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Investigation on volatile profile, lipid fraction degradation and antioxidant content of tomato-based pâtés as a function of ingredient formulation

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Abstract

Various studies are present in literature about the nutritional and sensorial characteristics of preserved tomato products and minimally processed products. To the best of our knowledge, there are no data in literature concerning the tomato-based pâtés, suitable as seasoning for pasta, salads and sandwiches. The aim of this work was to characterize two types of tomato-based pâtés in terms of volatile compounds profile, lipid fraction degradation and antioxidant contents as a function of the ingredient formulation. The tomato-based pâtés showed a different aromatic profile, with particular reference to volatile compounds deriving from the raw materials and lipid autoxidation. Significant differences were also observed for the oxidative and hydrolytic degradation level of the lipid fraction, as well as total phenols and flavonoids content. The differences observed were linked to the ingredient formulation used. In particular, the addition of minced mushrooms, chilli and parsley involved a development of terpenic volatile compounds, while when extra virgin olive oil was used significantly higher percent contents of aldehydes and ketones were found, as well as a minor oxidative degradation of lipid fraction. Also total phenols and flavonoids content were influenced by the ingredient formulation, while no differences were observed for the lycopene content.

Introduction

Vegetables are considered as high nutritional value products with peculiar characteristics in terms of colour, flavour and taste, as well as naturalness image that binds the consumption of these products to human welfare (Patras *et al*., 2009; Oey *et al.*, 2008). Recent researches have focused the attention on health aspects in relation to the content in bioactive compounds, including nutritional compounds (vitamins and mineral salts) and non-nutritive compounds (antioxidants, phytoestrogens, dietary fiber), whose consumption plays a preventive role in reducing risk of a number of chronic diseases, such as atherosclerosis and cancer (Gundgaard *et al*., 2003; Gosslau and Chen, 2004).

Among vegetables, tomato (*Solanum lycopericum* L.) is, after potato, the second most consumed vegetable in the world (Savatović *et al.*, 2010). Tomato is a rich source of antioxidant compounds, such as: carotenoids, among which the most important is lycopene, a fat soluble carotenoid, precursor of β-carotene (Sandmann, 1994), having at least twice the antioxidant capacity of β-carotene (Di Mascio *et al*., 1989); phenolic compounds, including flavonoids able to withstand industrial processing methods, being detected in a variety of tomato-based products (Stewart *et al*., 2000; Sahlin *et al*., 2004); ascorbic acid, generally used as a marker for nutrient degradation (Rickman *et al*., 2007); tocopherols, lipid soluble vitamins less affected than water-soluble nutrients by processing steps such as washing and blanching, as well as cooking at home (Toor and Savage, 2006).

Although tomatoes are commonly consumed fresh, over 80% of the tomato consumption comes from processed products (Rao *et al.*, 1998) such as preserved canned tomato (tomato paste and purèes, peeled tomatoes), tomato juice, minimally processed products, semi dried tomatoes and vegetable-based sauces (ketchup, ready sauces including pesto and pâtés). The tomato-based pâtés are usually consumed as seasoning for pasta, suitable to dress meat, salads and sandwiches (Baiano *et al*., 2005), able to satisfy the consumer's growing demand for value-added products with good flavour and adequate shelf-life.

Vegetable industrial processing such as blanching, canning, sterilization and freezing, as well as domestic cooking, is expected to affect the content, composition, antioxidant activity and bioavailability of antioxidants (Podsędek, 2007). Operations such as cutting and slicing may induce a rapid enzymatic depletion of several naturally occurring antioxidants as a result of cellular disruption which allows contacts of this substrates with oxygen and enzymes; the thermal stabilization process, despite stabilizing

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the product from the microbiological point of view and extending shelf-life, causes degradation of the product, especially with reference to colour, odour, taste and nutritional values (Fabiano *et al.*, 2000).

Generally, the antioxidant concentrations and activities in processed vegetables are lower than those of the corresponding raw samples. This was caused by their degradation, but also by absorption of water during boiling, which dilutes the compounds and decreases their content per weight unit (Podsędek, 2007). Literature is rich of studies regarding the nutritional and sensorial characteristics of preserved tomato products (Anese *et al.*, 2002; Zanoni *et al.*, 2003; Lavelli and Giovanelli, 2003), minimally processed products (Pingulkar *et al.*, 2001; Abano *et al.*, 2011), while no studies are present about the chemical characteristics of tomato-based pâtés that represent an alternative method of preparation of tomatoes based food products. The aim of this work was to characterize the tomato-based pâtés in terms of volatile compounds profile, antioxidant contents and lipid fraction degradation as a function of the ingredient formulation.

Materials and Methods

Sampling

The research was performed on two kinds of tomato-based pâtés (TP1 and TP2), purchased from production plants and obtained using the same processing technology (figure 1) and the same batch of dried tomatoes. Table 1 reports the ingredient formulation of the two types of tomato-based pâtés under investigation. Three different lots were taken for each sample.

Headspace analysis

Volatile compounds were extracted by solid phase micro-extraction (SPME) and analyzed by gas-chromatographic system equipped with mass spectrometer (GC/MS). In particular, 100 µL of a solution of 1-propanol (internal standard), at a concentration of 200 mg kg^{-1}, were added to an aliquot of sample (1 g ± 0.05), placed inside 12 mL glass vials, closed by butylic rubber septa and an aluminum seal. The sample was homogenized for 2 min using a laboratory vortex shaker. Before extraction, stabilization of the headspace in the vial was achieved by equilibration for 10 min at 40°C. The extraction was performed by exposing a 75 µm Carboxen/polydimethylsiloxane (CAR/PDMS) fiber (Supelco, Bellefonte, Pa., U.S.A.) in the headspace of the sample at 40°C for 25 min. When the extraction process was completed, the fiber was removed from the vial and desorbed in the injection port of the GC in splitless mode. The GC/MS instrumentation included an Agilent 6850 gas-chromatograph (Milan, Italy) equipped with an Agilent 5975 mass-spectrometer. Compounds were resolved on a HP-Innowax (60 m × 0.25 mm, 0.25 µm film thickness) polar capillary column (Agilent) under the following conditions: injector temperature, 250°C; helium as the carrier gas at a flow rate of 1 mL/min. The oven temperature was held for 3 min at 40°C, then increased at 1°C/min to 60°C and held constant for 2 min, then raised to 180°C at 5°C/min for 10 min and finally held at 230 °C for 5 min. The mass spectrometer was operated in the electron impact mode (electron energy = 70 eV) and the ion source temperature was 250°C. The mass range was m/z 20–260. Peak identification was performed comparing the retention times with those of the standards (purchased from Sigma-Aldrich, Buchs, Switzerland) and by computer matching with the reference mass spectra of NIST and Wiley. The volatile compounds were quantified by standardizing the peak areas of compounds of interest with the peak area of the internal standard (1-propanol). The results

Table 1. Ingredient formulation of tomato-based (TP) pâtés under investigation

Ingredients	TP1	TP2
Dried tomatoes (g kg^{-1})	560	367
Extra virgin olive oil (mL L^{-1})	346	67.2
Sunflower oil (mL L^{-1})	-	268.8
Minced *Champignon* mushrooms (g kg^{-1})	-	157
Chilli (g kg^{-1})	5.6	52
Vinegar (mL L^{-1})	56	52
Parsley (g kg^{-1})	-	26
Garlic (g kg^{-1})	5.6	3
Sugar (g kg^{-1})	22	-
Basil (g kg^{-1})	11	-
Wild marjoram (g kg^{-1})	2	-
Ascorbic acid (g kg^{-1})	0.5	-

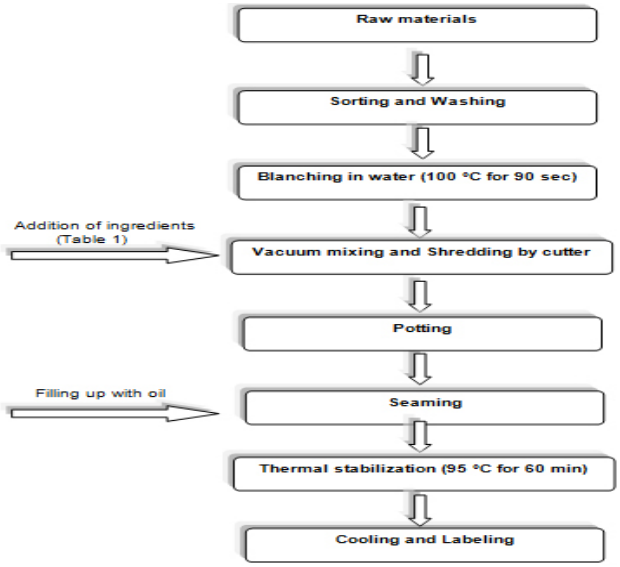

Figure 1. Flow sheet of the tomato-based pâtés technological process

were expressed as μg g^{-1}.

Lipid fraction extraction

The lipid fraction was extracted from pâtés with petroleum ether in a 1:2 ratio (w:v). After 60 min of maceration, maintaining the mixture under stirring on shaker at 180 rpm, the mixture was filtered through Whatman no. 1 papers. Extraction was repeated once more to ensure complete separation of oil and final filtration was conducted on anhydrous sodium sulfate to remove water traces. The solvent was evaporated using a rotavapor.

Analytical determinations

The extracted oil was analyzed to determine free fatty acids (FFA), peroxide value (PV) and UV absorption (extinction coefficients K_{232} and K_{270}), according to the Official Journal of the European Communities (1991). The polar compounds (PC) were separated from the oil by silica gel column chromatography according to the AOAC method no. 928.27 (2003). The PC, recovered in THF, were then submitted to High Performance Size-Exclusion Chromatography (HPSEC) analysis, using THF as eluent at a flow rate of 1 mL/min. The HPSEC analysis enables separating and quantifying the various classes of substances constituting the PC, such as triacylglycerol oligopolymers (TAGP), oxidized triacylglycerols (ox-TAG) and diacylglycerols (DAG). The HPSEC system consisted of a series 200 pump (Perkin-Elmer, Norwalk, CT, USA) with Rheodyne injector, a 50 μL loop, a PL-gel guard column (Perkin-Elmer, Beaconsfield, UK) of 5 cm length and 7.5 mm i.d., and a series of two PL-gel column (Perkin-Elmer, Beaconsfield, UK) of 30 cm length and 7.5 mm i.d. each. The columns were packed with highly cross-linked styrene-divinylbenzene copolymer with particles of 5 μm and a pore diameter of 500 Å. The detector was a series 200 refractive index (Perkin-Elmer, Norwalk, CT, USA). Peaks on the chromatograms were identified and quantified as reported in a previous paper (Gomes and Caponio, 1999).

The extraction of hydrophilic antioxidants was performed on pâtés following the procedure reported by Gambacorta *et al.* (2010), with some modifications. About 1 g of homogenised sample was prepared by adding 1 mL of hexane and extracted using 5 mL of methanol/water (70:30 v/v) for 10 min. The mixture was centrifuged (Beckman Coulter, Fullerton, Ca., U.S.A) at 9,000 rpm for 10 min and the supernatant decanted into polypropylene tubes. The pellets were extracted under identical conditions. Supernatants were combined, centrifuged at 10,000 rpm for 5 min, recovered with a syringe and then filtered through nylon filters (pore size 0.45 μm, Sigma, Ireland) to obtain a clear supernatant liquid and stored at -20°C for subsequent. The clear extracts were analysed both for determination of total phenols and flavonoids content.

Total phenolics were determined spectrophotometrically using colorimetric method as proposed by Cerretani *et al.* (2003). An aliquot of the aqueous-methanolic solution of phenolic compounds (100 μL) is diluted in 6 mL of water, followed by the addition of 0.5 mL of Folin-Ciolcateu reagent; the mixture was incubated for 2 min at room temperature and 2 mL of sodium carbonate (200 g L^{-1}) was added to the reaction mixture, which is finally mixed and diluted with water to 10 mL. The mixture was vortexed for 20 s and incubated for 60 min at room temperature in the dark. The absorbance of the sample was read at 750 nm using gallic acid as a standard (10-1000 mg L^{-1}). Results were expressed as mg of gallic acid kg^{-1} of sample.

Total flavonoids content was determined spectrophotometrically using the method of Zhishen *et al.* (1999), based on the formation of a complex flavonoid-aluminum, with some modifications. An aliquot (0.5 mL) of the extract solution was mixed with distilled water (2 mL) and subsequently with $NaNO_2$ solution (50 g L^{-1}, 0.15 mL). After 6 min, $AlCl_3$ solution (100 g L^{-1}, 0.15 mL) was added and allowed to stand further 6 min; thereafter, NaOH solution (40 g L^{-1}, 2 mL) was added to the mixture. Immediately, distilled water was added to bring the final volume to 5 mL. Then, the mixture was properly mixed and allowed to stand for 15 min. The intensity of pink colour was measured at 510 nm. (+)-Catechin was used to calculate the standard curve and results were expressed as mg of (+)-catechin kg^{-1} of sample.

Lycopene was extracted following the method of Fish *et al.* (2002). Approximately 0.6 g of sample (determined to the nearest 0.01 g) were weighed into two 40 mL amber screw-top vials that contained 5 mL of 0.05% (w/v) butylated hydroxytoluene (BHT) in acetone, 5 mL of 95% USP grade ethanol and 10 mL of hexane. Samples were extracted on an orbital shaker at 180 rpm for 15 min on ice. After shaking, 3 mL of deionized water were added to each vial; the samples were then agitated for an additional 5 min on ice and left at room temperature to allow phase separation. The absorbance of the upper hexane layer was measured in a 1 cm path length quartz cuvette at 502 nm blanked with hexane. Lycopene content was estimated as mg kg^{-1} of sample using molar the extinction coefficient (E%) of 3150 (Binoy, 2004) at 502 nm and the molecular weight 536.9 g mol^{-1}.

Statistical analysis

All the determinations were carried out in triplicate. Analysis of variance (ANOVA) followed by Tukey HSD test for multiple comparisons was carried out on the experimental data by the XLStat Software (Addinsoft, New York, NY, USA).

Results and Discussion

Figure 2 shows the mean percent values and the results of the statistical analysis (one-way ANOVA) on the classes of volatile compounds identified in the tomato-based pâtés under investigation. Ester compounds were the most abundant class of volatile compounds determined in headspace of the both pâtés with no statistical differences.

In TP1, characterized by the use of extra virgin olive oil, a significantly higher percent contents of aldehydes and ketones were found, while in TP2, characterized by the use of sunflower oil, minced mushrooms, chilli and parsley, a significantly higher percent content of terpenic volatile compounds was observed.

In Table 2, the composition of headspace, obtained by SPME/GC-MS analysis of the two types of tomato-based pâtés under investigation was reported. A total of 89 volatile compounds were identified and grouped in relation to the chemical class they belonged to.

Regarding the terpenic volatile compounds, deriving from raw materials, significant differences were observed for most of these. In particular, α-phellandrene, β-phellandrene, α-terpinolene, γ-terpinene, α-terpinene and p-mentha-1,3,8-triene, were found only in TP2, probably associated to the use of mushrooms and parsley (Díaz-Maroto *et al*., 2002; Leffingwell and Alford, 2011). Compounds such as eucalyptol and p-allyl anisole were found, instead, only in TP1 in association to the use of basil (Truta *et al.*, 2010).

In TP2, moreover, significantly higher values were also observed for β-myrcene, α-pinene, β-pinene, that together to p-mentha-1,3,8-triene, are considered principal components of profile volatile of parsley (López *et al.*, 1999; Díaz-Maroto *et al*., 2002). As regards aldehydes, all aliphatic aldehydes, present in both types of tomato-based pâtés, are produced by chemical or enzymatic oxidation of lipids (Di Cesare *et al*., 2003). One of the most important was hexanal, considered an important aroma volatile in fresh tomato (Krumbein and Auerswald, 1998) and also in the initial flavor of virgin olive oil, produced from linoleic acid through the lipoxygenase pathway, while in refined vegetable oils its presence is linked to oxidation process (Morales *et al*., 1997).

Table 2. Volatile compounds identified in tomato-based pâtés (TP) under investigation

Volatile compounds	TP1		TP2		Volatile compounds	TP1		TP2	
Terpenes					2-Pentylfuran	*	*A*	*	*B*
α-Farnesene	*	-	*	-	Furan, 3-(4-methyl-3-pentenyl)	*	-	*	-
α-Terpinene	nd	*B*	*	*A*	*Acids*				
β-Mircene	*	*B*	**	*A*	Propanoic acid	**	*B*	**	*A*
α-Pinene	*	*B*	*	*A*	Butanoic acid	*	*B*	**	*A*
p-Mentha-1,3,8-triene	nd	*B*	**	*A*	Pentanoic acid, 3-methyl	*	*B*	*	*A*
γ-Terpinene	nd	*B*	*	*A*	Hexanoic acid	*	*B*	*	*A*
α-Phellandrene	nd	*B*	*	*A*	*Alcohols*				
β-Pinene	*	*B*	*	*A*	1-Butanol, 3-methyl	*	*B*	**	*A*
p-Cimene	*	*B*	**	*A*	1-Pentanol	*	-	*	-
p-Cimene	*	*B*	**	*A*	1-Hexanol	*	-	**	-
β-Phellandrene	nd	*B*	**	*A*	1-Penten-3-ol	*	*A*	nd	*B*
α-Terpinolene	nd	*B*	*	*A*	1-Propanol, 2-methyl	*	*B*	*	*A*
Geranial	*	-	*	-	2-Propen-1-ol	*	-	*	-
d-Limonene	*	-	*	-	2-Butanol	*	*B*	*	*A*
Linaool	*	-	*	-	2-Penten-1-ol	*	-	*	-
p-Allyl anisole	*	*A*	nd	*B*	*trans*-2-Hexen-1-ol	**	-	**	-
Eucalyptol	*	*A*	nd	*B*	2-Ciclohexen-1-ol	*	*A*	nd	*B*
Sulfur compounds					2-Furanmethanol	*	*B*	*	*A*
1,3-Dithiane	*	-	*	-	*cis*-3-Hexen-1-ol	**	*B*	***	*A*
Diallyl disulphide	*	*B*	**	*A*	*trans*-3-Hexen-1-ol	*	*B*	*	*A*
Dimethyl sulfide	**	-	**	-	3-Methylbenzyl alcohol	*	-	*	-
Dimethyl sulfoxide	*	*B*	*	*A*	Benzyl alcohol	*	*B*	*	*A*
3-Vinyl-1,2-dithiacyclohex-4-ene	*	*B*	*	*A*	Ethanol	***	*B*	****	*A*
Aldehydes					Phenylethylalchol	nd	*B*	*	*A*
trans,trans-2,4-Hexadienal	*	*B*	*	*A*	*Ketones*				
trans,trans-2,4-Heptadienal	*	-	*	-	Acetone	***	*A*	***	*B*
trans,trans-2,4-Decadienal	*	*B*	*	*A*	Ethanone, 1-(2-furanyl)	*	-	*	-
trans-2-Hexenal	***	-	***	-	2,4-Heptanone	*	*A*	nd	*B*
trans-2-Heptenal	*	*B*	**	*A*	1-Penten-3-one	*	-	*	-
trans-2-Octenal	*	-	*	-	2,3-Butanedione	**	*B*	**	*A*
trans-2-Nonenal	*	*B*	*	*A*	2-Butanone, 3-hydroxy	**	*B*	***	*A*
5-Heptenal, 2,6-dimethyl	nd	*B*	*	*A*	3-Penten-2-one	**	-	**	-
Acetaldehyde	*	*B*	*	*A*	5-Hepten-2-one, 6-methyl	**	-	**	-
Benzaldehyde, 2-methyl	*	-	*	-	3,5-Heptadien-2-one, 6-methyl	*	-	*	-
Benzaldehyde	*	*B*	**	*A*	*Esters*				
Benzenacetaldehyde	*	-	*	-	1-Butanol, 3-methyl-, acetate	*	*B*	*	*A*
Butanal, 2-methyl	*	*B*	*	*A*	*cis*-3-Hexen-1-ol, acetate	**	*A*	*	*B*
Butanal, 3-methyl	*	-	*	-	Acetic acid, methyl ester	**	-	**	-
2-Butenal, 3-methyl	*	*A*	nd	*B*	Ethyl acetate	****	*B*	****	*A*
Furfural	**	*B*	**	*A*	Propanoic acid, 2-hydroxy-, ethyl ester	*	*B*	*	*A*
Pentanal	**	-	**	-	Acetic acid, exyl ester	*	*A*	nd	*B*
Hexanal	**	-	***	-	Benzoic acid, methyl ester	*	*A*	nd	*B*
Heptanal	*	-	*	-	*Other compounds*				
Nonanal	*	*A*	nd	*B*	Octane	**	*A*	**	*B*
Furans					1-Methoxy-3-hexene	*	*A*	nd	*B*
Benzofuran, 2,3-dihydro-2-methyl	nd	*B*	*	*A*	*p*-Xylene	*	-	*	-
2-Methylfuran	**	-	*	-	1,5-Heptadiene, 4-methyl	*	*A*	*	*B*
2-Ethylfuran	*	*B*	**	*A*	Toluene	*	*A*	nd	*B*

*concentration detected < 1 μg g^{-1}; **concentration detected between 1 μg g^{-1} and 5 μg g^{-1}; ***concentration detected between 5 μg g^{-1} and 10 μg g^{-1}; ****concentration detected > 10 μg g^{-1}; nd, not detected.
AB, different letters indicate significant differences for $p < 0.05$. A, higher values; B, lower values; -, not significant.

In tomato-based pâtés under investigation, hexanal was found in higher amounts in TP2 than in TP1. The higher amounts of linoleic acid in sunflower oil than in extra virgin olive oil justified the presence of other aldehydes, such as trans-2-heptenal, trans-2-nonenal, trans,trans-2,4-decadienal, trans,trans-2,4-hexadienal, related to the linoleic acid oxidation, in significantly higher amounts in TP2 than TP1. The presence of nonanal only in TP1 can be related to use of extra-virgin olive oil in which the predominant fatty acid is oleic acid.

Furfural, a small heterocyclic and highly volatile compound, is generated during heating of food by thermal degradation of food constituents, such as vitamin C, carbohydrates, proteins, polyunsaturated

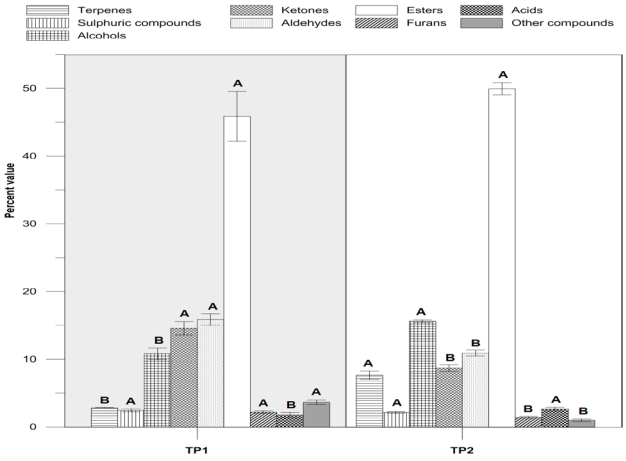

Figure 2. Percent values (± SD) and results of statistical analysis of the volatile compounds classes identified in the tomato-based pâtés under investigation. AB, different superscript letters indicate significant differences for $p < 0.05$.

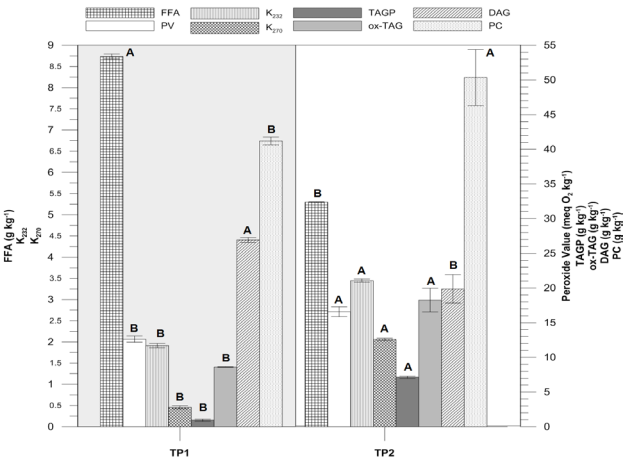

Figure 3. Mean values (± SD) and results of statistical analysis of the analytical indices used for determination of oxidative and hydrolytic degradation of oil extracted from tomato-based pâtés under investigation. AB, different superscript letters indicate significant differences for $p < 0.05$. FFA, free fatty acids; PV, peroxide value; TAGP, triacylglycerol oligopolymers; ox-TAG, oxidized triacylglycerols; DAG, diacylglycerols.

fatty acids and also by interactions between these compounds (Crews and Castle, 2007). Considering that both tomato-based pâtés were produced with the same technological process, the significantly higher amount of furfural in TP2 could be attributed to the acidic composition of oils used, because linoleic acid has been shown to be a more efficient precursor of furans than oleic acid (Becalski and Seaman, 2005). Also 2-ethylfuran, which might be useful in distinguishing oxidation at the late stage (Kalua *et al*., 2007), was detected in significantly higher amounts in TP2, as well as some carboxylic acids such as propanoic, butanoic and hexanoic acids.

The lower concentration of volatile compounds

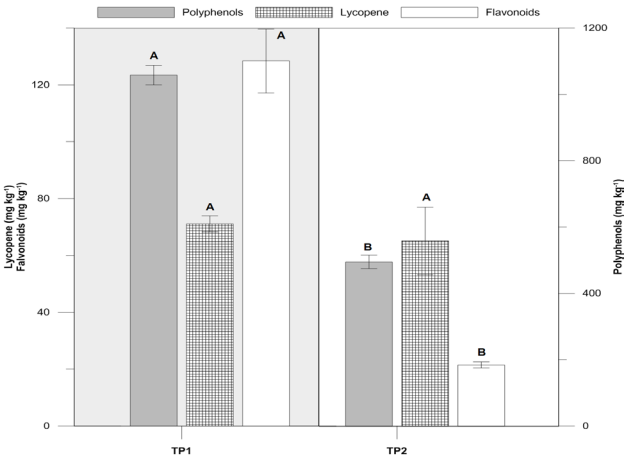

Figure 4. Mean values (± SD) and results of statistical analysis of the total phenols, flavonoids and lycopene content. AB, different superscript letters indicate significant differences for $p < 0.05$.

derived from oxidative processes in TP1 suggests a minor level of oxidative process in this pâté, that could be related to the use of extra virgin olive oil and to a greater stability to the thermal treatments conferred by this type of oil. The alcohols have different origins; in fact, some ingredients such as vinegar could be the main source of ethanol that represents the most abundant one. Alcohols are also by-products of some pathways where aldehydes are involved. Once formed, some aldehydes such as hexanal and *trans*-2-hexenal, suffer a series of enzymatic transformations mediated by isomerases and alcohol dehydrogenases forming C6 alcohols (Malheiro *et al*., 2011). Among lipid-derived alcohols, there were *cis* and *trans*-3-hexen-1-ol, typical compounds contributing to the aroma of tomato, giving the green and bitter sensory perception, respectively (Carbonell-Barrachina *et al.*, 2006), and present in significantly higher concentrations in TP2.

As regards ketones, acetone was the most representative in both the tomato-based pâtés with significantly higher values detected in TP1. It is one of the most important volatile compounds in tomato (Yilmaz, 2001) thus a higher concentration of this compound in TP1 could be attributable to the use of a greater amount of tomato compared to that used in TP2. Moreover, 2,3-butanedione and 2-butanone,3-hydroxy are important flavor components detected in a significant higher amount in TP2; the former is a Maillard reaction product (Wnorowski and Yaylayan, 2000) while the latter could derive from both the oxidation of 2,3-butanedione and of vinegar. No significant difference was observed for 5-hepten-2-one, 6-methyl, an important compound in the aroma of tomato, formed from the thermal degradation of carotenoids and regarded as a marker compound

of these (lycopene, γ-, δ-, ζ-carotene) (Sieso and Crouzet, 1977).

Among esters, ethyl acetate was the most abundant; it is commonly detected in olive oil (Kalua *et al.*, 2007), and together to the others esters above all in vinegar (Blanch *et al.*, 1992). Figure 3 shows the mean values and the results of the statistical analysis of the analytical indices used to assess the oxidative and hydrolytic degradation of extracted oil from the tomato-based pâtés under investigation. The oil extracted from TP2 showed mean values of FFA significantly lower than TP1, attributable to the use of refined oil, in which FFA are removed during neutralization. As regards the conventional indices of oxidative degradation, PV, K_{232} and K_{270} showed significantly higher mean values in the oil extracted from TP2 than TP1.

The level of TAGP, stable substances including all forms of triacylglycerol polymerization, and of ox-TAG were also significantly higher in the TP2, to indicate higher oxidative degradation of this oil compared to TP1, already verified by the SPME/GC-MS analyses of volatile compounds. Besides, it has been proved that TAGP and ox-TAG act in oils as pro-oxidants and as precursors of volatile oxidation products (Gomes *et al*., 2011), so high concentrations could reduce the shelf-life of the product.

Regarding the DAG content, significantly higher values were found in the oil extracted from TP1. The findings are in accordance with those reported in literature on oils used as liquid medium of in-oil preserved vegetables (Caponio *et al*., 2003) and are linked to the DAG content of the starting oils used. Finally, figure 4 shows the mean values and the results of the statistical analysis of total phenolics, flavonoids and lycopene – natural substances able to perform a strong antioxidant activity – in the tomato-based pâtés analyzed.

TP1 had a significantly higher total phenols content compared to TP2, due to the use of extra virgin olive oil, naturally rich in phenolic compounds respect to the sunflower oil in which the extraction and refining process induces a removal and/or destruction of this compounds (Pellegrini *et al*., 2001). Also the contribute of spices (in this case of basil and wild marjoram), considered among those with higher content of polyphenols and strong antioxidant activity (Muchuwety *et al.*, 2007), should not be neglected.

The same considerations can be extended also to flavonoids, among the major phenolic compounds of tomatoes. A reason that can explain the lower amount of these compounds in TP2 could be the use of a smaller incorporation of dried tomatoes in the formulation of ingredients (560 g kg^{-1} in TP1 versus 367 g kg^{-1} in TP2), as well as the use of extra virgin olive oil and of spices. As regards the lipophilic components, the amount of lycopene, the carotenoid responsible of the red colour of tomatoes, appeared instead comparable in both tomato-based pâtés.

Conclusions

The two types of tomato-based pâtés showed marked differences in the volatile composition and oxidative/antioxidant pattern. Notably, the headspace solid-phase micro-extraction and GC/MS analysis reported in TP1 higher contents of compounds ascribable to lipid oxidation, such as trans-2-heptenal, trans,trans-2,4-hexadienal, trans,trans-2,4-decadienal and carboxylic acids, confirmed by chemical determination. Also the antioxidant compounds, in particular hydrophilic components (polyphenols and flavonoids), showed differences between the two tomato-based pâtés, that could be attributed to a more complex ingredient list and to the use of extra virgin olive oil in TP1, that, compared to TP2 showed lower amounts of oxidation compounds.

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