Scientia Horticulturae 165 (2014) 163–170

Contents lists available at ScienceDirect

Scientia Horticulturae

journal homepage: www.elsevier.com/locate/scihorti

Quality parameters, bio-compounds, antioxidant activity and sensory attributes of Spanish quinces (*Cydonia oblonga* Miller)

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ARTICLE INFO

Article history:
Received 9 September 2013
Received in revised form 22 October 2013
Accepted 14 November 2013

Keywords:
Fatty acids
Hydrophilic antioxidant activity
Lipophilic antioxidant activity
Organic acids
Polyphenols
Sugars

ABSTRACT

Quinces are attracting interest due to their health promoting properties. Quality parameters, bioactive compounds, antioxidant activity and the main sensory parameters were determined in six Spanish quince clones. Quinces are rich in phytic, malic and quinic acids and also in fructose, sorbitol and glucose, which gives them an interesting equilibrium among sourness, astringency and sweetness. Total polyphenols content (TPC) and total antioxidant activity (TAA), in both hydrophilic (H-TAA) and lipophilic (L-TAA) extracts, were found to be significantly higher in quince peel than in pulp; for instance, the ratio TPC_{peel}/TPC_{pulp} was ~4.7. The predominant fatty acids were linoleic (54.7%) and oleic (35.5%) acids, leading to a ratio of unsaturated to saturated fatty acids of ~9–10. The studied parameters were finally used to establish appropriate applications for quinces: (i) PUM fruits are better suited for preparation of functional quince-based products because of their high TPC and TAA (e.g. 5810 mg gallic acid kg^{-1} peel and 5430 mg Trolox kg^{-1} peel), while (ii) other clones, such as OHM14, ZM6 and OHM13, are appropriate for fresh consumption because of their equilibrated levels of sourness and sweetness and their high quince flavor.

1. Introduction

Recent studies have revealed the potential health benefits associated with a diet rich in fruits and vegetables (Du Toit et al., 2001). Nutritional studies recommended the regular consumption of fruits and vegetables, because they are rich in vitamins, an excellent source of fibre and naturally low in fat. Quinces are attracting interest due to their health promoting properties, mainly related with their antioxidant capacity, phenolic composition, hypoglycemic, anti-inflammatory, anti-carcinogenic, antimicrobial, anti-allergic, and anti-ulcerative activities and because it might act as a tonic for heart and brain (Wojdyło et al., 2013; Legua et al., 2013; Sharma et al., 2011). Besides, quince has low fat content and it is an important source of organic acids, sugars, crude fibre and minerals like potassium, phosphorous and calcium (Sharma et al., 2011; Rodríguez-Guisado et al., 2009; Shinomiya et al., 2009). Due to these healthy properties, quince extracts have been traditionally used as dietary supplements and for medical treatment for infections and inflammatory diseases.

Quince fruits are not very appreciated for fresh consumption mainly due to pulp hardness, woodiness, bitterness and astringency; however, when ripe, quince fruits have pleasant, lasting and powerful flavor. Nevertheless even nowadays, quinces are intended primarily to the manufacture of marmalade, jams, jelly and cakes (Silva et al., 2002, 2004a,b, 2005, 2006); the most popular quince product in Spain is a jam called “quince sweet”.

Because native quince resources are almost vanished nowadays in Spain and throughout the European Union, the Plant Science and Microbiology Department of the Miguel Hernandez University established in their facilities in Orihuela (Alicante, Spain) a gene bank with a total of 25 quince accessions with a wide genetic diversity. Thus, the aim of this research line is to develop strategies and methodologies to classify quince clones according to their suitability for fresh consumption or further processing. In this particular study, six of the most interesting clones, according to previous research (Legua et al., 2013), were selected and a full characterization of their quality was conducted. The parameters that have been evaluated included: bioactive compounds (polyphenols), the total antioxidant activity (TAA), measured in the hydrophilic (H-TAA) and lipophilic (L-TAA) fractions separately, in the peel and pulp, organic acids, sugars, and fatty acids. Finally, principal component analysis (PCA) and cluster analysis (CA) were applied to these data to assess the relationship among clones.

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http://dx.doi.org/10.1016/j.scienta.2013.11.028

The results will provide information about the potential interest of quince accessions for fresh fruit consumption (with a proper varietal selection it will be possible to obtain quinces which are fully suitable for fresh consumption) or for manufacturing quince-based products, such juice, jam, jelly and liquors, with high content on bioactive compounds and health benefits.

2. Materials and methods

2.1. Plant material

Six quince clones (PUM, OHM2, OHM13, OHM14, ZM6 and ZM9) were used in this research; all of them being appropriated for fresh market and/or processing. The selected plant materials belong to the quince gene bank located at the experimental field station of the Miguel Hernández University (Alicante, Spain). Trees are planted at a spacing of 4 m × 3 m; they are 9 year-old and are in full production age. The experiment was established in a randomized block design with four single-tree replications and grafted onto quince BA-29 rootstock. Fruits were harvested at commercial ripening stage (farmers usually consider normal harvest date, colour and total soluble solids) at the end of September and first October, and 40 homogeneous fruits (based on colour, size and absence of defects) were selected from each clone (10 fruits from each tree) for analytical determinations. The study was conducted twice in the years 2011 and 2012 and results are the mean ± SE of two years.

2.2. Main quality parameters

For the following analyses, samples of 30 quinces per clone were randomly selected from the 40 picked from the field (rejecting any slightly damaged fruits), and then divided into 3 subsamples of 10 fruits. They were hand-peeled and peel and pulp were cut in small pieces to obtain homogeneous samples. Samples were immediately frozen in liquid N_2, ground and stored in freezer at −40 °C until analysis. All analyses were run in triplicate for each year; this is, a total of 6 replicates (3 replicates per year × 2 years) were conducted for each analysis.

For TSS and TA determination 10 g of pulp samples were squeezed using a commercial blender and the extracted juice was later sieved and centrifuged at 8,000 × *g* for 20 min (Sigma 3–18K, Osterode and Harz, Germany). TSS were determined using a digital refractometer Atago N1 (Atago Co. Ltd., Tokyo, Japan) at 20 °C. TA was determined in 1 mL of the above supernatant diluted in 25 mL of distilled water by titration with 0.1 N NaOH up to pH 8.1, using an automatic titration device (877 Titrino plus, Metrohm ion analyses CH9101, Herisau, Switzerland) and results expressed as g of malic acid L^{-1}. Later, maturity index (MI) was calculated as the ratio TSS/TA.

Moisture percentage was determined by oven drying until constant weight and crude fibre content was determined by a digester, Ankon fibre analyser model A22 (Ankom Technology, Macedon, NY, USA), and quantified following the official methodology established by the Spanish Ministry of Agriculture, Fisheries and Food as described by Rodríguez-Guisado et al. (2009).

2.3. Total polyphenols content (TPC)

Total polyphenols content (TPC) was quantified using Folin–Ciocalteu reagent (Singleton et al., 1999). Briefly, for each sample, 2 g of pulp or 1 g of peel tissues was homogenized in 5 mL of MeOH/water (80:20 v/v) + 2 mM NaF and then centrifuged at 10,000 × *g* for 20 min. Absorption was measured at 760 nm using a spectrophotometer ThermoSpectronic (Heγios, UK). Results (mean ± SE) were expressed as mg of gallic acid 100 g^{-1} fw.

2.4. Total antioxidant activity (TAA)

TAA was quantified as described by Díaz-Mula et al. (2008). This procedure allowed the determination of both the hydrophilic and lipophilic TAAs in the same extraction. Briefly, for each subsample, 5 g of pulp or 1 g of peel tissues were homogenized in 5 mL of 50 mM phosphate buffer pH 7.8 and 3 mL of ethyl acetate, then centrifuged at 10000 × *g* for 15 min at 4 °C. The upper fraction was used for TAA due to lipophilic compounds (L-TAA) and the lower for TAA due to hydrophilic compounds (H-TAA). In both cases, TAA was determined in triplicate in each extract using the enzymatic system composed of the chromophore 2,2′-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS), the horse radish peroxidase enzyme and its oxidant substrate (hydrogen peroxide), in which $ABTS^{\bullet+}$ radicals are generated and monitored at 730 nm. The decrease in absorbance after adding the extract was proportional to TAA of the sample. A calibration curve was performed with Trolox ((R)-(+)-6-hydroxy-2,5,7,8-tetramethyl-croman-2-carboxylic acid) (0–20 nmol) from Sigma (Madrid, Spain), and results (mean ± SE) are expressed as mg of Trolox equivalent 100 g^{-1}.

2.5. Organic acids and sugars

For organic acids and sugars, the methodology by Calín-Sánchez et al. (2013) was used. The 50 g of quinces were squeezed and extracted juice was sieved and centrifuged at 10,000 × *g* for 20 min (Sigma 3–18K, Osterode and Harz, Germany). One millilitre of the centrifuged juice was passed through a 0.45 μm Millipore filter and then injected into a Hewlett-Packard series 1100 HPLC (Wilmington Del., USA). The elution system consisted of 0.1% phosphoric acid with a flow rate of 0.5 mL min^{-1}. Organic acids were separated on a Supelcogel TM C-610H column (30 cm × 7.8 mm i.d., Supelco, Bellefonte, PA., USA) and kept at 30 °C with a precolumn Supelguard-H (5 cm × 4.6 mm, Supelco), and detected using a diode-array detector set up at 210 nm. For sugar analyses, the same HPLC equipment, elution system, flow rate, and columns were used. The detection of sugars was performed using a refractive index detector (HP 1100, G1362A). Standards of organic acids, monosaccharides, oligosaccharides and sugar alcohols were obtained from Supelco. Peaks were identified by comparison with retention time of the standards and quantified by regression formula obtained with standards. Sugars and organic acids were determined in triplicate.

2.6. Fatty acids

Grinded quince seeds were extracted in a Soxhlet apparatus for 4 h with petroleum ether. The organic solvent was evaporated at 30 °C under vacuum to constant weight, and the oil content was gravimetrically determined. The extracted oils were immediately analysed for fatty acids (FA) by GC-MS after conversion into their corresponding methyl esters (FAMEs).

Fatty acids were *in situ* methylated according to Park and Goins (1994) with some modifications. Basically, 50 mg of quince seeds oil were transferred into a test tube together with 80 μL of C17:0 *n*-hexane solution (20 mg mL^{-1}) as internal standard. Then, 100 μL of dichloride methane and 1 mL of 0.5 N NaOH in methanol were added and the tubes were heated in a water bath at 90 °C for 10 min. One millilitre of BF_3 in methanol were added and the mixture was left at room temperature (25 °C) for 30 min. One millilitre of distilled water and 600 μL of hexane were added and then fatty acid methyl esters (FAME) were extracted by vigorous shaking for about 1 min. Following centrifugation, the aliquots were dried with anhydrous Na_2SO_4 and the top layer was transferred into a vial flushed with nitrogen which was stored at −20 °C until analyzed by GC-MS.