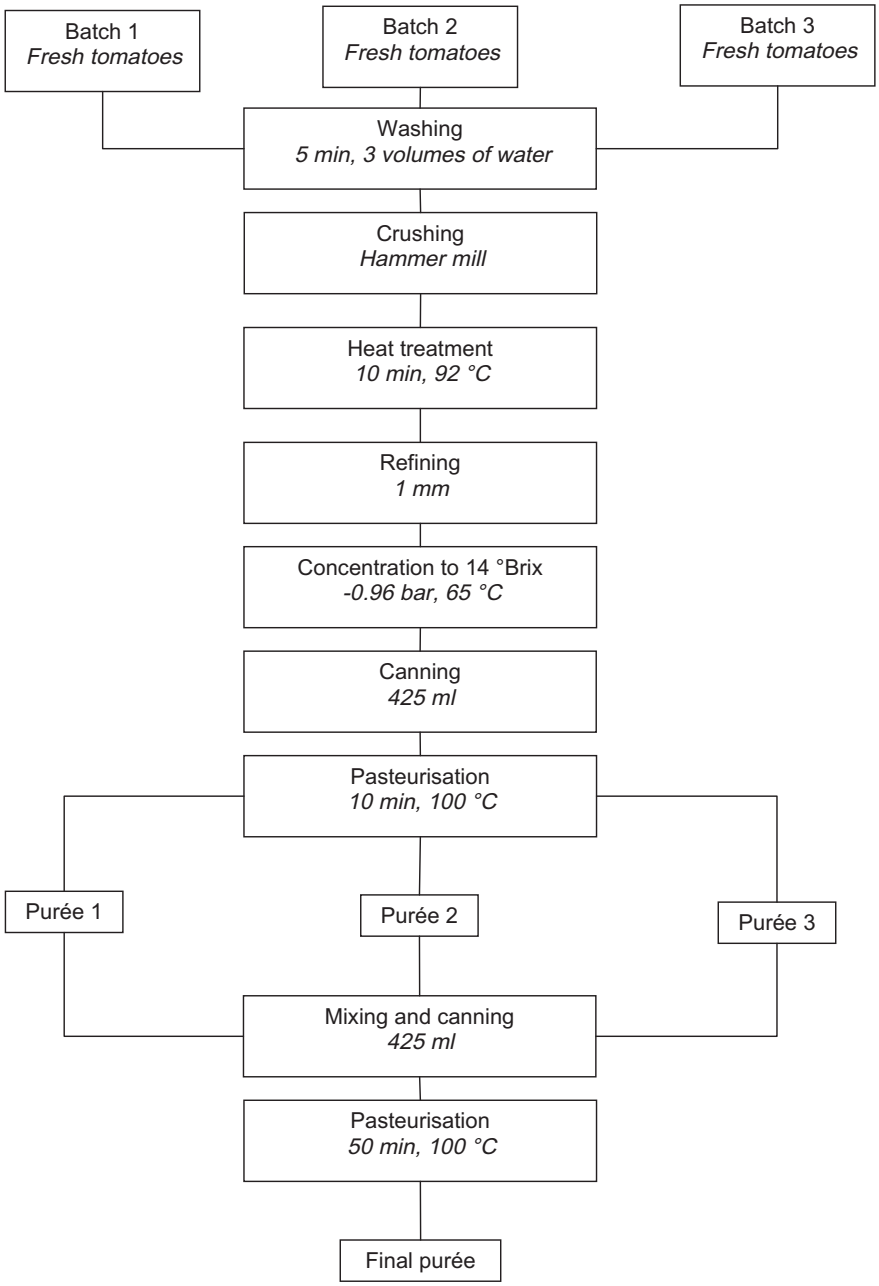

Fig. 1. Description of the process used to obtain red and yellow tomato purées.

where C is the concentration of carotenoid expressed in μg/ml, and A_{450} and A_{503} represent the absorbance at 450 nm and 503 nm, respectively.

2.6.3. Qualitative analysis

Fresh tomatoes were analysed by reverse-phase HPLC using an HP 1100 system equipped with a quaternary pump, an autosampler and a diode array detector. Separation was achieved using an Atlantis 150 × 4.6 mm C_{18} column (Waters, Saint Quentin en Yvelines, France). A linear gradient of acetonitrile (35–77%) in methanol was used as the mobile phase with a flow rate of 1 ml/min for a maximum elution time of 30 min at a temperature of 27 °C.

2.7. Polyphenol analysis

2.7.1. Total polyphenol content

Fresh, processed and freeze-dried tomato samples (from 300 mg to 1 g) were homogenised with 10 ml extraction solution (acetone/water, 7/3, v/v) for 10 min. The raw extract was obtained after filtration through Whatman paper (Whatman, Limonest, France). Phenolic compounds are commonly determined using the Folin–Ciocalteu reagent; however, it interacts with other non-phenolic reducing substances and thus overestimates the polyphenol content. In our method, solid-phase extraction (Oasis HLB; Waters, Milford, MA) was carried out on the raw extract to eliminate the water-soluble reducing interferences, including vitamin C. Colorimetric correction was thus performed by subtracting interfering substances contained in the aqueous washing extract from the raw extract. The complete analytical procedure was performed as previously described by George, Brat, Alter, and Amiot (2005).

2.7.2. Qualitative analysis

An HPLC chromatograph (Agilent 1100 Series) equipped with a diode array detector was used to analyse the phenolic compounds

in fresh tomato extracts, prepared as described above, according to the following method. A 150 × 4.6 mm C_{18} column (Alltima 5 μm, Alltech; Grace, Deerfield, IL) and a C_{18} guard column with the same packing were used. Phenolic compounds were eluted with a gradient of water (0.5% (v/v) formic acid) and acetonitrile: 10% acetonitrile in the first 10 min, 10–50% acetonitrile from 10 to 35 min, and 100% acetonitrile from 35 to 50 min. The total elution time was 50 min and the flow rate was 1.0 ml/min. LC–MS analysis was also performed using an HPLC chromatograph (HP Model 1050) equipped with a diode array detector (Agilent 1100 Series) coupled to a Micromass LCZ mass spectrometer (Waters). The following method was used. A 4.6 × 150 mm C_{18} column (Alltima 5 μm, Alltech) and a C_{18} column guard with the same packing were used, kept at 35 °C. Phenolic compounds were eluted with a gradient of water (1% (v/v) formic acid) and methanol/acetonitrile (1.5/1, v/v): 10% methanol/acetonitrile in the first 10 min, 10–15% methanol/acetonitrile from 10 to 16 min, 15% methanol/acetonitrile from 16 to 26 min, 15–30% methanol/acetonitrile from 26 to 40 min, 30–45% methanol/acetonitrile from 40 to 60 min and 45–50% methanol/acetonitrile from 60 to 65 min. The total elution time was 65 min and the flow rate was 0.8 ml/min. Mass spectra were recorded in the negative electrospray mode. Parameters, especially the cone voltage (−25 and −30 V), were optimised to avoid fragmentation. The Masslynx program was used for data analysis.

2.8. Vitamin C analysis

We determined the total vitamin C as the sum of L-ascorbic acid (AA) and dehydroascorbic acid (DHAA). The method is based on (i) extraction with an acidic solution (trichloroacetic acid, 0.3 M), (ii) enzymatic conversion of AA to DHAA with ascorbate oxidase (as a ready-to-use ascorbate oxidase spatula), (iii) derivatisation with 1,2-*o*-phenylenediamine. Quantification of vitamin C was performed by HPLC (Waters system) with a reversed-phase C_{18} column (Waters Spherisorb ODS 2, 250 × 4.6 mm i.d., 5 μm particle size) maintained at 30 °C. The mobile phase was 0.1 M K_2HPO_4/0.08 M KH_2PO_4/CH_3OH, (55/25/20, v/v/v), and the flow rate was 1.5 ml/min. Detection was performed with a III-1311 Milton Roy fluorimeter (Ivyland, PA) with $\lambda_{excitation}$ = 350 nm and $\lambda_{emission}$ = 430 nm. The injection volume was 20 μl and total run time was 10 min. Quantification was carried out by external calibration with L-ascorbic acid. The calibration curve was set from 1 to 7 μg/ml.

2.9. Statistical analysis

Levels of micronutrients in fresh red and yellow tomatoes were compared using analysis of variance (ANOVA). When a significant difference was detected, means were compared using the *F*-test. A *p* value under 0.05 indicates that samples are statistically different. The same procedure was used to compare the micronutrient contents in fresh red and yellow tomatoes with either processed or lyophilised red and yellow tomatoes. These statistical comparisons were performed using STATGRAPHICS Plus software, Version 5.1 (Statpoint Technologies, Inc., Warrenton, VA).

3. Results and discussion

3.1. Tomato colour measurement

Indices used to characterise fruit colouration were all very significantly different among yellow and red fruits ($p < 0.0001$). Lightness L^* had greater value for yellow tomatoes than for red tomatoes (57.2 *vs* 39.8, respectively, Table 1) and the index b^* was also greater for yellow tomatoes than for red tomatoes (49.9 *vs* 23.7, respectively, Table 1). In contrast, index a^* was very low for yellow tomatoes compared to red tomatoes (1.6 *vs* 21.8, respectively, Table 1). Consequently, the ratio a^*/b^* was dramatically lower in yellow tomatoes than in red tomatoes (0.03 *vs* 0.92, respectively), which correlated with the absence of lycopene in yellow fruits. These data corroborate the results reported by (Arias, Lee, Logendra, and Janes (2000), who found a good correlation between colours measured with a chromameter and the lycopene content measured by HPLC. They even proposed an equation to relate the lycopene content to the ratio a^*/b^*. The absence of red colour in YT was also confirmed by the higher hue angle compared to RT. The high chroma value for both genotypes indicates the purity of their colour. The parameter b^* was higher in yellow tomato than in red tomato; however, the β-carotene content is lower in yellow tomato than in red tomato (results shown later). Consequently, the b^* parameter was not a good indicator of the β-carotene content.

3.2. Choice and validation of the carotenoid extraction method

The separation efficiency of a mixture of hexane/acetone/ethanol (50/25/25, v/v/v, HAE) was compared to that of acetone/petroleum ether on the solid/liquid extraction of carotenoids from red tomato purée. The acetone/petroleum ether solvent system was shown to be as efficient as HAE for lycopene extraction; however, it was significantly more efficient than HAE regarding β-carotene extraction (+24.4%). Moreover, with the acetone/petroleum ether system, the intra-day variation (2.64% and 9.78% for lycopene and β-carotene, respectively ($n = 6$)) and inter-day variation (1.59% and 8.15% for lycopene and β-carotene, respectively, ($n = 6$)) were suitable. Therefore, the extraction method using acetone/petroleum ether was selected for all the extractions, due to its greater efficiency.

3.3. Choice of the analysis method for carotenoids

Quantitative analyses were performed using spectrophotometry because it is as efficient, quicker and cheaper than HPLC for measuring the carotenoid content in red and yellow tomatoes. We compared the carotenoid content of red and yellow tomatoes using the spectrophotometric technique given in the quantification method by Lime, Griffiths, O'Connor, Heinzelman, and McCall (1957) and the HPLC technique. The carotenoids contents of both extracts were very similar using both methods (data not shown).

Table 1
Contents of carotenoids, total polyphenol and vitamin C in fresh red and yellow tomato[a] and colorimetric parameters.

	Red tomatoes	Yellow tomatoes	*p* value
Lycopene	3.7 ± 0.5	n.d.[e]	n.c.[f]
β-Carotene	1.0 ± 0.0	0.3 ± 0.1	<0.0001
TPC[b]	16.0 ± 0.6	17.8 ± 0.9	0.0403
Vitamin C	15.8 ± 1.1	17.1 ± 1.1	0.13
L^*	39.8 ± 1.6	57.2 ± 3.4	<0.0001
a^*	21.8 ± 2.8	1.6 ± 2.7	<0.0001
b^*	23.7 ± 2.1	49.9 ± 3.6	<0.0001
C^*[c]	32.3 ± 2.8	50.0 ± 3.5	<0.0001
Hue (°)[d]	47.5 ± 3.6	88.2 ± 3.1	<0.0001

[a] Data are expressed as the mean ± SD, $n = 3$, in mg/100 g of FW.
[b] TPC = total polyphenol content.
[c] C = chroma value.
[d] Hue (°) = hue angle expressed in degree.
[e] n.d.: not detected.
[f] n.c.: not calculated.

3.4. Micronutrient analyses in fresh red and yellow tomatoes

Quantitative analysis of fresh red tomatoes showed the presence of lycopene as a major carotenoid (3.7 mg/100 g FW) together with β-carotene (1.1 mg/100 g FW) (Table 1). The lycopene content lies in the range of values given in the USDA database (0.88–4.2 mg/100 g FW), whereas the β-carotene content lies slightly above the maximum values in the USDA database (0.1–0.7 mg/100 g FW) (<http://www.nal.usda.gov/fnic/foodcomp>) and in a German database (0.150–0.739 mg/100 g FW) (Souci, Fachmann, & Kraut, 2000). The slight differences between our data and those of the literature can be explained by the high dependence of various factors, such as maturity, variety, cultivar and also agronomic conditions, on the carotenoid content in tomatoes (Davies & Hobson, 1981; Dumas, Dadomo, Lucca, & Grolier, 2003). Other minor carotenoids – lutein, neurosporene and 1,2-epoxy-lycopene – were tentatively identified using qualitative HPLC analysis by comparing their UV/Vis spectra with literature data (Britton, Liaaen-Jensen, & Pfander, 2004). In yellow tomatoes, no lycopene was detected and the major carotenoid found was β-carotene, although its content was four times lower than that of red tomatoes (0.3 mg/100 g FW). Lutein and neurosporene were tentatively identified by HPLC as minor carotenoids of yellow tomatoes. β-Carotene was the main carotenoid (0.11 mg/100 g FW) in a yellow flesh (r) mutant tomato together with a minor amount of lycopene (0.004 mg/100 g FW) (Lewinsohn et al., 2005). In another yellow mutant, do Rego, Finger, Casali, and Cardoso (1999) found β-carotene and also lycopene in similar amounts (0.09 mg/100 g FW and 0.07 mg/100 g FW, respectively). Again, the difference in the β-carotene and lycopene contents that we obtained and those of the literature could be due to the studied genotypes and/or cultural practices and/or environment.

Our value for the total phenolic content (TPC) in red tomatoes (16.0 mg/100 g FW, Table 1) was in the range of those already found in five varieties of tomatoes by Brat et al. (9.8–23.0 mg/100 g FW; Brat et al., 2006) and slightly below the values determined by Hernandez et al. (19.7–21.1 mg/100 g FW; Hernandez, Rodriguez, & Diaz, 2007). We found that TPC was significantly higher in yellow tomatoes than in red ones ($p = 0.0403$, Table 1). These results agree with those of Chang and Liu (2007), who showed that TPC in yellow tomato was higher (>35 mg/100 g) than in red ones (<25 mg/100 g). The difference in values between our study and the results of Chang and Liu could be due, at least in part, to the improved method we used, which minimises the influence of vitamin C and other interfering substances that could lead to an overestimation of TPC (George et al., 2005).

The chromatographic profile of the phenolic compounds was very similar in both red and yellow tomatoes (Fig. 2). The phenolic compounds were identified using their absorption spectra in the UV–Visible range and their mass spectra. The main hydroxycinnamic acid derivatives were identified as caffeic acid derivatives: glucoside, chlorogenic acid and an unidentified derivative. Main flavonoids present in the red and yellow tomato extracts were rutin and naringenin. The results obtained in our study on the qualitative analysis of phenolic compounds are consistent with those of the literature. Hydroxycinnamic acid derivatives have already been found in red tomatoes (Macheix, Fleuriet, & Billot, 1990); chlorogenic acid is the most commonly encountered (Fleuriet & Macheix, 1981). Rutin, naringenin, and chalconaringenin have been reported (Benard et al., 2009; Caris-Veyrat et al., 2004) as the main flavonoids in different varieties of red tomatoes.

Vitamin C content was similar in both red and yellow tomatoes. The vitamin C content of red tomatoes (15.8 mg/100 g FW, Table 1) is close to the value given in the CIQUAL database (18 mg/100 g FW; <http://www.afssa.fr/TableCIQUAL/index.htm>) as well as the values reported by Souci et al. (10–29 mg/100 g; Souci et al., 2000) and in the USDA database (12.7 mg/100 g FW; <http://fnic.nal.usda.gov>). With respect to yellow tomato, the value obtained in our study (17.1 mg/100 g FW) is higher than the value found in the USDA database (9.0 mg/100 g FW), which is the mean value of two tomato samples only but is lower than the values found by Simonne et al. (35.0–44.8 mg/100 g FW; Simonne, Fuzere, Simonne, Hochmuth, & Marshall, 2007) for a yellow grape tomato variety.

3.5. Effect of processing

In our processed tomato purée, the β-carotene content was 16.0 mg/100 g DW (Table 2). This value is above the range of β-carotene contents in canned tomato purée with and without added salt that are given in the USDA database: 2.5 mg/100 g DW (<http://www.nal.usda.gov/fnic/foodcomp>). In contrast, the lycopene content in the tomato purée made in our study (60.3 mg/100 g DW, Table 2) is below the lycopene content in canned tomato

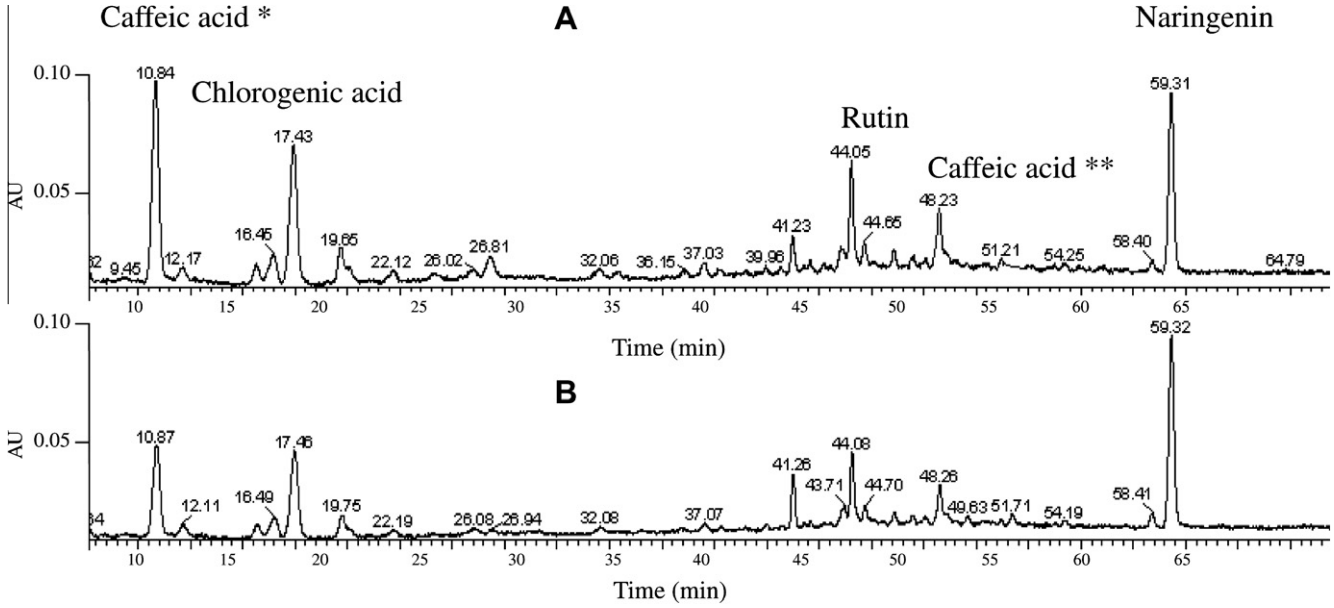

Fig. 2. HPLC polyphenol profile of fresh red tomatoes (A) and fresh yellow tomatoes (B) at 280 nm. *Glucoside. **Derivative.

Table 2
Contents of carotenoids, vitamin C and total polyphenol in fresh, purée and lyophilised red and yellow tomato[a].

	Red tomato			Yellow tomato		
	Fresh	Purée	Lyophilised	Fresh	Purée	Lyophilised
β-Carotene	17.4 ± 0.8	16.0 ± 0.4	14.9 ± 0.8	3.6 ± 0.7	2.0 ± 0.1	3.2 ± 0.5
Lycopene	61.1 ± 9.4	60.3 ± 0.7	32.4 ± 4.9	n.d.	n.d.	n.d.
TPC[b]	268.0 ± 10.7	153.4 ± 1.4	269.2 ± 33.0	254.1 ± 8.9	183.1 ± 1.8	177.5 ± 20.2
Vitamin C	262.4 ± 17.7	50.0 ± 2.4	290.0 ± 14.3	251.2 ± 17.0	50.0 ± 1.9	237.7 ± 7.7

n.d.: not detected.
[a] Data are expressed as the mean ± SD, $n = 3$, in mg/100 g of DW.
[b] TPC = total polyphenol content.

purée with and without added salt given in the USDA database (179.5 mg/100 g DW). These differences could be attributed to the initial carotenoid content in the fresh tomatoes used for processing, which might be very different, and also to differences in processes used. No data on processed yellow tomato products were found either in databases or in other published work.

Processing red tomatoes did not significantly affect their carotenoid content, whereas the β-carotene content was greatly reduced (−44%) in yellow tomatoes (Fig. 3). The results obtained in our study on red tomatoes are comparable to those of Perez-Conesa et al. (2009), who also found that a hot-break treatment (vapour stream at 82 °C for 2 min) of a tomato purée did not change the content of lycopene or β-carotene. Other authors found that the lycopene content was stable in tomatoes submitted to different thermal treatments (Graziani et al., 2003; Sanchez-Moreno, Plaza, de Ancos, & Cano, 2006). However, conflicting data on tomato carotenoid stability during thermal processing of red tomato can be found in the literature. For instance, Sharma and LeMaguer (1996) found a 20% loss of lycopene in heated tomato pulp. During preparation of a tomato paste, Capanoglu et al. (2008) showed a significant decrease in the content of both lycopene (32%) and β-carotene (36%). The final product in this study was a tomato paste, which is more concentrated than the tomato purée obtained in our study (28–39 °Brix for tomato paste *vs* 14 °Brix for our tomato purée). The paste was probably submitted to a more drastic evaporation process than our prepared purée, which could have lead to the loss of carotenoids. In contrast, several authors have found an increase in lycopene content in processed tomato products compared to raw tomatoes. Abushita et al. (2000), who used a comparable process to the one in our study to make a tomato paste (dry matter content 28–30%), measured an increase of 36% for lycopene and a stable β-carotene content. Re et al. (2002) found a systematic increase in the lycopene content in several processed products, with up to 30% in a tomato paste. The different thermal treatments applied in these studies probably increased the bioaccessibility of lycopene, making it more easily extractable from the tomato matrix during the solvent-assisted extraction step. Indeed, thermal processing disrupts cell membranes and cell walls, thus facilitating release of lycopene from the insoluble portion of the tomatoes.

In summary, processing of red tomato can generate a wide variability with respect to the carotenoid content, which mainly depends on the time and temperature conditions used. In our case, we observed stable carotenoid contents in red tomato purée, which suggests that our process does not destroy carotenoids. The parameters we used for the different processing steps – hot-break treatment, concentration and pasteurisation – seemed to be mild enough to preserve the carotenoids and/or the plant matrix. The applied hot treatments may have inactivated carotenoid-oxidising enzymes such as peroxidases. However, it is also possible that our improved analytical method allowed us to extract most of the lycopene from the raw tomato.

The difference in stability of β-carotene between the two types of tomatoes could be linked to different factors related to the composition of the tomatoes because they do not have a specific genetic relationship. Their content in the three main families of phytomicronutrients that we analysed does not allow us to explain the instability of β-carotene in yellow tomatoes. It would be interesting to repeat these experiments with other red and yellow tomato cultivars, and particularly with genetically related tomatoes that only differ in their lycopene content, to see whether these results can be generalised and linked to the absence of lycopene in yellow tomatoes.

The total polyphenol content decreased significantly during processing both in red (43%) and yellow (28%) tomatoes (Fig. 3). Our results agree with those of Perez-Conesa et al. (2009), who also found a significant decrease in total phenolic content that they attributed to the pasteurisation step. In contrast, an increase in the total phenolic content was observed by Gahler et al. (2003) during processing of tomato juice and tomato sauce; this result is possibly due to liberation of phenolics from the tomato matrix. In another study by Dewanto et al. (2002), no significant change in total phenolic content was observed. It should be noted that Re et al. (2002) found a drastic loss of naringenin (90%), but an increase in chlorogenic acid content (30%) in hot-broken tomatoes. Altogether these data suggest that the extent of polyphenol degradation might depend not only on the thermal treatment, but also on the phenol type. Degradation could be explained by oxidation of the molecules due to oxidative and hydrolytic enzymes that were released during the process but not fully deactivated.

The vitamin C losses were high and similar for both red and yellow tomatoes: ~80% (Fig. 3). These results are consistent with data from the literature, where numerous examples can be found of vitamin C degradation during thermal processing of tomato products. For instance, Perez-Conesa et al. (2009) found up to 90% degradation of vitamin C after pasteurisation of tomato purée. In other studies, around half of the vitamin C was lost during thermal processing of tomatoes (Abushita et al., 2000; Capanoglu et al., 2008). Loss of vitamin C in different tomato products increased with heating time and number of processing steps (Gahler et al., 2003). This important loss is probably due to the well-known sensitivity of vitamin C to heat and oxygen.

3.6. Impact of lyophilisation

In both red and yellow tomatoes, the carotenoid content was significantly lower in lyophilised material than in fresh tomatoes. The decrease of β-carotene was 14% and 11% in red and yellow tomatoes, respectively, and lycopene decreased by 47% in red tomatoes (Fig. 4). Such decreases could be due either to degradation of the carotenoids during lyophilisation, and/or to a lower extractability of carotenoids in lyophilised compared to fresh material. Very few examples of the effect of freeze-drying on tomato carotenoids have been described. Chang, Lin, Chang, and Liu (2006) found that the lycopene content of freeze-dried tomatoes was reduced by 33% and 48% in two varieties of tomatoes. Our results also agree

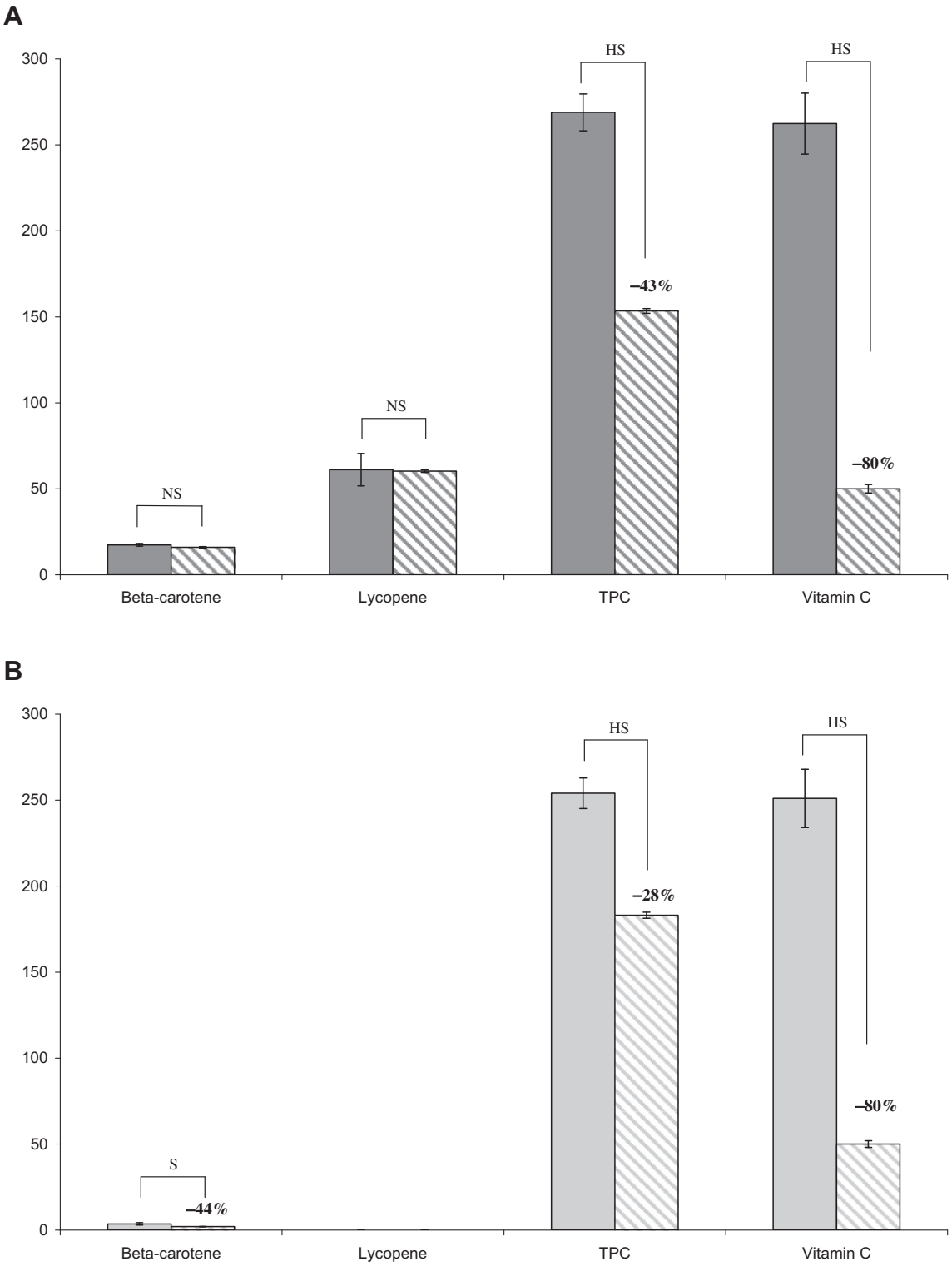

Fig. 3. Effect of processing on the contents of carotenoids, total polyphenol and vitamin C in red (A) and yellow (B) tomato[a]. [a]Concentrations are expressed as the mean ± SD, $n = 3$, in mg/100 g of DW Solid dark grey: fresh red tomatoes; hatched dark grey: red tomato purée; solid light grey: fresh yellow tomatoes; hatched light grey: yellow tomato purée. NS: non-significant ($p > 0.05$); S: statistically different ($p < 0.05$); HS: highly statistically different ($p < 0.00001$) Percentage values correspond to significant micronutrient losses after processing or lyophilisation.

with those found in grapefruits in which lycopene and β-carotene contents were reduced by a factor of five and two, respectively, after lyophilisation (Vanamala et al., 2005). Freeze-drying increases the sample porosity; thus the carotenoids could be exposed to more oxygen, which could have a significant effect on their stability. We also suggest that the extractability of carotenoids is reduced in lyophilised material, compared to fresh material.

The total polyphenol content in red tomato was not affected by lyophilisation (Fig. 4). Our results on red tomatoes agree with the study carried out by Chang et al. (2006), who showed that there

was no significant difference in the total polyphenol content after freeze-drying of two varieties of red tomatoes. In yellow tomatoes, the amount of total polyphenols decreased by 30% in lyophilised tomatoes, compared to fresh ones (Fig. 4). These results could be related to the presence of lycopene in red tomato that might protect polyphenolic compounds from degradation during lyophilisation; however, there is little literature data available on the interaction of carotenoids and phenolic compounds (Mortensen & Skibsted, 1996).

The vitamin C content was not affected by lyophilisation both in red and yellow tomato (Fig. 4). Chang et al. (2006) found 8–10% loss of ascorbic acid in lyophilised red tomatoes. Data on other fruit (grapefruit) indicate that lyophilisation did not affect the vitamin C content (Vanamala et al., 2005).

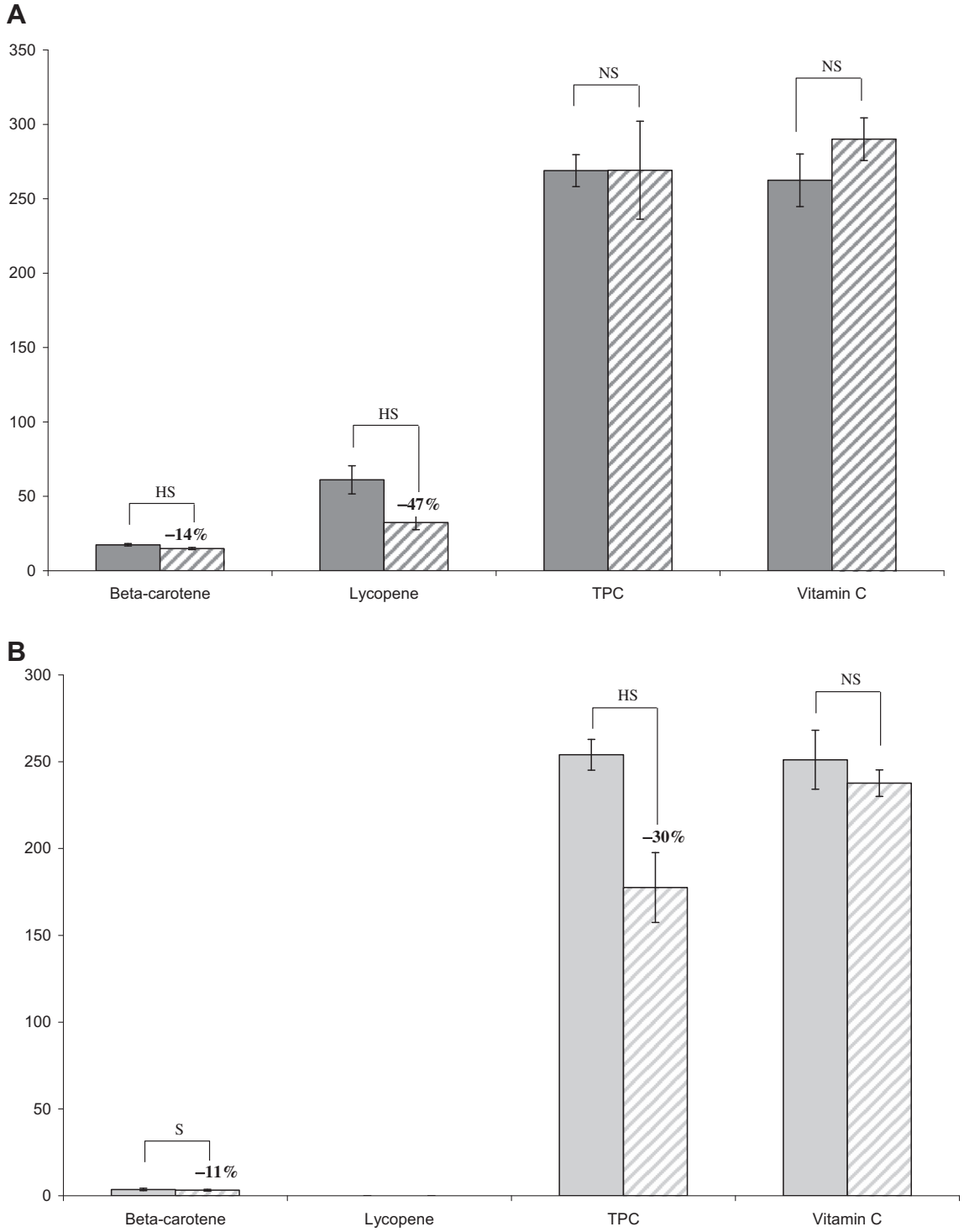

Fig. 4. Impact of lyophilisation on the contents of carotenoids, total polyphenol and vitamin C in red (A) and yellow (B) tomato[a]. [a]Concentrations are expressed as the mean ± SD, $n = 3$, in mg/100 g of DW Solid dark grey: fresh red tomatoes; hatched dark grey: red tomato purée; solid light grey: fresh yellow tomatoes; hatched light grey: yellow tomato purée. NS: non-significant ($p > 0.05$); S: statistically different ($p < 0.05$); HS: highly statistically different ($p < 0.00001$) Percentage values correspond to significant micronutrient losses after processing or lyophilisation.

4. Conclusion

In summary, the content of antioxidant micronutrients may vary during a lyophilisation step, and this has to be taken into account when preparing samples for further analyses, especially when carotenoid analyses are planned. Since the lyophilisation process is a widely-used technique to stabilise plant samples over a long period of time, it could be of interest to perform a kinetic study in order to follow the stability of the micronutrients during storage at different temperatures and to compare the results to those of fruit samples kept in the frozen state.

For the first time, we compared the nutritional composition of red and yellow tomatoes by analysing three different families of phytonutrients (carotenoids, polyphenols and vitamin C).

We identified which micronutrient was more affected by classical thermal processing and a freeze-drying process. These results could be significant in terms of human nutrition and could serve as the basis for suggesting changes in the industrial processing of tomatoes.

From a more fundamental point of view, it would be interesting to understand the reasons for the differing behaviour of the micronutrients in the two types of tomatoes, i.e., the selective decrease in β-carotene content during thermal processing and TPC during lyophilisation in yellow tomato. In view of this, experiments are planned to study other varieties over several years of cultivation. Furthermore, analyses of the newly-formed molecules in the tomato purée and the lyophilised material are currently being carried out to obtain more information on the mechanisms involved in possible protection/interaction effects between antioxidant micronutrients.

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