International Food Research Journal 23(2): 816-821 (2016)
Journal homepage: *http://www.ifrj.upm.edu.my*

Comparative evaluation of the proximate composition and antioxidant properties of processed products of quince (*Cydonia oblonga* Miller)

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Article history

Received: 28 November 2014
Received in revised form: 7 August 2015
Accepted: 13 August 2015

Keywords

Cydonia oblonga Miller
Quince
Health benefits
Processed products
Antioxidants

Abstract

Quince (*Cydonia oblonga* Miller) was processed into different products (candy, jam and dehydrated slices) and these were evaluated for their proximate composition and antioxidant properties. Total phenolics, reducing power, H_2O_2 value, FRAP and DPPH of the processed products of quince fruit varied significantly and were found in the range of 69.12-78.67 mg GAE/100g, 70.9-89.5%, 36.02-51.20%, 1.40-1.68 µM and 79.91-82.61% respectively. The present study revealed that processed products of quince have higher total phenolic content and antioxidant properties as compared to fresh pulp.

Introduction

Quince (*Cydonia oblonga* Miller) is a simple pome fruit which belongs to family Rosaceae. It is a small tree or a shrub which is native of Turkey and Iran. Quince is like a pear or apple shaped golden yellow fruit with leathery skin and is not consumed fresh because of its astringency, strong acidity and hard flesh (presence of stone cells). On ripening the hairs on the peel disappear and this stage is highly demanded for processing it into candy, jam, jelly, marmalade and cakes (Silva *et al.*, 2005). In India it is mostly grown in Kashmir valley, where it is known as bamchount. (Mir *et al*., 2015)

Quince is considered as a rich source of functional compounds like dietary fibre, pectin, polysaccharides, phenolic acids and flavonoids (Oliveira *et al.*, 2007), which are potent antioxidants. The phytochemical composition of quince has been extensively investigated. It contains considerable amounts of hydroxycinnamic derivatives mainly characterized by 3-caffeoylquinic and 5-caffeoylquinic acids as well as polymeric procyanidins (Fiorentino *et al*., 2008). The pulp is characterized by 3-O- and 5-O-caffeoylquinic acids, 3, 5-O-dicaffeoylquinic acid and rutin. Caffeoylquinic acids are the major phenolic compounds (99%), the most abundant being 5-O-caffeoylquinic acid (57%). However, in the earlier studies, 4-O-caffeoylquinic acid has also been found in quince pulp (Silva *et al.*, 2005), although in small amounts only. In addition to caffeoylquinic acids, several kaempferol and quercetin glycosides have also been found in peel extracts. Quince is also enriched with minerals like calcium, potassium and phosphorus (Gora, 1979; Mukhamedova, 1979).

Quince fruit is recognized as an important dietary source of health promoting compounds, due to its antioxidant, antimicrobial and antiulcerative properties (Fiorentino *et al.*, 2008). Due to presence of different functional compounds and phytochemicals the fruit has received increasing attention for its role in the prevention and treatment of human diseases (Oliveira *et al*., 2009). The medicinal value of these plants is related to their phytochemical components which produce definite physiological actions on human body (Mushtaq and Wani, 2013). The consumption of quince has been practised long ago, as it was commonly recognized that there is a positive relationship between a diet rich in plant foods and reduced incidence of the degenerative diseases (Gibney *et al.*, 2009).

Quince has not been explored well for its use as a fresh fruit because of its poor sensory attributes. As an attempt in the path of food security, to increase the use of quince fruit in the form of different processed food products due to the presence of the various above described compounds and their health benefit in quince, the fruit pulp and its processed

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products (pulp, candy, jam and dehydrated slices) were evaluated for their comparative antioxidant properties and proximate composition.

Materials and Methods

Materials

The fruits were collected from Sheri Kashmir University of Agriculture Science and Technology (SKUAST) Kashmir and care was taken to select the fruits with uniform ripening and maturity.

Chemicals and reagents

All the chemicals, solvents and reagents used for assessing the antioxidant screening were purchased from Sigma-Aldrich Chemie (Buchs, Switzerland), Himedia India.

Preparation of processed products

Extraction of the pulp was done by the hot break process. The fresh pulp so obtained was stored at -18°C for further analysis. A portion of the fresh pulp was used for the preparation of jam as per the FPO specifications. For the preparation of candy, the quince fruits were cut into pieces, boiled in a large pan, to which sugar was added at regular intervals in order to achieve the total solids up to 65°B. Finally, the fruit pieces were dried by the tunnel drying process to the desired moisture content. For dehydration, quince was sliced to uniform thickness and was dried by the tunnel drying process.

Sensory evaluation

Nine point hedonic scale method was followed for the sensory evaluation of the quince Jam, candy and dehydrated slices.

Proximate analysis

Moisture content of the fresh fruit and its processed products was determined by digital moisture analyzer (Sartorius-MA100). Crude fat was estimated by Soxhlet extraction method. Total soluble solid (TSS) was determined by using a hand refractometer. Ascorbic acid content, titrable acidity, ash content Protein content was determined by the standard Kjeldahl procedure of the AOAC (2000). The quantification of reducing and total sugars in the samples was carried out using Lane & Eynon method (AOAC, 2000).

Antioxidant activity

Extraction

Methanolic extracts of the processed products of quince for antioxidant activity and total phenolic content were prepared according to the method of Swain and Hillis (1959), with minor modifications. 2 g of each sample were mixed with 8 mL methanol and homogenized. The homogenates were incubated at 4°C for 12 h and then centrifuged at 15,000 rpm using a cooling centrifuge (Eppendorf, 5810R). The supernatants were recovered and stored at -18°C for analysis.

Determination of total phenolic content

Total phenols were determined using the Folin-Ciocalteu reagent assay according to the method of Singleton *et al.* (1999). 2.5 mL of Folin-Ciocalteau reagent was added to 100 µL of the double diluted methanolic extracts of processed products. 2 mL of 2% sodium carbonate was added to this solution after 4 minutes. The samples were then incubated in the incubator at 30°C for about 2 hours. The absorbance was taken at 760 nm against a blank (Methanol). The results were expressed as mg gallic acid equivalents per 100 g sample (mg GAE /100 g) using a gallic acid (0-0.1 mg/mL) standard curve.

Determination of 2, 2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging activity

The method of Brand-Williams *et al.* (1995) was adopted for measuring the DPPH radical scavenging ability of methanolic extracts obtained from the various processed products. The methanolic extracts of all samples were dissolved in 1.0 mL of 0.1mM DPPH methanol solution at room temperature. After 30 min of incubation the absorption at 515 nm was measured by a spectrophotometer (Hitachi, U-2900) with reference to a blank (Methanol). The results were expressed as percentage inhibition by using the equation

$$\% \text{ inhibition} = (A_0 - A_s/A_0) \times 100$$

A_0 is the absorbance of the control
A_s is the absorbance of the sample

Determination of reducing power

For determination of reducing power, the method described by Oktay *et al.* (2003) with minor modifications was followed. Methanolic extracts of different processed products were dissolved in 2.5 mL of 0.2 M phosphate buffer solution (pH 6.6). After adding 2.5 mL of 10% potassium ferricyanide, the mixture was incubated at 50°C for 20 minute. 2.5 mL of 10% tricholoro acetic acid (w/v) was added to the solution and centrifuged at 3000 rpm for 10 minutes. Then 2.5 mL of the supernatant was diluted

with 2.5 mL of distilled water and 0.5 mL of 0.1% $FeCl_3$ solution was added to it. The absorbance was measured at 700 nm against a blank (methanol). The increase in absorbance of the reaction mixture indicates increase in reducing power. The percentage reduction was calculated by

$$\% \text{ reduction} = (A_{(test)} / A_{(blank)} - 1) \times 100$$

A_{test} = absorbance of the sample
A_{blank} = absorbance of the control

Determination of the FRAP (Ferric reducing antioxidant power)

The antioxidant capacity of processed products was estimated according to the procedure described by Benzie and Strain (1996) modified by Pulido *et al.* (2000). Fe (III) reduction is often used as an indicator of electron donating activity which is an important mechanism of phenolic antioxidants action.

$$Fe(TPTZ)_2(III) + ArOH \rightarrow Fe(TPTZ)_2(II) + ArOH^{+-} \quad (1)$$

The FRAP assay is based on the ability of the antioxidants to reduce Fe^{3+} to Fe^{2+} in the TPTZ solvent, resulting an intense blue Fe^{2+}-TPTZ complex with an absorption maximum at 593 nm. The mechanism behind the chemical reaction of the FRAP method involves a single electron transfer between Fe (TPTZ) 2 (III) and a single electron donor ArOH.

The FRAP reagent was prepared by mixing 10 mL of 300 mM acetate buffer (pH 3.6), 1 mL of 10 mM TPTZ in 40 mM hydrochloric solution and 1 mL of 20 mM $FeCl_3$ solution. The FRAP reagent was incubated for 10 min at 37^{0}C immediately after its preparation. 3 mL of the reagent was added to 0.1 mL of the sample extracts and the reaction mixture was incubated for 4 min at room temperature before the absorbance was taken at 593 nm against a blank reagent. The results were expressed as µM FRAP/g, which was calculated by

FRAP (µM) = (Change in absorbance of sample from 0 to 4 min / Change in absorbance of standard from 0 to 4 min) × FRAP value of standard.

Estimation of H_2O_2 scavenging activity

The H_2O_2 scavenging activity was determined according to the method of Pick and Keisari (1980). The antioxidant property of the antioxidants was optimized against 3.5 mM H_2O_2 at 20 and 50 mg/mL of the extracts in phosphate buffer (pH 7.4) and absorbance was taken at 230 nm at specific time intervals against a blank reagent. The percentage of scavenging of H_2O_2 against antioxidant was calculated as follows

H_2O_2 value = $[(A_0 - A_1)/ A_0] \times 100$
A_0 = absorbance of control
A_1 = absorbance of the sample.

Statistical analysis

The data was analyzed statistically for interpretations of results using analysis of variance technique for CRD factorial (Gomez and Gomez, 1984).

Results and Discussion

Sensory evaluation

Sensory scores of the processed quince products are given in Table 1. The score of the jam for color (7.13), taste (6.98) and texture (6.95) were found to be satisfactory for its overall acceptability (7.02). The candy in terms of its color (7.99), taste (7.32), texture (7.21) and overall acceptability (7.50) was ranked well. For dehydrated slices scores for color (6.89), taste (6.81), texture (6.11) and overall acceptability (6.60) were found to be appreciable. All the products developed and evaluated were satisfactory.

Table 1. Sensory evaluation of the processed quince products

Sample	Color	Taste	Texture	Overall Acceptability
Jam	7.13 ± 0.09^a	6.98 ± 0.19^a	6.95 ± 0.17^b	7.02 ± 0.15^{ab}
Candy	7.99 ± 0.13^b	7.32 ± 0.15^a	7.21 ± 0.14^b	7.50 ± 0.31^{bc}
Dehydrated Slices	6.89 ± 0.13^a	6.81 ± 0.11^a	6.11 ± 0.11^a	6.60 ± 0.42^a

Proximate composition

The proximate composition of the fresh quince pulp and its processed products has been presented in Table 2. A significant difference was observed in the moisture, TSS, titrable acidity, ascorbic acid, total sugar, reducing sugar, protein, fat and ash content of the processed products and in the fresh pulp. The moisture content of the fresh pulp, candy, jam and dehydrated slices varied as 84.10%, 18.00%, 27.62% and 11.98%, respectively. The TSS recorded in fresh pulp, candy, jam and dehydrated slices was 14.10°B, 70.00°B, 69.35°B and 85.40°B, respectively. Titrable acidity recorded in fresh pulp and other products was as 1.18% in the fresh pulp, 1.51% in candy, 0.68% in jam and 1.39% in dehydrated slices. Ascorbic acid content observed was (15.32 mg/100 ml) in the fresh pulp, (11.78 mg/100 ml) in the candy, (11.05 mg/100 ml) in the jam and (10.13 mg/100 ml) in the dehydrated slices. Total sugar content varied as

Table 2. Proximate composition of quince & its processed products

Sample	Moisture (%)	TSS (°B)	Titrable acidity (%)	Ascorbic acid	Total Sugars (%)	Reducing sugars (%)	Protein (%)	Fat (%)	Ash (%)
Pulp	84.10±0.19^{d}	14.10±0.16^{a}	1.18±0.13^{c}	15.32±0.19^{d}	8.13±0.23^{a}	5.04±0.13^{a}	0.47±0.02^{a}	0.21±0.02^{c}	0.53±0.12^{c}
Candy	18.00±0.17^{b}	70.00±0.19^{b}	1.51±0.13^{a}	11.78±0.19^{c}	46.09±0.31^{c}	26.43±0.14^{c}	2.22±0.03^{a}	0.33±0.01^{a}	2.01±0.14^{b}
Jam	27.62±0.17^{c}	69.35±0.17^{c}	0.68±0.14^{b}	11.05±0.14^{b}	46.95±0.18^{d}	27.88±0.31^{d}	2.36±0.03^{b}	0.97±0.01^{a}	1.80±0.16^{b}
Dehydrated slices	11.98±0.17^{a}	85.40±0.17^{d}	1.39±0.12^{b}	10.13±0.15^{a}	26.83±0.28^{b}	21.50±0.20^{b}	3.47±0.03^{b}	1.16±0.07^{b}	2.34±0.13^{a}

Means in the rows with different superscripts are significantly ($p \leq 0.05$) different.

8.13%, 46.09%, 46.95% and 26.83% in the fresh pulp, candy, jam and dehydrated slices, respectively. Similar results for total sugars and reducing sugars were reported by Dar *et al.* (2011). The Reducing sugar content was observed to be 5.04% in fresh pulp, 26.43% in candy, 27.88% in the jam and 21.50% in dehydrated slices. A very small percentage of crude protein and fats was seen in the fresh pulp and the processed products. The fresh quince pulp showed protein content of 0.47%, 2.22% in the candy, 2.36% jam while its percentage was 3.47% in the dehydrated slices. The fat content of the fresh quince pulp was 0.21 %, 0.33% in candy, 0.97% in jam and 1.16% in dehydrated slices fat. The ash content in the fresh quince pulp was (0.53%), ash content of the candy was seen (2.01%), while (1.80%) ash content was seen in the jam and (2.34%).in dehydrated slices.

Total phenolics

Total phenolics of the various processed quince products have been presented in Figure 1. Among the processed products of quince, the dehydrated slices showed the highest total phenolics (78.67 mg GAE/100g), while as the lowest total phenolics were recorded in the candy (69.12 mg GAE/100g), which varied non-significantly with the fruit pulp (67.44 GAE/100g). The total phenolics in the quince jam were found to be 73.41 mg GAE/100g. The total phenolics varied significantly among the different products of quince fruit and were observed to increase in the processed products as compared to the fresh pulp which might be due to leaching of the bound phenolic compounds. Previous reports on fruits and vegetables indicated that thermal processing increased antioxidant potential due to formation of novel compounds such as Maillard reaction products (MRPs) having antioxidant activity (Nicoli *et al.*, 1997; Manzocco *et al.*, 2001). The more value of

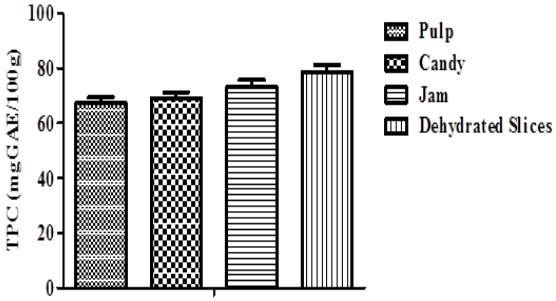

Figure 1.Total Phenolic content of different products of quince

total phenolics for the dehydrated slices as compared to candy and jam is probably due to high convective forces acting at the air-solid interface. The glycosides of phenolics, being localised in hydrophilic regions of cell such as vacuoles and apoplasts, or as other soluble phenols in the cytoplasm and in the cell nuclei (Sakihama *et al.*, 2002), seemed to get a protective heat shield by the cell wall material. It is important to note that the rate of increase in phenolic contents primarily depends on the type of samples and the preparation procedure used. However, data on the effects of drying on total phenolics and antioxidant activity of fruits are rather conflicting due to several factors, such as the drying method, the type of extraction solvent, the antioxidant assays and the interactions of several antioxidant reactions (Manzocco *et al.*, 2001).

DPPH radical scavenging activity

The DPPH radical scavenging activity of the various processed quince products is presented in Figure 2. An insignificant difference in the DPPH radical scavenging activity among the various processed products of quince fruit was observed in the analysis. The highest DDPH radical scavenging

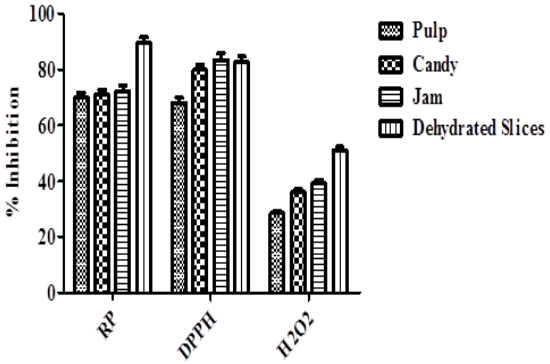

Figure 2. Reducing power (RP), DPPH and H_2O_2 scavenging activities of quince products

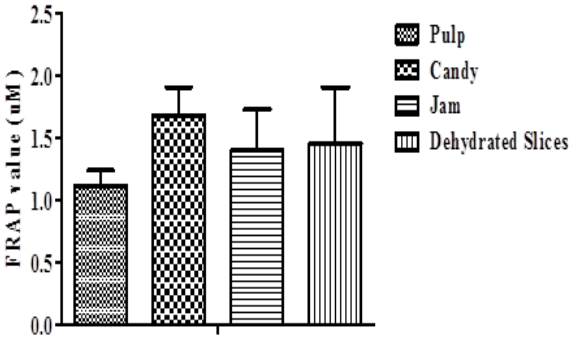

Figure 3. FRAP value of quince products

activity was recorded in quince jam (83.56%), which varied non-significantly with the dehydrated slices (82.61%) and the candy (79.91%). The DPPH radical scavenging activity of the processed quince products was seen to increase significantly as compared to the fresh pulp. The release of various bound phenolics during processing are supposed to be responsible for enhanced DPPH activity in the processed products. It has been reported in the past as well that processing causes either no change to antioxidant potential of quince fruit or enhances it due to the improvement of antioxidant properties of the naturally occurring compounds or by the formation of novel compounds like the Maillard reaction products that have antioxidant potential (Manzocco *et al*., 2001).

Reducing power

The reduction of Fe^{3+} to Fe^{2+} measured as the comparative reducing power showed a significant difference among the different processed products of the quince fruit. It has been shown that the reducing power is related with antioxidant activity and may give a significant indication of the antioxidant activity (Oktay *et al*., 2003). The reducing power of the processed quince products have been presented in Figure 2. The highest reducing power was seen in the dehydrated slices (89.5%) that varied significantly with the candy (70.9%) and jam (72.2%). Among the processed quince products, only the dehydrated slices showed a significant difference in the reducing power as compared to the fresh pulp. The concentration of different phenolic compounds and formation of new compounds during processing might be responsible for enhanced reducing power in case of different processed products.

Determination of H_2O_2 scavenging activity

The H_2O_2 scavenging activity values obtained for the different processed products of the quince fruit are presented in Figure 2. Among the different processed products of the fruit, highesH_2O_2 scavenging activity was observed in the dehydrated slice (51.20%) and lowest in the candy (36.02%) that varied non-significantly with the quince jam (39.13%). The H_2O_2 scavenging activity of the different processed products was significantly higher than the fresh pulp, which may be attributed to combined effects of the Maillard reaction products. Yen and Hsieh (1995) reported that Maillard reaction products have dose dependent scavenging activity on hydroxyl radical, which might be attributed to the combined effects of reducing power, donation of hydrogen atoms and scavenging of active oxygen.

Ferric reducing antioxidant power (FRAP)

It has been reported that reducing potential is associated with antioxidant activity and may serve as a significant reflection of the antioxidant activity (Oktay *et al.*, 2003). The FRAP values obtained for the different processed products of the quince fruit are presented in Figure 3. A non significant difference in the FRAP values among the various processed products of quince fruit was reported in the analysis. The highest FRAP value was reported in quince candy (1.68 µM), which varied insignificantly with the jam (1.40 µM) and the dehydrated slice (1.46 µM). However the FRAP values of the processed quince products was seen to increase with respect to the fresh pulp that may be due to the release of more phenolic compounds and changes in their profile.

Conclusion

The emerging research on dietary antioxidants and the protective role of the phytochemicals and pure metabolites have favoured the development of the functional food market. Processing of quince involving cooking and dry heat treatment increased the total phenolic contents and antioxidant activities significantly. These changes in the overall

antioxidant properties of the processed products could be attributed to the synergistic combinations or counteracting of several types of factors including oxidative reactions, leaching of water-soluble antioxidant compositions, formation or breakdown of antioxidant compositions and solid losses during processing. However, dry heat processes caused smaller losses in the total phenolic content and antioxidant activity. The results of this study are expected to provide sufficient baseline information for further exploration and development of new, cheaper and safe quince products for nutraceuticals, bio-pharmaceutical and other technological purposes.

Acknowledgement

The authors are highly thankful to the Department of Biotechnology, Government of India for financial support.

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