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RESEARCH ARTICLE

Characteristics of the raw fruit, industrial pulp, and commercial jam elaborated with Spanish quince (*Cydonia oblonga* Miller)

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ABSTRACT

Quince fruit and two industrial derivates (pulp and jam) were characterized from physicochemical, nutritional and microbiological viewpoint. Quinces were collected at maturity (September) in Murcia (Spain). Quinces were converted at a processing factory in pulp (intermediate product) and, in the same factory, this pulp was transformed in jam. The pH, soluble solids, acidity, color, moisture, water activity, total phenolic compounds, antioxidant activity, vitamin C and flavonoids were measured for all samples, while for microbiological analysis was only used quince jam. There were significant differences among quince fruit, industrial pulp and commercial jam. Processing caused pH, moisture and water activity decrease, while soluble solids increase. Total phenolic compounds and antioxidant activity increased in the pulp and in the jam. The effect of cooking and storage was a decrease of vitamin C and flavonoids in the jam. Quince jam presented a total number of molds and yeasts lower than 2 log cfu/g. Although the production parameters affect to the quality of the quince jam, it is a sensory attractive food with healthy properties.

Keywords: Quince; Pulp; Jam; Industrial processing; *Cydonia oblonga*

INTRODUCTION

Persons are more and more conscius of the necessity to have a sufficient amount of vegetables in the diet, with the purpose of to obtain a complete intake of bioactive compounds, which will help to prevent several illnesses of the human organism and also to have a good health. The seasonal nature of the agricultural production of vegetables, the short life of the harvested vegetables in good conditions for human consumption and, sometimes, the impossibility of eating fresh vegetables, have developed the widespread use of processed vegetables (González-Hidalgo et al., 2019a,b).

Quince (*Cydonia oblonga* Miller) is considered a healthy fruit. Quince is recognized as a good, cheap and important dietary source of health-promoting compounds (Sut et al., 2019). The content of these compounds, beside the variety, may be affected by many factors, also climatic conditions, and the agrochemical composition of the soil (Bystrická et al., 2017). The bioactive phytochemicals present in the peel and pulp of the quince, such as flavonoids, phenolic acids, ascorbic acid and carotenoids, have received attention due to their high antioxidant potential (Baroni et al., 2018; Bystrická et al., 2017; Maghsoudlou et al., 2019; Mir et al., 2016), capable in preventing and treating pathologies. On the basis of these biologically active constituents, quince has antioxidant (Magalhaes et al., 2009), anti-influenza (Hamauzu et al., 2005), anti-inflammatory (Sharma et al., 2011), antimicrobial (Fattouch et al., 2007), anticancer (Carvalho et al., 2010; Pacifico et al., 2012), antidiabetic (Sharma et al., 2011) and antiulcerative (Hamauzu et al., 2006) properties.

It is not possible a direct consumption of fresh quince, due to its hardness and a very acidic taste combined with an astringency sensation in the mouth (Silva et al., 2002a). For that reason, quince is consumed processed as jam (Ferreira et al., 2004), jelly (Silva et al., 2002a), marmalade (de Almeida Lopes et al., 2018), juice (Yıkmış et al., 2019), nectar (Yilmaz and Karadeniz, 2014) and snack (Torres et al., 2019). Quince pomace, a processing

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by-product, has been used for pectin extraction (Brown et al., 2014). The factories for quince fruit processing are located in the countries where take place its cultivation. Industrially elaborated products from quince are also rich in those bioactive compounds, in the measure that those compounds survival processing conditions. The consumption of quince derived products is a via for the ingestion of antioxidants, among others (Silva et al., 2006).

There are only a few references concerning industrial samples, such as the work of Ramos and Ibarz (2006) on the viscoelastic behavior of quince processed pulp, and the work of Baroni et al. (2018) on the changes in antioxidant properties of quince fruit during jam production at industrial scale.

During raw quince processing, sodium benzoate as preservative can be added to the industrial pulp. If added, then quince derived products will contain sodium benzoate. Altough this preservative is allowed at a final concentration of a maximum of 750 ppm (Ferreira et al., 2004), from a marketing point of view, and also from food safety, it is much better the no presence of preservatives in the confections. But preservatives are necessaries for quince pulp conservation in barrels at room temperature for its industrial use throughout the year. This storage of the pulp until processing take place between a campaign (September-October) and next campaign one year later. In this sense, other reason to perform this research is to establish the basis for an industrial storage of the quince pulp without the use of preservatives.

Considering these previous ideas on quince and quince pulp, the aim of this research was to characterize quince fruit and its industrially derived products from physicochemical, nutritional and microbiological viewpoint. With this purpose, the changes of the characteristics of the quince fruit industrially processed, and the changes of the pulp and jam during their storage has been investigated, in a real situation of a Spanish quince processing factory.

MATERIALS AND METHODS

Plant material and industrial samples

Quince trees (*Cydonia oblonga* Miller) were cultivated in the province of Murcia, south-east Spain, 38º 2´ north and 2º 32´ east. The quinces (Fig. 1) were harvested at maturity in September 2018 and transported to the processing factory.

Quinces were directly processed or stored at 6.0±0.5 ºC for a few days until processing. The raw fruit was washed with water at room temperature, and sieved for the obtention of the fresh pulp, separated seeds and by-products. The pulp was cooked at 95.0±1.0 ºC for microorganismes elimination and enzymes inactivation, and cooled to room temperature. The cooked pulp can be used directly for quince products elaboration or stored until processing. Usually the cooked pulp is stored at ambient temperature in high density polyethylene barrels of 250 kg. In order to avoid microorganismes spoilage during the months of storage until pulp processing, sodium benzoate (E-211) at a final concentration in the pulp of 1000 ppm was added. There are two samples from the storage barrel, the pulp from the the internal (central) part and external (top) part of the storage barrel.

When the pulp is used for quince jam (Fig. 2) elaboration, an amount of the 80% of the pulp weight of sucrose is added. Then, the mix is cooked at 90.0±1.0 ºC until 66.0±0.5 ºBrix were reached, usually lasts 15-30 min. At this value of soluble solids, cooking is stoped and the quince jam is packed in different formats before to cool at room temperature. Usually, the formats are 800 g and 5000 g. The pack containing the quince jam is closed, cooled by air and sealed. The jam can be stored or shipped for its sale. Both pulp and jam storage were carried out at ambient temperature.

Fig 1. Quince (*Cydonia oblonga* Miller) fruits.

Fig 2. Quince jam.

pH and soluble solids

To determine the pH and the soluble solids of fresh quince, 100 g of sample were crushed with a Moulinex blender to obtain the juice. The pH of the juice, pulp and jam was measured with a pHmeter according to Ros et al. (2004). The soluble solids (ºBrix) were measured with an Atago N-1E refractometer according to Ros et al. (2004).

Titratable acidity

The titratable acidity was measured according to the method developed by Rodríguez-Guisado et al. (2009), with some changes. A sample of 2 g (quince juice, pulp or jam) was homogenized in Ultraturrax (Heidolph) with 8 ml of distilled water. The titratable acidity was determined by potenciometry with 0.1 M NaOH up to pH 8.1. Results were expressed as grams of anhidrous citric acid (ACA) per 100 g of sample.

Color

The color was measured using a hand held tristimulus reflectance colorimeter (Chromameter II CR-200, Minolta) according to González-Hidalgo et al. (2019b). The results were expressed as International Commission on Illumination (CIE) CIELab units: L* (lightness), a* (redness) and b* (yellowness). Triplicate readings were taken at room temperature in three different outer sections of each sample.

Moisture

The moisture was determined by dehydration in an oven according to Nielsen (2010). 5 g of sample was weighed (Pi). After a period of 24 h in the oven at 80°C, the final sample weight (Pf) was measured. The moisture was calculated as humidity (%) = (Pi - Pf / Pi) x 100

Water activity

Water activity was measured in a Novasina water activity meter at 25°C according to Kitic et al. (1986). 3 g of sample were placed in a plastic case and proceeded to read. The meter's settling time was until constant water activity was reached, among 5 to 10 minutes.

Total phenolic compounds

The total phenolic compounds (TPC) content was determined using the Folin-Ciocalteu reagent following the procedure described by Zhou et al. (2004). The reaction mixture contained 100 µl of extract, 500 µl of Folin-Ciocalteu reagent, and 1.5 ml of 20% sodium carbonate. The extract was obtained according to Zhou et al. (2004) by extraction of 1 g of sample with 10 ml of absolute ethanol. The final volume was brought up to 10 ml with pure water. After 2 h of reaction at ambient temperature, the absorbance at 765 nm was measured and used to calculate the total phenolic content, with gallic acid (Sigma-Aldrich) solutions as standard. Results were expressed as mg of gallic acid per 100 g.

Antioxidant activity

The antioxidant activity was determined by the method described by Benzie and Strain (1996) with some changes (González-Hidalgo et al., 2019b). 3 ml of FRAP reactive containing TPTZ (Sigma-Aldrich) was added to 300 µl of water and 100 µl of the extract. The sample was prepared by extraction with Ultraturrax of 1 g of sample in 2 ml of the acetate buffer and centrifugation at 14450 x g, using the supernatant. The unit used was µmol Fe^{2+} per 100 g.

Radical scavenging capacity

The determination of the antioxidant activity due to free radical scavenging capacity (DPPH) was carried out as described by Vega-Gálvez et al. (2009). Different dilutions of the extracts were prepared in triplicate. 2 ml of DPPH radical was added to 1 ml of the extract. The extract was obtained according to Turkmen et al. (2005) by extraction of 1 g of sample with 4.5 ml of 80% aqueous methanol. Total antioxidant capacity was expressed as the percentage inhibition of the DPPH radical. More details were published previously (González-Hidalgo et al., 2019b). Results were expressed as the half maximal Inhibitory Concentration (IC_{50}), the concentration required to obtain a 50% antioxidant capacity.

Vitamin C

Vitamin C was determined by the method of AOAC (2000) 967.21, titration with 2,6-dichlorophenolindophenol. 5 g of sample was mixed with 10 ml of a solution of metaphosphoric acid and acetic acid, being titrated with the 2,6-DCPIP solution until a stable pink color apeared. It is recorded the consumed volume for calculations using a calibration curve made by titration of ascorbic acid standard solutions. The results were expressed in mg of ascorbic acid per 100 g.

Total flavonoids

The total flavonoid (TF) content was determined according to Chang et al. (2002) and Lin and Tang (2007), with some changes. The extract was obtained according to Lin and Tang (2007), by extraction of 1 g of sample with 10 ml of methanol. This extract (0.5 ml) was mixed with 0.1 ml of 10% aluminium chloride hexahydrate, 0.1 ml de 1 M potassium acetate, and 2.8 ml of deionized water. After reaction at room temperature for 40 minutes, the absorbance was measured at 415 nm againt a deionized water reference, with quercetin (Sigma-Aldrich) solitions as standard. The results were expressed as miligram of quercetin per 100 g.

Microbiology

To establish a profile of the microbiological population of the quince jam, molds and yeasts were quantified. The

culture medium used was Dichloran Glycerol Agar (DG18), supplemented with glycerol. The medium was sterilized in autoclave at 121ºC for 20 minutes. Samples were analyzed in duplicate. From each sample, a portion of 10 g with sterile scissors and spoons was taken and then it was introduced in Stomacher pouches. 90 ml of buffered water pectona (BPW) were added to each bag and then proceeded with Stomacher homogenization, using two cycles of 90 seconds for shredding the samples, obtaining dilution 10^{-1}. From this dilution, successive dilutions were obtained putting into tubes containing 9 ml of BPW and 1 ml of previous dilution. The seeding process was carried out under laminar flow hood. For the analysis of mold and yeast, plates were incubated at 25°C for 5-7 days. After this, was carried out the manual recount of the plates, expressing the result as log cfu/g.

Statistical analysis

Results are presented as the mean±standard deviation. In order to establish the statistic significance of the results and make comparisons among them, some physicochemical data of the Tables 1 and 2 are also in the Table 3. The same occurs with the nutritional data (Tables 4-6). The analysis of the variance was used to compare the results obtained

Table 1: Physicochemical characteristics of some industrial derived products: pulp with added sodium benzoate and pulp without added sodium benzoate, both pulps being sampled at initial storage, and pulp with added sodium benzoate being sampled after four months of storage from the internal (central) part and external (top) part of the storage pulp barrel (mean±standard deviation)

		Quince pulp (initial)		Quince pulp with added sodium benzoate (4 months)	
		With added sodium benzoate	Without added sodium benzoate	Internal part	External part
pH		3.4±0.0^{a}	3.5±0.1^{a}	3.5±0.0^{a}	3.5±0.0^{a}
Soluble solids (ºBrix)		12.7±0.1^{c}	13.1±0.1^{b}	13.3±0.1^{a}	12.7±0.1^{c}
Total acidity (g ACA/100 g)		0.8±0.1^{b}	0.5±0.0^{c}	0.8±0.0^{b}	1.2±0.0^{a}
Color	L*	62.3±0.1^{b}	64.5±1.0^{a}	50.8±0.2^{c}	48.9±0.1^{d}
	a*	-1.0±0.3^{a}	-1.0±0.1^{a}	2.4±0.1^{b}	3.4±0.1^{c}
	b*	22.2±0.2^{b}	25.5±0.6^{a}	14.9±0.1^{c}	14.0±0.2^{d}
Moisture (%)		87.1±1.2^{a}	86.1±0.2^{a}	86.3±0,76^{a}	84.2±2.1^{b}
Water activity		0.98±0.00^{a}	0.98±0.00^{a}	0.98±0.01^{a}	0.98±0.01^{a}

Means in line with different letters (a, b, c, d) are significantly different ($p < 0.05$)

Table 2: Physicochemical characteristics of quince jam elaborated with pulp without added sodium benzoate at the initial and after four months of jam storage, for 800 g and 5000 g format of the quince jam bar (mean±standard deviation)

		Initial		After 4 months	
		800	5000	800	5000
pH		3.0±0.0^{a}	3.0±0.0^{a}	3.2±0.0^{a}	3.1±0.0^{a}
Soluble solids (ºBrix)		65.4±0.2^{c}	66.3±0.3^{b}	66.8±0.9^{a}	65.3±0.1^{c}
Total acidity (g ACA /100 g)		0.9±0.1^{a}	0.8±0.1^{a}	0.7±0.0^{b}	0.7±0.1^{b}
Color	L*	28.8±2.1^{a}	27.8±2.6^{a}	21.1±1.1^{b}	21.0±1.3^{b}
	a*	5.1±0.7^{a}	5.0±0.8^{ab}	4.5±0.4^{ab}	3.8±0.3^{b}
	b*	-1.9±0.3^{a}	-2.5±0.2^{b}	-2.1±0.4^{ab}	-2.0±0.2^{a}
Moisture (%)		37.5±0.9^{a}	36.1±0.8^{a}	30.9±1.6^{b}	32.5±1.6^{b}
Water activity		0.81±0.00^{a}	0.80±0.00^{a}	0.72±0.02^{b}	0.73±0.02^{b}

Means in line with different letters (a, b, c) are significantly different ($p < 0.05$)

Table 3: Physicochemical characteristics of fresh quince and some industrial derived products: pulp* without added sodium benzoate sampled at initial storage, pulp with added sodium benzoate after four months of storage, and quince jam from pulp without added sodium benzoate at the initial and after four months of storage (mean±standard deviation)

		Quince fruit (fresh)	Quince pulp without sodium benzoate* (initial)	Quince pulp with sodium benzoate (4 months)	Quince jam without sodium benzoate (initial)	Quince jam without sodium benzoate (4 months)
pH		3.4±0.1^{a}	3.4±0.0^{a}	3.5±0.0^{a}	3.0±0.0^{b}	3.1±0.0^{b}
Soluble solids (ºBrix)		13.4±0.4^{b}	12.9±0.1^{b}	13.0±0.1^{b}	65.8±0.3^{a}	66.1±0.3^{a}
Acidity (g ACA/100 g)		0.9±0.1^{ab}	0.7±0.0^{b}	1.0±0.0^{a}	0.9±0.0^{ab}	0.7±0.0^{b}
Colour	L*	78.4±1.6^{a}	63.4±0.5^{b}	49.8±0.1^{c}	28.3±2.3^{d}	21.1±1.2^{e}
	a*	-1.2±1.1^{c}	-0.5±0.2^{c}	2.9±0.1^{b}	5.0±0.7^{a}	5.2±0.4^{a}
	b*	28.3±2.9^{a}	23.8±0.4^{b}	14.4±0.1^{c}	-2.0±0.3^{d}	-2.2±0.3^{d}
Moisture (%)		84.4±1.1^{a}	86.6±0.7^{a}	85.2±1.8^{a}	36.8±0.8^{b}	31.7±1.6^{c}
Water activity		0.99±0.01^{a}	0.98±0.00^{a}	0.98±0.01^{a}	0.80±0.00^{b}	0.72±0.02^{c}

*The initial quince pulp with added sodium benzoate has very similar physicochemical characteristics to those of the initial pulp without added sodium benzoate.
Means in line with different letters (a, b, c, d, e) are significantly different ($p < 0.05$)

Table 4: Nutritional characteristics of fresh quince and some industrial derived products: pulp* without added sodium benzoate sampled at initial storage, pulp with added sodium benzoate after four months of storage, and quince jam from pulp without added sodium benzoate at the initial and after four months of storage (mean±standard deviation)

	Quince fruit (fresh)	Quince pulp without sodium benzoate (initial)*	Quince pulp with sodium benzoate (4 months)	Quince jam without sodium benzoate (initial)	Quince jam without sodium benzoate (4 months)
TPC (mg GA/100 g)	104.6±24.3^{c}	170.7±8.9^{a}	127.5±2.6^{bc}	131.7±11.9^{bc}	140.4±2.5^{b}
FRAP (μmol Fe^{+2}/100 g)	712±145^{c}	1379±44^{a}	1005±38^{b}	945±49^{b}	1357±33^{a}
DPPH (IC_{50})	11.3±2.3^{d}	12.6±0.3^{cd}	18.6±0.2^{b}	15.9±0.9^{bc}	25.4±0.6^{a}
Vit. C (mg AA/100 g)	26.0±2.0^{a}	7.3±0.1^{b}	4.1±0.1^{bc}	3.5±0.3^{bc}	2.2±0.2^{c}
TF (mg QE/ 100 g)	4.7±0.8^{c}	13.7±0.9^{b}	18.7±0.7^{a}	10.2±3.8^{b}	11.0±0.5^{b}

*The initial quince pulp with added sodium benzoate has very similar nutritional characteristics to those of the initial pulp without added sodium benzoate. Means in line with different letters (a, b, c, d) are significantly different ($p < 0.05$)

Table 5: Nutritional characteristics of some industrial quince derived products: pulp with added sodium benzoate and pulp without added sodium benzoate, both pulps being sampled at initial storage, and pulp with added sodium benzoate being sampled after four months of storage from the internal (central) part and external (top) part of the storage pulp barrel (mean±standard deviation)

	Quince pulp (initial)		Quince pulp with added sodium benzoate (4 months)	
	With added sodium benzoate	Without added sodium benzoate	Internal part	External part
TPC (mg GA/100 g)	164.4±10.8^{b}	177.0±7.1^{a}	130.9±2.3^{c}	124.1±2.8^{d}
FRAP (μmol Fe^{+2}/100 g)	1361±24^{a}	1397±65^{a}	1102±25^{b}	908±50^{c}
DPPH (IC_{50})	13.2±0.4^{c}	12.1±0.3^{d}	17.1±0.1^{b}	20.1±0.4^{a}
Vit. C (mg AA/100 g)	6.2±0.0^{b}	8.3±0.1^{a}	4.1±0.0^{c}	4.1±0.0^{c}
TF (mg QE/ 100 g)	15.8±0.5^{c}	11.7±1.3^{d}	17.8±0.6^{b}	19.5±0.8^{a}

Means in line with different letters (a, b, c, d) are significantly different ($p < 0.05$)

Table 6: Nutritional characteristics of quince jam elaborated with pulp without added sodium benzoate at the initial and after four months of jam storage, for 800 g and 5000 g format of the quince jam bar (mean±standard deviation)

	Initial		After 4 months	
	800	5000	800	5000
TPC (mg GA/100 g)	143.9±9.5^{b}	119.4±14.2^{d}	146.1±1.7^{a}	134.8±3.2^{c}
FRAP (μmol Fe^{+2}/100 g)	932±64^{b}	958±35^{b}	1330±24^{a}	1386±42^{a}
DPPH (IC_{50})	17.1±1.2^{ab}	14.7±0.7^{b}	25.1±0.7^{a}	25.7±0.6^{a}
Vit. C (mg AA/100 g)	3.5±0.6^{a}	3.5±0.5^{a}	2.4±0.4^{b}	2.0±0.1^{b}
TF (mg QE/ 100 g)	13.0±3.0^{a}	13.5±4.7^{a}	10.3±0.3^{b}	11.7±0.8^{b}

Means in line with different letters (a, b, c, d) are significantly different ($p < 0.05$)

among the quince and its derived products, and was also used to determinate the effects of content of sodium benzoate and pulp changes between the inner and outer part of the storage container. All extractions and measures were made at least in triplicate. The statistical model was a random design and the different industrial processes were considered as treatments. The effect of the treatments was determined using an ANOVA analysis. Scheffé's homogeneity means test ($p < 0.05$) was used. The statistical computer program used was Statistix 8 for Windows.

RESULTS AND DISCUSSION

pH and soluble solids

The Table 3 shows the mean values for pH and soluble solids of fresh quince and derived products. Quince, quince pulp (initial) and quince pulp with added sodium benzoate after four months of storage in a barrel show no significant differences in pH and soluble solids, while there were significant differences among quince fruit or quince pulp pH and soluble solids and quince jam pH and soluble solids.

The Table 1 shows the mean values for pH and soluble solids of the quince pulp at initial time, with and without added sodium benzoate, and also pulp with sodium benzoate from the barrel, after four months of storage. The results indicate that there were no significant differences in pH among quince pulp with added sodium benzoate and quince pulp without sodium benzoate, at initial conditions of availability and storage. After four months of storage in closed barrels, there were also no significant differences among the pH value of the pulp from the internal part and the external part of the barrel. Also, for these same samples, the soluble solids were similar.

The Table 2 shows the mean values for pH and soluble solids of the quince jam elaborated as 800 g and 5000 g formats and stored, being sampled at initial and after four

months of storage. There were similar pH values without statistic significant differences among 800 g and 5000 g formats in quince jam without sodium benzoate at both initial and after four months of storage. In the same samples, some minor statistic significant differences were found for the soluble solids.

Our value found for the pH (3.4) of quince fruit was a bit lower than the pH values (3.6-4.2) in fresh quinces from Brazil, depending of the cultivar (Leonel et al., 2016). Our values found for the pH were in the same range of those (3.5 and 2.8) reported by Roger et al. (2006) in quince fruit and jelly, respectively. Ramos and Ibarz (2006) reported a pH of 3.6 in an industrial sample of quince pulp. In our quince derived products, the pH decreased due to the industrial processing, such as also ocurrs in raspberry, strawberry, peach and prune puree obtention (Maceiras et al., 2007).

The soluble solids that we found in quince (13.4 ºBrix) were similar to those of Rodríguez-Guisado et al. (2009), who reported soluble solids among 11.5 and 14.7 ºBrix in five quince clones, also similar to the soluble solids (12.6-14.9 ºBrix) of fresh quinces from Brazil, depending of the cultivar (Leonel et al., 2016), and lower than the 14.2 ºBrix (Sharma et al., 2011) and the 15.4 ºBrix (Gheisari and Abhari, 2014), both in fresh quince. The main free sugars of quinces are fructose, sorbitol and glucose (Rodríguez-Guisado et al., 2009; Szychowski et al., 2014). Ramos and Ibarz (2006) reported a soluble solids value of 12.3 ºBrix for an industrial sample of quince pulp, which is similar to ours (12.9 º Brix). Torres et al. (2019) reported 14.4 ºBrix in quince puree. In our quince jam, soluble solids were similar to those (63-70 ºBrix) reported in Portuguese quince jams by Ferreira et al. (2004).

Titratable acidity

The Tables 3, 1 and 2 show the mean values of the titratable acidity in fresh quince and derived products. There were significant differences among quince, quince pulp (initial) and quince pulp with added sodium benzoate after four months of storage (Table 3). There were significant differences among quince pulp with added sodium benzoate and quince pulp without sodium benzoate and also among the quince pulp from both internal and external parts of the storage barrel (Table1). There were no significant differences among 800 g and 5000 g formats in quince jam without preservative, both initial and after four months of storage (Table 1).

The acidity (0.9 g ACA/100 g) value of our fresh quince is of the same order of magnitude (0.4-1.0) that fresh quinces from Brazil, depending of the cultivar (Leonel et al., 2016). All these values of acidity were lower than the 1.2 g ACA/100 g reported by Sharma et al. (2011) in fresh quince. Our industrial quince pulp has an acidity value of 0.7 g ACA/100 g, which is higher than the 0.4 g ACA/100 g reported by Ramos and Ibarz (2006) in industrial quince pulp. The organic acids of quinces are malic, tartaric, citric, ascorbic, quinic, shikimic, fumaric, oxalic, succinic and phytic acid (Silva et al., 2002b; Ferreira et al., 2004; Rodríguez-Guisado et al., 2009; Szychowski et al., 2014).

Color

The color differences of quince jam in relation to the fresh fruit and to quince pulp appear in the Tables 3, 1 and 2.

Color parameter lightness (L*). Parameter lightness values decreased from quince fruit (78.4) and pulp (63.4) to quince jam (21.1, 4 months) (Table 3). Leonel et al. (2016) reported values of parameter lightness in fresh quince from Brazil among 74.5 and 80.1, depending of the cultivar, being these values of the same order of magnitude than ours, indicating no differences in luminosity. Quince pulp darkened with temperature and time as pineapple puree during thermal processing (Chutintrasri and Noomhorm, 2005). Parameter lightness also decreased due to storage at room temperature of quince pulp and jam (Tables 1 and 2). There were significant differences among the lightness of quince pulp with added sodium benzoate and without sodium benzoate, and among both internal and external part of the barrel pulp (Table 1), due to water loss and browning during storage. There were no significant differences among the lightness of the 800 g and 5000 g formats in quince jam without sodium benzoate, both at initial and after four months of storage (Table 2).

Color parameter redness (a*). The Table 3 provides the redness (-1.2) value of fresh quince, which is of the same order of magnitude that the parameter redness values ((-0.9)-(-1.8)) in fresh quinces from Brazil, depending of the cultivar (Leonel et al., 2016), indicating no differences in the red-green axis. The Table 3 shows an increase in redness values during heat treatment and storage, from quince fruit to jam, which is in agreement with Garza et al. (1999) on non-enzymatic browning in peach puree during heating, and with Chutintrasri and Noomhorm (2005) on color degradation of pineapple puree during thermal processing. There were no significant differences (Table 1) among quince pulp with added sodium benzoate and without sodium benzoate, while there were significant differences among both internal and external part of the barrel, due to water loss and browning during storage. There were significant differences (Table 1) among 800 g and 5000 g formats in quince jam without sodium benzoate, both formats at initial and after four months of storage.

Color parameter yellowness (b*). The Table 3 provides the yellowness (28.3) value of fresh quince, which is a bit

lower than the parameter yellowness values (28.8-35.1) in fresh quinces from Brazil, depending of the cultivar (Leonel et al., 2016), indicating small differences in the yellow-blue axis. The parameter yellowness decreased (Table 1) from quince fruit to jam (4 months) with statistic significant differences among all the samples, due to the heat treatment and storage time, which is in agreement with Chutintrasri and Noomhorm (2005), as mentioned before. The Table 1 shows that among quince pulp with added sodium benzoate and quince pulp without sodium benzoate there were significant differences, and that the parameter yellowness of the quince pulp from the external part of the barrel was lower than the internal part of the barrel. There were significant differences among quince jam of 800 g and 5000 g formats, or among these quince jams after four months of storage (Table 2).

Moisture and water activity

The Tables 3, 1 and 2 show the mean values for moisture and water activity of fresh quince and derived products. The Table 1 provides the moisture (84.4%) value of fresh quince, which is a bit higher than the moisture values (76.5-84.0) in fresh quinces from Brazil, depending of the cultivar (Leonel et al., 2016). Sharma et al. (2011), Gheisari and Abhari (2014) and de Almeida Lopes et al. (2018) reported a moisture content of 85%, 79% and 81% in fresh quince, respectively, being our result (84.4%) of the same order of magnitude, even higher, to those.

There were no significant differences among quince fruit and quince pulp after four months of storage, for moisture and for water activity (Table 3). The values of these two parameters were significantly decreased when quince pulp is transformed in quince jam, as shown in the Tables 3, 1 and 2. This result is in agreement with Shin et al. (2007), who described the effect of thermal treatments on the moisture content of strawberry, and with Igual et al. (2010), who reported on non-conventional techniques to obtain grapefruit jam.

There were no significant differences in moisture and water activity values among the quince pulp with added sodium benzoate and without sodium benzoate, the quince pulp from the internal part and external part of the storage barrel, quince jam in 800 g and 5000 g formats and among quince jam, the two formats, after four months of storage (Tables 3, 1 and 2).

The water activity (0.98) in quince pulp is the same to that reported by Ramos and Ibarz (2006). The water activity (0.8-0.7) in quince jam is the same to that reported in grapefruit and kiwifruit jams (Igual et al., 2010; García-Martínez et al., 2002).

Total phenolic compounds

The Tables 4, 5 and 6 show the mean values for total phenolic compounds of fresh quince and derived products. Total phenolics in quince fruit were 104.6 mg galic acid 100 g^{-1} of quince (Table 4), which is higher than the 41-98 mg 100 g^{-1} reported in sub-Hymalaya quinces (Mir et al., 2015a), and the 66-104 mg 100 g^{-1} reported in Slovak quinces (Bystrická et al., 2017). Phenolic compounds increase in the quince pulp (170.7 mg 100 g-1, Table 4). The sieving of the quince fruit, which has an effect of partial cell-wall breaking, and the cooking of the obtained pulp, which break more the cell-walls and the cell membranes, facilitates the extraction effectiveness of phenolic compounds during their analysis. The same extraction applied to quince fruit, which has a more structured cell-wall material, yields a lower phenolic compounds content. In quince jam (131.7 mg 100 g^{-1}), total phenolic increased (consider the sugar addition) due to pulp cooking (Silva et al., 2004a; Mir et al., 2016; Baroni et al., 2018) and storage (Shin et al., 2007). Processed products of quince have higher total phenolic content as compared to fresh pulp (Mir et al., 2016).

The Table 5 shows that there were no significant differences among quince pulp with added sodium benzoate and quince pulp without sodium benzoate, unlike the quince pulp from the internal part and external part of the storage barrel, being phenolics from the internal part higher than those from the external part, due to not being in contact with the air. There were no significant differences among the phenolics of the 800 g and 5000 g formats in quince jam without preservative, both formats at initial and after four months of storage (Table 6). The main phenolic compounds in quince are 3-O-, 4-O-, and 5-O-caffeoylquinic acids and 3,5-O-dicaffeoylquinic acid (Silva et al. 2002a, 2005; Karar et al., 2014; Baroni et al., 2018). Sut et al. (2019) add 4-caffeoylshikimic acid. The most abundant was 5-O-caffeoylquinic acid with 26–48 mg 100 g^{-1} in peel and 10–22 mg 100 g^{-1} in quince pulp (Stojanović et al., 2017).

Antioxidant activity

FRAP. The Tables 4, 5 and 6 show the mean values for the FRAP assay of fresh quince and derived products. FRAP values increase with the process of quince, due to the increased extraction effectiveness by the crushing of the fruit. Quince pulp (initial) FRAP values were higher than quince pulp (4 months) and these were higher than quince jam too, due to the storage and the thermal treatment. There were no significant differences among quince pulp with added sodium benzoate and without sodium benzoate, unlike the quince pulp from the internal and external part of the storage barrel. The FRAP values from the internal part were higher than these from the external part, due to not being in contact with the air (Table 5). There

were no significant differences among 800 g and 5000 g formats in quince jam without sodium benzoate, both at initial and after four months of storage (Table 5). The chlorogenic acids and the flavonols of quince exhibited more antioxidant capacity than the positive standards α-tocopherol and ascorbic acid (Fiorentino et al., 2008).

DPPH. Table 4 shows the concentrations required to scavenge DPPH as IC_{50} scavenging values, which increase from quince fruit to jam, in agreement with Silva et al. (2004b). The pulp with added sodium benzoate shows a higher value of IC_{50} than the pulp without sodium benzoate, due to the effects of the presence of sodium benzoate. The trend of DPPH with the processing is similar to that reported by Mir et al. (2015b, 2016), when comparing fresh quince with jam, jelly and candy, concluding that processed products have higher antioxidant properties than fresh pulp. There were significant differences among the IC_{50} of the pulp from the internal and external part of the storage barrel (Table 5). There were no significant differences among the 800 g and 5000 g formats in quince jam without preservative, both at initial and after four months of storage (Table 6). The antioxidant activities cannot only be attributed to their phenolic and/or organic acid contents, also to the result of the action of different compounds present in quince and jam, and to possible synergic and antagonist effects (Silva et al., 2004b). The IC_{50} values of quince pulp, peel, and jam phenolic extracts were strongly correlated with caffeoylquinic acids and total phenolics contents (Silva et al., 2004b). The chlorogenic acids and the flavonols exhibited more radical scavenger capacity than the positive standards α-tocopherol and ascorbic acid (Fiorentino et al., 2008).

Vitamin C

The Tables 4, 5 and 6 show the mean values of the vitamin C of fresh quince and derived products. The content of vitamin C in our quince was 26 mg 100 g^{-1}, with a variation in the range 20-32 mg ascorbic acid 100 g^{-1}. This result is in agreement with the 6-26 mg 100 g^{-1} reported by Wojdyło et al. (2013), although there are cultivars very rich (79 mg 100 g^{-1}) in vitamin C (Rop et al., 2011), and others with a lower (15 mg 100 g^{-1}) content (Gheisari and Abhari, 2014; de Almeida Lopes et al., 2018) and 17 mg 100 g^{-1} (Sharma et al., 2011). Bystrická et al. (2017) reported an ascorbic acid content in the range from 15 to 22 mg 100 g^{-1} in Slovak cultivars of quince. This content for quince is similar to citrus fruits: orange 25-80, mandarin 30-50, grapefruit 25-60 and lemon 30-70 mg 100 ml^{-1} (Ros et al., 2004), raspberry 25, strawberry 55, prune 5 and peach 7 (Maceiras et al., 2007). The effect of cooking and storage is shown in the Table 4, since it is observed that vitamin C content is lower in jam than in fresh fruit, in agreement with Maceiras et al. (2007) and Shin et al. (2007). Vitamin C content of pulp without sodium benzoate was higher than quince pulp with added sodium benzoate, having this difference statistic significance, while there were no significant differences among the internal and the external part of the storage barrel (Table 5). There were no significant differences between 800 g and 5000 g formats in jam without added sodium benzoate, both at initial and after four months of storage (Table 6). Our values of vitamin C in fresh quince are acceptable for edible quince (15 mg 100 g^{-1}), according to the Food Data Central (ARS-USDA, 2020). Considering that the Daily Recommended Intake of vitamin C is among 70 and 90 mg for an adult, an intake of 100 g of quince jam contributes to 5% of the Daily Recommended Intake.

Total flavonoids

The Tables 4, 5 and 6 show the mean values of the total flavonoids of fresh quince and derived products. Total flavonoid (Table 4) in quince is lower than in other fruits, as described by Lin and Tang (2007), due to the fact that the total of phenolic compounds and flavonoids in fruit and vegetables varied considerably. After four months of storage, total flavonoids (Table 4) increased in pulp and jam, which confirmed the findings of Rodrígez-Guisado et al. (2009). The application of heat treatment on quince pulp caused a significant reduction in the content (Table 4) of total flavonoids in quince jam, in agreement with Igual et al. (2011) and Cilla et al. (2018). The content of flavonoids in pulp with added sodium benzoate was significantly higher than in pulp without sodium benzoate (Table 5). Total flavonoids in the internal part of the storage barrel were lower than in the external part. We have no logical explanation of this result. It is concluded that flavonoids present in quince are not stable during the storage (Table 5). There were no significant differences among 800 g and 5000 g formats in jam without sodium benzoate, both at initial and after four months of storage (Table 6). The main flavonoids in quince are quercetin 3-galactoside, rutin, quercetin-3-glucoside, kaempferol glycoside, kaempferol 3-glucoside, kaempferol 3-rutinoside, quercetin glycosides acylated with p-coumaric acid, and kaempferol glycosides acylated with p-coumaric acid (Silva et al., 2002a, 2005; Stojanović et al., 2017; Baroni et al., 2018). Sut et al. (2019) add quercetin-3,7-diglucoside, kaempferol-3-*O*-rhamnoside and kaempferol-7-*O*-glucoside.

Microbiology

Quince jams presented an intermediate humidity (36%) and a water activity relatively high (0.80) (Table 2) and could be vulnerable to some microbial alterations. However, jams will be safe from development of the majority of bacteria, since their water activity is lower than 0.86 (El-Gerssifi, 1998). Due to the low pH values of quince fruit (3.4), the main typical flora consists of moulds and yeasts. Microbiological analyses revelated that quince jam without preservative samples presented a total number of molds

and yeasts lower than 2 log cfu/g. Ferreira et al. (2004) performed microbiological analyses of molds and yeast of eighteen brands of quince jam randomly purchased from the retail market. These analyses revealed that four quince jam samples presented a total number of molds and yeast higher than 3 log cfu/g. Further, crude extract of quince fruit polyphenols showed antibacterial activity against the Gram-negative bacterium *Escherichia coli* (Karar et al., 2014).

CONCLUSIONS

Quince characteristics changed as a consequence of the heat treatment and sugar addition, during fruit processing for industrial pulp and commercial jam elaboration. Quince jam had a lower amount of vitamin C and a higher total phenolic compounds content, antioxidant activity and total flavonoid content than quince fruit. There was no effect of the sodium benzoate in any parameters except, total flavonoids, which were higher in pulp with sodium benzoate. During quince pulp storage, color, moisture, total phenolic compounds, antioxidant activity and vitamin C decreased. The characteristics of quince jams are more dependent of the raw materials and on the production parameters, than of added food preservatives. During quince jam storage, moisture, water activity and vitamin C decreased, and total phenolic compounds content and antioxidant activity increased. On the basis of their characteristics, quince and quince jam are healthy food. Future research will be focused in actions to avoid the use of sodium benzoate for industrial quince pulp conservation and, as a consequence, the presence of sodium benzoate in the commercial quince jam.

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Authors' contributions

This manuscript contains the main results of Esther Vidal Cascales's master thesis. This master thesis was carried out by Esther at the University of Murcia (Spain), under the direction of Dr. José María Ros García, who design the research. Esther carried out the work at laboratory and industrial level taking samples, making the physicochemical, nutritional and microbiological analysis and also the statistic analysis of the data. Finally, the manuscript has been prepared by Esther and José María.

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