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Valorisation of low quality edible oil with tomato peel waste

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Abstract

The aim of this study is to enrich edible oils with carotenoids and lycopene from tomato purée or tomato peel, an industrial tomato waste. These tomato derivatives were incorporated in refined olive oil, extra virgin olive oil and refined sunflower oil. The incorporation of peel enhanced the concentration of β-carotene and lycopene more than tomato purée. Furthermore, the incorporation of both tomato purée and peel induced better thermal stability of the refined olive oil compared to extra virgin oil and sunflower oil. A decrease on total phenols as well as some prooxidant activity account for this, when tomato purée was incorporated. In our oil preparations, rutin and naringenin, as flavonoids coming exclusively from tomato purée or peel, were detected. The enrichment of oils with tomato carotenoids and lycopene, in particular low quality oils like refined olive oils, might be an alternative approach to elaborate new functional foods.

Keywords: Tomato by-product; Antioxidant activity; Olive oil; Phenolics

1. Introduction

The protective effect of the Mediterranean diet against the risk of cancer and cardiovascular disease has been attributed to various dietary components (Kushi, Lenart, & Willet, 1995). Recently, there has been renewed attention given to the antioxidant content of tomatoes because many epidemiological studies suggest the association of this crop with a range of health benefits such as the prevention of prostate cancer (Heber, 2000).

Tomatoes (*Lycopersicon escullentum*) are widely consumed either raw or after processing and can provide a significant proportion of the total antioxidants in the diet (Martínez-Valverde, Periago, Provan, & Chesson, 2002). This is largely in the form of carotenes (Nguyen & Schwartz, 1999) and phenolic compounds (Hertog, Hollman, & Katan, 1992). However, when tomatoes are processed into products like catsup, salsa and sauces, 10–30% of their weight becomes waste or pomace (King & Zeidler, 2004). Al-Wandawi, Abdul-Rahman, and Shaikhly (1985) reported that tomato skin contains high levels of lycopene compared to the pulp and seeds. Stewart et al. (2000) reported that the majority of the flavonols in tomatoes are present in the skin. Recently, George, Kaur, Khurdiya, and Kapoor (2004) studied the antioxidant components in 12 fieldgrown tomato genotypes and reported that, on average, the tomato skin had 2.5 times higher lycopene levels than the pulp, with significant amounts of phenolics and ascorbic acid. In a more detailed analysis, Toor and Savage (2005) determined the major antioxidants and antioxidant activity in different fractions (skins, seeds and pulp) of three tomato cultivars and found that the skin fraction of all

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cultivars had significantly higher levels of total phenolics, total flavonoids, lycopene and ascorbic acid; the antioxidant activity was also higher than the pulp and seed fractions.

Many factors have contributed over the last few years to the development of waste-handling technology, including the cost of disposing the waste, the growing interest in natural food additives and the increased restrictions brought about by the challenge of environmental protection. Many proposals and processes (Knoblich, Anderson, & Latshaw, 2005; Toor & Savage, 2005) are already applied for the exploitation of tomato pomace, as for example their use in animal feed, manifesting equivalence to soybean meals as a protein and carotenoid source (Knoblich et al., 2005).

In the present study another approach for the exploitation of this waste is considered. This alternative approach is based on the lipophilic properties of carotenoids for their extraction into edible oils and phenolics to some extent in view of upgrading low quality oils and thus suggesting new functional food products. In our work, refined olive oil was chosen because it is a low quality virgin olive oil with high acidity, which undergoes physical and chemical treatment to improve its quality. It has been found to protect LDL from oxidation at a lesser extent as compared with virgin olive oil (Ramirez-Tortosa et al., 1999). The other reason is the fact that intake of lycopene-rich foods cooked with monounsaturated fat has been suggested to have an added benefit against coronary heart disease (Ahuja, Ashton, & Ball, 2003).

2. Materials and methods

2.1. Materials

Tomato purée (in tetra packs) and fresh tomatoes were purchased from the local market in April 2006. After opening the packet, the product was stored at −20 °C. The skin of the tomatoes was separated from the flesh using a sharp knife and was frozen immediately (the flesh was discarded). The sample was then freeze-dried, placed in oxygen barrier bags and stored frozen at −20 °C until analysis. Three types of oils were used for the test of incorporation: a refined olive oil of low quality, an extra virgin olive oil and BHT-free sunflower oil.

2.2. Sample preparation

Amounts of 1.00 g, 2.25 g, 5.00 g and 8.60 g of tomato purée were added to 20.00 g of the oil samples, to give final concentrations of 5%, 10%, 20% and 30%, respectively, and homogenized with a cyclone I.Q.[2] Virtis blender for 3 min, followed by centrifugation at 6240*g* for 15 min on a HERAEUS Megafuge 1.0 R centrifuge (Germany). The organic phase was recovered and stored at 4 °C until analysis. The peel was mixed with the refined olive oil only at ratios of 5% and 10%; higher proportions could not be applied due to mechanical difficulties resulting in inadequate mixing. Samples were left to diffuse for 24 h at 4 °C in the dark and then centrifuged at 6240*g* for 15 min; the resulting oils were stored at 4 °C until analysis. The commercial oils were also stored under the same conditions to be used as blanks for all the tests.

2.3. Peroxide value

The peroxide value was determined according to EC regulation 2568/91, Annex III.

2.4. Acidity

The acidity was measured according to EC regulation 2568/91, Annex II.

2.5. Phenolic extraction

The tomato purée and tomato peel were washed with hexane (weight (g):volume (ml) 1:5 and 1:20, respectively), then both resulting extracts were mixed with ethanol (1:10) and left overnight under stirring. The ethanolic phase was then concentrated on a rotary evaporator and the residue was taken up in methanol for the LC–MS analysis. Twenty five grams of the oils and oil mixes were partitioned between 50 ml of hexane and 30 ml of MeOH–H_2O (60/40). The upper phase was washed twice with MeOH–H_2O and the three methanolic extracts were combined, washed with 50 ml hexane and concentrated under vacuum. The residue was recovered in 5 ml MeOH for the Folin–Ciocalteu total phenol test (Waterman & Mole, 1994); results were expressed as caffeic acid equivalents. The phenolic profile of the sample of 20% tomato purée in refined oil and that of 10% tomato peel in the same oil were examined by LC–MS.

This analysis was performed using the LC/DAD/MS system with a Finnigan MAT Spectra System P4000 pump coupled with a UV6000LP diode array detector and a Finnigan AQA mass spectrometer. The separation was performed on a 125 × 2 mm Superspher 100-4 RP 18 column (Macherey-Nagel, 4 μm particle size) at a flow rate of 0.33 ml/min. The detection was monitored at 290, 340 and 365 nm and also by MS-ESI(+) spectroscopy at a probe temperature of 400 °C, probe voltage of 4.0 kV and at 12 and 40 eV in the mass analyzer. The following gradient program was used: (A) AcOH (2.5%) and (B) MeOH, 90% A at 0 min with an isocratic gradient for 2 min, at 37 min 0% A. The data were processed using the Xcalibur 1.2 software.

2.6. Carotenoid analysis

Carotenoids were extracted according to Rodriguez-Amaya (2001). A homogenous sample of 10 g of tomato purée and 5 g of peel were macerated with acetone for 15 min and after filtration the residue was macerated again with fresh acetone. The extraction was repeated until exhaustion of colour. The extracts were collected and evaporated under vacuum (<30 °C). The residues were then

stirred overnight in the dark with 25 ml of a methanolic solution of potassium hydroxide (10%) and 25 ml of petroleum ether containing 0.1% BHT. The mixture was partitioned with water, and the upper phase washed with a water:MeOH mixture (v:v, 1:1) until neutral pH and dried over anhydrous sodium sulphate. The organic phase was concentrated under vacuum (<30 °C), redissolved in 2 ml of acetone and stored at −20 °C prior to analysis. The analyses were carried out in triplicate. For the measurement of carotenoids in the final product samples, 2 g were used following the procedure above.

The carotenoid analysis was carried out according to Soto-Zamoraa, Yahia, Brecht, and Gardea (2005). The concentration was expressed as mg/100 ml of extract, as follows:

$$\text{Lycopene (mg/100 ml extract)} = -0.0458(\text{Abs}_{663}) + 0.204(\text{Abs}_{645}) + 0.372(\text{Abs}_{505}) - 0.0806(\text{Abs}_{453}).$$

$$\beta\text{-Carotene (mg/100 ml extract)} = 0.216(\text{Abs}_{663}) - 1.22(\text{Abs}_{645}) - 0.304(\text{Abs}_{505}) + 0.452(\text{Abs}_{453}).$$

2.7. Antioxidant activity assays

Three tests for the evaluation of the antioxidant activity were performed. The chemiluminescence test for the evaluation of hydrogen peroxide scavenging activity following a previously established method by Arnous, Petrakis, Makris, and Kefalas (2003) was carried out on all the samples and results were expressed as IC_{50}, the concentration of sample required to decrease the chemiluminescence intensity of the blank by 50%. The antiradical activity using the stable radical of 2,2-diphenyl-1-picrylhydrazyl (DPPH) was used according to the previously described method by Brand-Williams, Cuvelier, and Berset (1995). The decrease in the absorbance was determined at 580 nm because of the interfering carotenoids at 515 nm and the results were expressed as EC_{50}, which is the amount of sample necessary to decrease the initial DPPH concentration by 50%.

For the RANCIMAT test (Metrohm, Switzerland), oil samples (3 g) were oxidized at 120 °C, with an air flow of $20\,l \times h^{-1}$. The protection coefficient (P_c) was determined as the relationship between the induction period of the sample and the induction period of the control. P_c values >1 show antioxidant behaviour, whereas P_c values <1 suggest a prooxidant activity in the examined mixtures.

$$P_c = \frac{\text{Induction period of sample}}{\text{Induction period of control}}.$$

2.8. Statistical analysis

Data were analyzed using the analysis of variance ($p < 0.05$) to estimate the differences between values of compounds tested. Results were processed by the one-way analysis of ANOVA-MANOVA; the post-hoc test was performed (Duncan's test was applied) to indicate significant differences within individual groups.

3. Results and discussion

The acidity, the peroxide value and the total phenolic content of the oils and oil mixtures used are given in Table 1. The incorporation of the tomato purée or tomato peel in the refined oil and the extra virgin olive oil did not lead to any significant change in acidity and peroxide value. While the sunflower oil showed a significant increase in its peroxide value after the addition of 5% tomato purée, there was no significant change in the acidity.

The incorporation of tomato purée induced a significant decrease in the total polyphenols of the extra virgin olive oil mixtures, up to half of the initial content at 30% tomato purée. A light but significant decrease was noticed in the refined oil. However, a significant enrichment was observed with the addition of tomato purée to the sunflower oil and with tomato peel to the refined oil. The decrease observed in the case of virgin oil and even the refined oil could be attributed to the dissolution of polyphenols into the aqueous phase of the tomato purée during centrifugation. With sunflower oil, where the phenolic concentration is negligible, after mixing and partitioning, the phenolic content increased only slightly. Therefore, the use of peel circumvents this point, accounting for a phenol increase in the oil bulk.

3.1. Carotenoids

Carotenoid content of the oils used tended to increase significantly by increasing incorporation of tomato purée and/or peel. A higher diffusivity of lycopene was observed in virgin olive oil with 5% tomato purée, whereas at higher concentrations differences were not significant (Figs. 1 and 2). The effectiveness of the introduction of tomato peel was much higher with an average lycopene content of 1.99 mg/100 g oil with 10% of peel, corresponding approximately to the same content when 20% purée was added (1.84 mg/100 g oil) to the refined oil. An average β-carotene content of 1.07 mg/100 g oil was measured after the addition of 10% peel, which is 1.8 times higher than the content of β-carotene in the refined oil with 30% purée.

The lyophilized peel contains 5.85 mg of lycopene per 100 g, whereas in the purée the concentration is 2.91 mg/100 g. For β-carotene the respective concentrations are 2.90 mg/100 g of peel and 0.15 mg/100 g for tomato purée. This finding is consistent with the results of Toor and Savage (2005), showing that the skin contains the highest levels of lycopene, and with those of Sharma and Le Maguer (1996) who showed that lycopene is mostly attached to the fibre fraction of the pulp.

The non-significant difference in the solubility of carotenoids in the different types of oils is due to their similarity

Table 1
Acidity, peroxide value and total phenols of the oils and oil mixtures used

Characteristics		Acidity (% oleic acid/kg oil)	Peroxide value (meq O_2/kg)	Total polyphenol (mg/g oil expressed as caffeic acid equivalent)
Refined olive oil	0% Tomato	0.46 ± 0.08a	6.76 ± 0.35a	0.023 ± 0.001a
	5% Tomato purée	0.38 ± 0.08a	7.00 ± 0.50a	0.023 ± 0.001a
	10% Tomato purée	0.45± 0.05a	7.03 ± 0.40a	0.020 ± 0.001b
	20% Tomato purée	0.44 ± 0.07a	7.17 ± 0.25a	0.020 ± 0.001b
	30% Tomato purée	0.45 ± 0.05a	7.62 ± 0.41a	0.020 ± 0.001b
	5% Tomato peel	0.39 ± 0.09a	7.45 ± 0.18a	0.029 ± 0.001b
	10% Tomato peel	0.38 ± 0.04a	7.44 ± 0.24a	0.029 ± 0.001b
Virgin olive oil	0% Tomato	0.32 ± 0.03a	12.24 ± 0.25a	0.142 ± 0.002a
	5% Tomato purée	0.40 ± 0.02a	11.43 ± 0.40a	0.107 ± 0.002b
	10% Tomato purée	0.39 ± 0.04a	11.33 ± 0.33a	0.106 ± 0.001b
	20% Tomato purée	0.33 ± 0.03a	11.38 ± 0.38a	0.094 ± 0.003c
	30% Tomato purée	0.36 ± 0.04a	11.48 ± 0.40a	0.072 ± 0.001d
Sunflower oil	0% Tomato	0.07 ± 0.03a	2.39 ± 0.40a	0.003 ± 0.000a
	5% Tomato purée	0.14 ± 0.04b	4.30 ± 0.50a	0.004 ± 0.000a
	10% Tomato purée	0.08 ± 0.04b	4.37 ± 0.45a	0.005 ± 0.000b
	20% Tomato purée	0.12 ± 0.03b	4.50 ± 0.40a	0.010 ± 0.000c
	30% Tomato purée	0.44 ± 0.41b	4.58 ± 0.40a	0.010 ± 0.000c

Results are means ± SD ($n = 3$). Values of the same column, in the same treatment, followed by the same letter, are not statistically different at ($p < 0.05$) as measured by Duncan's test.

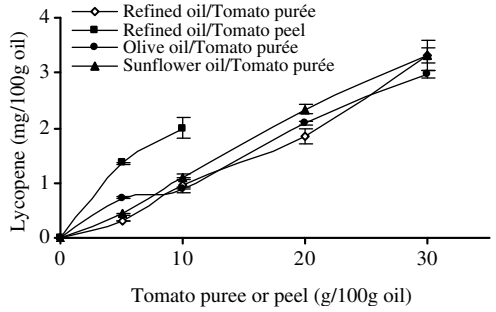

Fig. 1. Lycopene contents of different oils at various additions of tomato purée or peel.

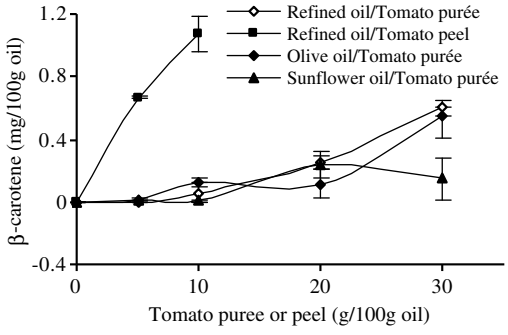

Fig. 2. β-Carotene contents of different oils at various additions of tomato purée or peel.

in the composition of fatty acids. From previous data concerning the fatty acid profile of the oils used (Codex Standard 210-1999, 2001; Codex Standard 33-1981, 2001), the differences concerned palmitic acid (7.5–20.0% for virgin olive oil against 5.0–8.0% for sunflower oil), oleic acid (55.0–83.0% for virgin olive oil against 13.0–40.0% for sunflower oil) and linolenic acid (3.5–21.0% for virgin olive oil against 40–74% for sunflower oil), while the solubility of lycopene and β-carotene was reported to increase when the chain-length of the triglyceride fatty acids decreased and there was no effect of the fatty acid unsaturation degree on the carotenoid solubility (Borel et al., 1996).

3.2. Antioxidant activity

3.2.1. DPPH test

The sunflower oil showed the best antiradical activity, expressed as EC_{50} of 3557.6 mg oil/mg DPPH against 4279.0 mg oil/mg DPPH and 12601.1 mg oil/mg DPPH for virgin olive oil and refined oil, respectively (Fig. 3). This could be due to the enrichment of the commercial sunflower oil with tocopherol. The incorporation of tomato purée into the refined oil increased the efficiency of the antioxidant activity of the oil up to 20%; after that, at 30%, a drop in the antioxidant activity was observed (Fig. 3). The incorporation of tomato peel showed similar results, while

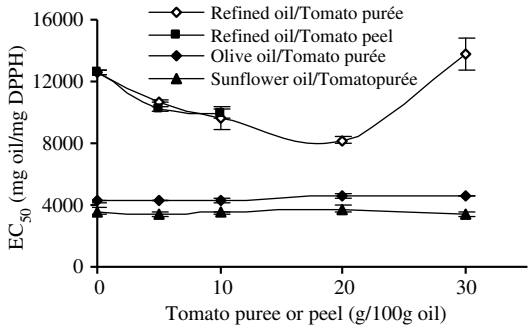

Fig. 3. EC_{50} of different oils at various additions of tomato purée or peel.

the antioxidant efficiency did not drop because of the enrichment in polyphenols. In the virgin olive oil mixtures, lower antioxidant efficiency was recorded after 5% incorporation. The difference in EC_{50} was not significant up to 20% incorporation, at which point the negative effect became obvious. The sunflower oil mixtures did not show a significant difference, presumably due to their enrichment in α-tocopherol. The lower antioxidant activities manifesting higher proportions of tomato purée could be due to polyphenol loss or to prooxidant activity of carotenoids at higher concentrations. It has been shown that lutein, lycopene and β-carotene increased the hydroperoxide formation of autoxidized triglycerides and that a combination of carotenoids and tocopherol inhibits this prooxidant activity (Terao, Yamauchi, Murakami, & Matsushita, 1980).

According to Krinsky (1993), antioxidant activity of carotenoids in organic solutions is related to oxygen concentration, the chemical structure of carotenoids and the presence of other antioxidants (e.g. polyphenols and tocopherol). Much research has shown that carotenoids maintained the oxidative stability of oils (Fakourelis, Lee, & Min, 1987). Montesano, Cossignani, D'Arco, Simonetti and Damiani (2006) reported that the addition of pure lycopene at 0.5% and 1% of extra virgin olive oil preserves it from natural oxidative events during storage by the preservation of phenolics and α-tocopherol. However, other works showed that β-carotene acts as a prooxidant during lipid oxidation in both the light (Terao et al., 1980) and the dark (Suzuki, Usuki, & Kaneda, 1989).

The phenolic compounds are active antioxidant ingredients present in tomato (Beecher, 1998). Shixian et al. (2005) mentioned that polyphenols contribute to the synergistic effects observed in lycopene. Martínez-Valverde et al. (2002) showed that the antioxidant capacity of tomato extracts is significantly related to the contents of the ferulic and caffeic acids, but not quercetin and chlorogenic acid. However, in other works the structures reported to be predominant in tomato extracts were rutin, quercetin, chalconaringenin and its degradation product, naringenin (Arabbi, Genovese, & Lajolo, 2004). While Miranda et al. (2000) showed that a flavonoid chalcone (chalconaringenin) and a flavanone (naringenin) with no prenyl groups act as prooxidant by promoting copper LDL oxidation.

Presumably, manifestation of antioxidant or prooxidant behaviour in this study is the result of various ratios among the carotenoids and the other compounds involved. This hypothesis is a challenge for further investigation.

3.2.2. Peroxyoxalate chemiluminescence

The peroxyoxalate chemiluminescence assay gave similar results to the DPPH assay (Fig. 4). Blank sunflower oil had the highest activity with an IC_{50} of 430.4 mg oil/ml followed, but with no significant difference, by virgin olive oil with 453.9 mg oil/ml and then by the refined oil with 552.2 mg oil/ml. The incorporation of tomato purée

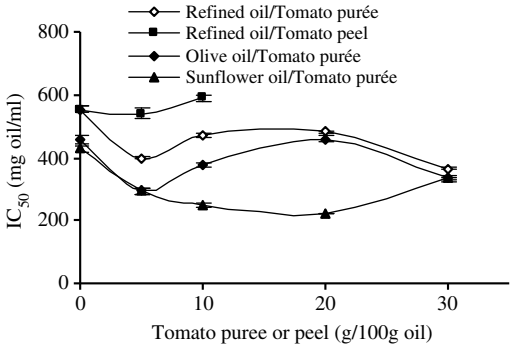

Fig. 4. IC_{50} of different oils at various additions of tomato purée or peel.

at 5% increased the antioxidant efficiency, but at higher concentrations the efficiency decreased. The same effect was shown by the incorporation of tomato peel at 5%, with virgin olive oil at 20% of tomato purée and sunflower oil after the addition of 30% of tomato purée. The delay in the manifestation of the prooxidant activity for commercial sunflower oil could be due to its enrichment with α-tocopherol.

3.2.3. Rancimat test

Oxidative stability is an important parameter in evaluating the quality of oils and fats, as it gives a good estimation of their susceptibility to oxidative degeneration, the main cause of their alteration. The greater or lesser stability of an oil means the conservation or not of the so-called dynamic parameters during the useful life of the product (Aparicio, Roda, Albi, & Gutiérrez, 1999). The stability tested by RANCIMAT was more indicative of the real state of the mixtures, suggesting in a more direct way the best mixture. The induction times of the different oils used in this experiment were 1.7, 9.4 and 1.7 h at 120 °C for the refined oil, virgin olive oil and sunflower oil, respectively. These values were enhanced for the refined oil with the incorporation of tomato purée to more than double (2.1 times) with 30% tomato purée and 1.4 times more with 10% tomato peel. Nevertheless, the induction time decreased to 6.9 and 0.8 h for virgin olive oil and sunflower oil, respectively, corresponding to 0.7 and 0.4 times the initial induction times (Fig. 5).

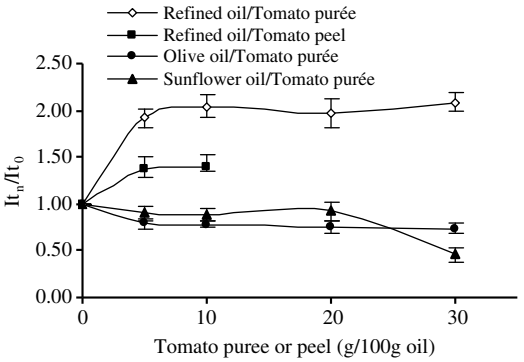

Fig. 5. Induction times of different oils at various additions of tomato purée or peel.

Table 2
Analysis of the HPLC and MS chromatograms for the tomato purée

R.T. (min)	$[M+H]^+$ (m/z)	Fragment ion (m/z) at 12 eV	Fragment ion (m/z) at 40 eV	λ_{max} (nm)	Identification
13.78	743	743	611, 465, 303	254, 354	Rutoside-tartrate
15.03	611	611	465, 303	256, 354	Rutin
19.12	273	273	273	240, 290	Naringenin
25.11	182	182	182, 167	280	2-(4-Hydroxy-3-methoxyphenyl) acetic acid
25.72	343	172	172	238, 282	Trihydroxybenzoic acid
26.79	277	171, 277, 294, 299	171, 299	250, 272	Ester of gallic acid
27.99	219	219, 236, 241	–	238, 280	8-Acetyl-7-hydroxy-4-methylcoumarin

Table 3
Analysis of the HPLC and MS chromatograms for the tomato peel

R.T. (min)	$[M+H]^+$ (m/z)	Fragment ion (m/z) at 12 eV	Fragment ion (m/z) at 40 eV	λ_{max} (nm)	Identification
6.01	287	231	163	240, 284	4′-4-5-Hydroxy-2′-methoxychalcone
14.98	611	611	303, 276	256, 352	Rutin
19.01	273	273	147, 153	238, 290	Naringenin

These results are not correlated to the two previous tests for antioxidant activity. The differences in mechanisms involved may account for this. Nevertheless, because of the importance of the last test from a technological point of view, we consider it as more indicative. In this view the optimal mixture for best valorisation of the refined olive oil was with 10% peel to enhance the nutritional quality and the stability of low quality olive oil.

3.3. Phenolic profile

The results of the LC–MS analysis on the tomato peel and purée (Tables 1 and 2) correlated with the previous research, where the most predominant flavonoids are rutin (Beecher, 1998), quercetin (Arabbi et al., 2004), chalconaringenin; the latter, being unstable, it easily converts to naringenin (Arabbi et al., 2004). In our oil preparations, only rutin and naringenin were recovered as flavonoids from the tomato purée and peel, rutin being detected in traces (Table 3). Miranda et al. (2000) reported that chalconaringenin and naringenin are both prooxidant flavonoids, which may contribute to a tentative explanation for the prooxidant behaviour changes of the oil preparations.

4. Conclusion

In this study we suggested an approach for the valorisation of tomato by-products by the extraction of carotenoids into edible oils and especially to low quality edible oils. The incorporation of tomato purée or peel did not lead to an increase of acidity and peroxide value except for the sunflower oil where a significant increase of its peroxide value was noticed. The enrichment levels on lycopene and β-carotene were similar in all the types of oils after incorporation of tomato purée independently of the percentage of incorporation. Interestingly, tomato peel incorporation in refined olive oil was more efficient to enhance its content on lycopene and β-carotenoids as compared to tomato purée. Moreover, tomato purée incorporation induced leaching of phenolic compounds, while tomato peel permitted to overcome this problem and enhance significantly the total phenol content of the refined olive oil.

All in all, the results of this study show that the incorporation of tomato peel, as agro-industrial tomato waste, is an efficient means to extract carotenoids and phenolics into the fatty substrate, to enhance their bioavailability, thus upgrading low quality edible oils.

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References

Ahuja, K. D. K., Ashton, E. L., & Ball, M. J. (2003). Effects of a high monounsaturated fat, tomato-rich diet on serum levels of lycopene. *European Journal of Clinical Nutrition, 57*, 832–841.

Al-Wandawi, H., Abdul-Rahman, M., & Shaikhly, K. (1985). Tomato processing wastes as essential raw material sources. *Journal of Agricultural and Food Chemistry, 33*, 804–807.

Aparicio, R., Roda, L., Albi, M. A., & Gutiérrez, F. (1999). Effect of various compounds on virgin olive oil stability measured by rancimat. *Journal of Agricultural and Food Chemistry, 47*, 4150–4155.

Arabbi, P. R., Genovese, M. I., & Lajolo, F. M. (2004). Flavonoids in vegetable foods commonly consumed in Brazil and estimated ingestion by the Brazilian population. *Journal of Agricultural and Food Chemistry, 52*, 1124–1131.

Arnous, A., Petrakis, C., Makris, D. P., & Kefalas, P. (2003). A peroxyoxalate chemiluminescence-based assay for the evaluation of hydrogen peroxide scavenging activity employing 9,10-diphenylanthracene as the fluorophore. *Journal of Pharmacological and Toxicological Methods, 48*, 171–177.

Beecher, G. R. (1998). Nutrient content of tomatoes and tomato products. *Proceedings of the Society for Experimental Biology and Medicine, 218*, 98–100.

Borel, P., Grolier, P., Armand, M., Partier, A., Lafont, H., Lairon, D., et al. (1996). Carotenoids in biological emulsions: Solubility, surface-to-core distribution, and release from lipid droplets. *Journal of Lipid Research, 37*, 250–261.

Brand-Williams, W., Cuvelier, M. E., & Berset, C. (1995). Use of a free radical method to evaluate antioxidant activity. *Lebensmittel-Wissenschaft und-Technologie, 28*, 25–30.

Codex Standard for Named Vegetable Oils. (2001). Codex Standard 210-1999. *Codex Alimentarius*, 8.

Codex Standard for olive Oil, Virgin and Refined, and for Refined Olive-Pomace Oil. (2001) Codex Standard 33-1981 (Rev.1-1989). *Codex Alimentarius*, 8.

Fakourelis, N., Lee, E. C., & Min, D. B. (1987). Effects of chlorophyll and β-carotene on the oxidation stability of olive oil. *Journal of Food Science, 52*, 234–235.

George, B., Kaur, C., Khurdiya, D. S., & Kapoor, H. C. (2004). Antioxidants in tomato (*Lycopersicon esculentum*) as a function of genotype. *Food Chemistry, 84*, 45–51.

Heber, D. (2000). Colorful cancer prevention: α-Carotene, lycopene and lung cancer. *American Journal of Clinical Nutrition, 72*, 901–902.

Hertog, M. G. L., Hollman, P. C. H., & Katan, M. B. (1992). Content of potentially anticarcinogenic flavonols of 28 vegetables and 9 fruits commonly consumed in the Netherlands. *Journal of Agricultural and Food Chemistry, 40*, 2379–2383.

King, A. J., & Zeidler, G. (2004). Tomato pomace may be a good source of vitamin E in broiler diets. *California Agriculture, 58*, 59–62.

Knoblich, M., Anderson, B., & Latshaw, D. (2005). Analyses of tomato peel and seed byproducts and their use as a source of carotenoids. *Journal of the Science of Food and Agriculture, 85*, 1166–1170.

Krinsky, N. I. (1993). Actions of carotenoids in biological systems. *Annual Review of Nutrition, 13*, 561–587.

Kushi, L. E., Lenart, E. B., & Willet, W. C. (1995). Health implications of Mediterranean diets in the light of contemporary knowledge. I. Plant foods and dairy products. *American Journal of Clinical Nutrition, 61*(Suppl. 6), 1407S–1415S.

Martínez-Valverde, I., Periago, M. J., Provan, G., & Chesson, A. (2002). Phenolic compounds, lycopene and antioxidant activity in commercial varieties of tomato (*Lycopersicon esculentum*). *Journal of the Science of Food and Agriculture, 82*, 323–330.

Miranda, C. L., Stevens, J. F., Ivanov, V., McCall, M., Frei, B., Deinzer, M. L., et al. (2000). Antioxidant and prooxidant actions of prenylated and nonprenylated chalcones and flavanones in vitro. *Journal of Agricultural and Food Chemistry, 48*, 3876–3884.

Montesano, D., Cossignani, L., D'Arco, G., Simonetti, M. S., & Damiani, P. (2006). Pure lycopene from tomato preserves extra virgin olive oil from natural oxidative events during storage. *JAOCS, 83*, 933–941.

Nguyen, M. L., & Schwartz, S. J. (1999). Lycopene: Chemical and biological properties. *Food Technology, 53*, 38–53.

Ramirez-Tortosa, M. C., Urbano, G., López-Jurado, M., Nestares, T., Gomez, M. C., Mir, A., et al. (1999). Extra-virgin olive oil increases the resistance of LDL to oxidation more than refined olive oil in free-living men with peripheral vascular disease. *Journal of Nutrition, 129*, 2177–2183.

Rodriguez-Amaya, D. B. (2001). *A guide to carotenoid analysis in foods*. Washington, DC: ILSI Press, pp. 1–64.

Sharma, S. K., & Le Maguer, M. (1996). Lycopene in tomatoes and tomato pulp fractions. *Italian Journal of Food Science, 8*, 107–113.

Shixian, Q., Dai, Y., Kakuda, Y., Shi, J., Mittal, G., Yeung, D., et al. (2005). Synergistic anti-oxidative effects of lycopene with other bioactive compounds. *Food Reviews International, 21*, 295–311.

Soto-Zamoraa, G., Yahia, E. M., Brecht, J. K., & Gardea, A. (2005). Effects of Postharvest hot air treatments on the quality and antioxidant levels in tomato fruit. *Lebensmittel-Wissenschaft und-Technologie, 38*, 657–663.

Stewart, A. J., Bozonnet, S., Mullen, W., Jenkins, G. I., Lean, M. E. J., & Crozier, A. (2000). Occurrence of flavonols in tomatoes and tomato-based products. *Journal of Agricultural and Food Chemistry, 48*, 2663–2669.

Suzuki, T., Usuki, R., & Kaneda, T. (1989). The role of carotenoids in the oxidative deterioration of edible oils. *Journal of Japan Oil Chemists' Society, 38*, 486–491.

Terao, J., Yamauchi, R., Murakami, H., & Matsushita, S. (1980). Inhibitory effects of tocopherols and β-carotene on singlet oxygen-initiated photooxidation of methyl linoleate and soybean oil. *Journal of Food Processing and Preservation, 4*, 79–93.

Toor, R. K., & Savage, G. P. (2005). Antioxidant activity in different fractions of tomatoes. *Food Research International, 38*, 487–494.

Waterman, P. G., & Mole, S. (1994). *Analysis of phenolics plant metabolites*. Oxford: Blackwell Scientific Publication, pp. 83–91.