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Phenolic fingerprint allows discriminating processed tomato products and tracing different processing sites

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Lycopene (PubChem CID: 446925)
Sesamolinol (PubChem CID: 443019)
Pinoresinol (PubChem CID: 73399)
Catechin (PubChem CID: 1203)
Isorhamnetin (PubChem CID: 5281654)
Quercetin 3-*O*-(6″-malonyl-glucoside) (PubChem CID: 5282159)
Myricetin 3-*O*-rhamnoside (PubChem CID: 5352000)
Coumaric acid (PubChem CID: 637542)

ABSTRACT

Tomatoes are important in human nutrition, as they are a source of carotenoids and phenolic compounds. However, transformation processes may alter the nutritional value of foods, decreasing the concentration of health-promoting compounds. This work aimed to explore the effects of industrial transformation on processed tomatoes (crushed pulp, puree and paste), as well as the effect of the different pre-processing technologies, rather than different manufacturing sites, in producing tomato paste. Results demonstrate that phenolics profiling can distinguish between different processed products as well as different paste pre-treatments (namely cold, warm and hot break), even though the latter underwent a final thermal treatment at >100 °C. Analogously, the different processing sites could be discriminated thanks to their characteristic phenolic fingerprint. The greatest differences identified were between conjugated forms of flavonoids, phenylpropanoids and lignans. The latter were the most labile phenolics, followed by flavonoids and then phenylpropanoids. Results provide evidence for the potential of phenolic fingerprint to support traceability of transformation processes and to investigate their effect on the nutritional value of processed tomatoes.

1. Introduction

The consumption of tomatoes and tomato-based products is correlated with a reduced incidence of chronic and degenerative diseases, including cancer (Grieb, Theis, Burr, Benardot, Siddiqui & Asal, 2009; Zhang, Ho, Chen, Fu, Cheng & Lin, 2009) and coronary heart disease (Stahl & Sies, 2005). These health-promoting properties can be related to several micronutrients, such as vitamins C and E, folate (Agarwal, Shen, Agarwal, & Rao, 2001), as well as several other bioactives, among which phenolic compounds and carotenoids are the most relevant. A wide variety of phenolic compounds have been identified in tomatoes, although they are mainly represented by flavanones and flavonols (Bahorun, Luximon-Ramma, Crozier, & Aruoma, 2004; Slimestad, Fossen, & Verheul, 2008; Stewart, Bozonnet, Mullen, Jenkins, Lean & Crozier, 2000). Antioxidant and radical scavenging properties of tomato-based foods have been ascribed to phenolics and to carotenoids with nine or more conjugated double bonds. These are capable of quenching singlet oxygen, lycopene is considered to be the most effective (Luterotti, Bicanic, Markovic, & Franko, 2015).

Industrial processing of tomatoes includes thermal treatment steps such as pasteurizing, heating and drying. These treatments increase product stability by inactivating enzymes and microorganisms. However, it has been reported that these treatments can alter appearance, nutritional value and organoleptic properties of the product (Capanoglu, Beekwilder, Boyacioglu, Hall, & de Vos, 2008), while decreasing the content of health-promoting

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compounds (Abushita, Daood, & Biacs, 2000; Takeoka et al., 2001).

Although the effects of industrial processing on lycopene content have been studied extensively (Goula, Adamopoulos, Chatzitakis, & Nikas, 2006; Sharma & Le Maguer, 2004), less information is available regarding phenolic compounds and antioxidant properties. Vallverdú-Queralt, Medina- Remón, Andres-Lacueva and Lamuela-Raventos (2011) evaluated individual phenolics and hydrophilic antioxidant capacity, reporting a gradual and significant decrease for both, throughout the processing steps of tomatoes. Chang and Liu (2007) reported an increase in total flavonoid and total phenolics content in processed tomatoes when compared to the corresponding levels in fresh tomatoes. However this may have been related to different moisture contents between fresh and processed products.

Additionally, the actual processing technology or processing facility might affect the phenolic profile of the end products, and therefore being of help to trace origin and identity of productions. Up to now, most of the work in tomato traceability has been carried out using multi-element (Fragni, Trifirò, & Nucci, 2015) or rare earths (Trincherini, Baffi, Barbero, Pizzoglio, & Spalla, 2014) mineral composition. These approaches benefit from the pedological fingerprint of the soil where plants are grown, and therefore can support geographical origin. However, this approach is not suitable to ensure food identity. On the other hand, the comprehensive profile of other secondary metabolites is affected by post-harvest treatments, thus representing a useful tool to guarantee food identity. Phenolic profile is very interesting in this sense, because it comprises a wide class of secondary metabolites, differing for their physical-chemical characteristics and stability. Indeed, this approach has been reported to be effective for establishing traceability and typicalness of raw plant materials and their processing products (Siracusa & Ruberto, 2014, pp. 15–33).

Therefore, it seems clear that processing conditions affect the quality of tomato product. This influences both the nutritional and organoleptic value of the product. Comprehensive information on this subject is still lacking, although it may be advisable to suggest changes to industrial processes, to support health promotion and to guarantee the traceability of productions. Nonetheless, it is possible that industrial transformation affect the actual phenolic profile of processed tomato in a characteristic manner, thus allowing tracing both origin and identity of tomato products. The aim of this work was to investigate and compare the phenolic profile and antioxidant capacity of three different processed tomato products (crushed pulp, puree, double concentrate paste). Additionally, the same approach was applied to identify differences in phenolics profile and lycopene content, in double concentrate tomato paste produced according to three processing approaches, namely the cold, warm and hot break. Finally, the potential of phenolic fingerprint to discriminate hot break tomato pastes coming from different processing sites was investigated.

2. Materials and methods

2.1. Processed tomatoes

Trials were conducted in an industrial processing facility, using a homogenous mixture of commercial varieties of tomato, typical for industrial transformation (Heinz, Fokker and Caliendo cultivars). From this mixture, the following processed products were obtained: crushed tomato pulp (CP), tomato puree (PU) and double concentrate tomato paste (DC). DC was produced using either cold break technology (DC-CB), hot break technology (DC-HB), or an intermediate process called warm break (DC-WB). The three technologies for DC paste differ for the pre-treatment temperature of raw tomatoes, from 60 to 70 °C in DC-CB (to facilitate peeling while preserving organoleptic properties) up to 105–110 °C in DC-HB (hence inactivating pectin esterases and *endo*-polygalacturonases, to gain optimal rheological properties in the final product). DC-WB is prepared at intermediate temperatures (75–80 °C), it therefore has intermediate technological properties. All end products were sterilized at about 105 °C for a minimum of three minutes, according to actual industrial processing. Three aliquots of each processed product (250 g each) were collected in three different time points, just before the packaging process. These aliquots were pooled, thoroughly homogenized and a portion of each processed product was immediately refrigerated at +4 °C until analysis.

Concerning the pastes produced at different processing sites, DC-HB products (about 250 g each, taken just before packaging) were kindly made available from factories located in the Po valley, North Italy. In more detail two DC-HBs were produced by the same brand in two different sites (Piacenza and Mantova, Italy), while two additional DC-HBs were manufactured by additional brands in Piacenza and Parma, respectively.

2.2. Antioxidant capacity

Five replicates (10 g) of each processed tomato sample were extracted in 50 mL of a dichloromethane/methanol (1:1, v/v) mixture for 30 min. The extract was filtered on Buchner and the filter cake re-extracted in 40 mL of a dichloromethane/methanol (5:3, v/v) mixture. The combined extracts were partitioned in a separator funnel with 50 mL of 20% NaCl in water and the organic phase was retained.

An Oxygen Radical Antioxidant Capacity (ORAC) test was performed on the extracts according to the protocol described by Lucini, Pellizzoni, Pellegrino, Molinari, and Colla (2015) and was carried out using a BioTek™ Synergy™ 2 Multi-Mode Microplate Reader Winooski, VT, USA, with Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) as the standard.

2.3. Lycopene content

The lycopene content in the processed products was determined in the extracts gained for antioxidant capacity, through liquid chromatography triple quadrupole tandem mass spectrometry, following the method reported by Lucini, Pellizzoni, Baffi, and Molinari (2012).

2.4. Total phenolics content and screening of individual compounds

Antioxidant compounds were screened through a hybrid quadrupole-time-of-flight mass spectrometer coupled to an UHPLC chromatographic system (LC-ESI/Q-TOF), on the basis of the approach described by Lucini, Rouphael, Cardarelli, Canaguier, Kumar and Colla (2015).

Samples were extracted in 10 vol of 80% methanol added to 50 mM formic acid, using an Ultra-Turrax, centrifuged and filtered through a 0.22 μm cellulose membrane, diluted 5 times in 50% methanol and transferred to an amber vial for LC-ESI/Q-TOF analysis. An aliquot was taken to measure total phenolic compounds (TP) using the Folin assay, as reported previously (Lucini, Pellizzoni et al., 2015) and expressed as Gallic Acid Equivalents (GAE). A 1290 liquid chromatograph system, equipped with a binary pump and a Dual Electrospray JetStream ionization system, coupled to a G6550 mass spectrometer detector (all from Agilent technologies Santa Clara, CA, USA) was used for the untargeted screening. The mass spectrometer was operated to acquire positive ions in MS-only mode, in the 50–1000 *m/z* range. Chromatographic separation was carried out using an Agilent Zorbax eclipse plus C18 column (50 × 2.1 mm, 1.8 μm) under a water-methanol gradient elution. A