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Fruit quality characterization of eleven commercial mandarin cultivars in Spain

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ABSTRACT

In this study, we characterized the chemical and physical aspects of eleven commercial mandarins ['Clementine' ('Clementina Fina', 'Clemenules', 'Hernandina'), tangor ('Ortanique', 'Afourer', 'Ellendale'), and hybrid cultivars ('Fortuna', 'Kara', 'Mor', 'Nova' and 'Yosemite')] in the Spanish southeast. The analysis revealed that 'Ellendale' showed the highest amount of juice, 'Nova' and 'Clementina Fina' displayed high total soluble solids and low titratable acidity, and 'Clementina Fina' showed a particularly high concentration of Potassium. The cultivars 'Clementina Fina' and 'Clemenules' were the mandarins most appropriate for fresh consumption, with small-medium sized fruits and a high percentage of excellent quality juice.

1. Introduction

In Spain, the major mandarin and orange producer, accounting for 50% and 45% of the total production, respectively (CAPA, 2009) is the Valencian community. At present, 35 mandarin cultivars with certain commercial importance are being cultivated, of which the major group is mainly clementine cultivars (*Citrus clementina* Hort. Ex Tan). The producing sector prefers cultivars with two clear requirements: (i) access to cultivars whose period of commercial supply is the maximum possible and (ii) cultivars of mandarins that have either no seeds or the minimum possible number. In order to best meet these two needs, the citrus growers and owners of nurseries of citrus plants are introducing new cultivars, principally varieties of hybrid and tangor mandarins. In order that citrus growers may be able to choose the right mandarin cultivar for a specific region or market, it is very important that they know the internal and external characteristics of the fruits. It is also useful to know the organoleptic and nutritional properties of these new mandarin cultivars, so as to identify any surplus value (added value) which would have the effect of expanding their market. In view of the low selling prices of citrus fruits, only those mandarin trees that produce high-quality fruits can be maintained.

The research groups of CEBAS–CSIC and University Miguel Hernández have done a study to identify the physicochemical properties of 11 commercial mandarins in south-east Spain. The results obtained during the 2011 campaign to study the fruit quality parameters of three different group cultivars of 'Clementine' ('Clementine Fina', 'Clemenules', 'Hernandina'); tangor ('Ortanique', 'Afourer', 'Ellendale'), and hybrid cultivars ('Fortuna', 'Kara', 'Mor', 'Nova' and 'Yosemite') are presented in this paper. All specimens of these cultivars were obtained from various farms located in Orihuela (Alicante, Valencian Community) and in the district of Santomera (Murcia).

2. Materials and methods

2.1. Plant material and experimental plot

Eleven cultivar mandarins were used in this test. The mandarin fruits were collected from orchards owned by small farmers located in different parts of the districts known as "La Murada" and "Virgen del Camino", which fall within the municipality of Orihuela, and in the citrus collection available from the CEBAS–CSIC experimental farm 'Tres caminos' in Santomera (Murcia). All these districts are considered to lie within the territory of 'Vega Baja del Segura'

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(38°11′ latitude North, 00°58′ longitude West). The area enjoys a Mediterranean climate with a scanty seasonal precipitation profile capped by a severe drought in summer. The evapotranspiration of reference according to Penman–Monteith and the average annual rainfall in the South of Alicante, is 1210 ± 60 and 305 mm, respectively.

The 11 cultivars mandarins studied were classified into three cultivar groups—'Clementine' group: Clemenules, Clementina Fina and Hernandina; 'Tangor' group: Afourer, Ellendale and Ortanique; and hybrid group: Fortune, Kara, Mor, Nova and Yosemite. Four trees at random locations were chosen from each cultivar variety on the corresponding farm, with 10 representative fruits being collected from each tree. All the cultivars were collected during the 21 or 22 of February 2011 except 'Clemenules' and 'Clementina Fina', which were collected on January 31. The trees were budded on 'Carrizo' citrange rootstock, had seven-year-old, were healthy, and showed no sign of any mineral deficiency.

2.2. Physical parameters of the fruit

To asses fruit quality attributes, the following physical variables were measured: index of color (IC), fresh weight (g), equatorial diameter (D_e; mm), longitudinal diameter (D_L), shape index ($100 \times D_L/D_e$), size index ($D_L + D_e/2$). Fruits were cut along their equatorial zone and their juice was extracted. Thus, juice volume (ml), pulp weight (g), peel weight (g), seed number and weight (g) were measured. Fruit skin surface and pulp color were assessed with a tri-stimulus color differencemeter (Minolta CR 300). Color index (CI) was calculated as $CI = a^* \times 10^3/(L \times b^*)$, where L indicates lightness and a^* and b^* are the chromaticity co-ordinates.

2.3. Chemical parameters of the fruit

The juice was filtered to separate the pulp and centrifuged at 1000 rpm. The following chemical variables were thereafter measured: pH, titratable acidity (TA; g/l citric), total soluble solids (TSS; °Brix), maturity index (MI = TSS × 10/TA), composition and concentration of sugars (%; g sugar/100 g fresh juice) and organic acids (%; g organic acids for 100 g fresh juice), mineral nutrients concentration (macronutrients and micronutrients; mg/l), total antioxidant activity (H-TAA and L-TAA), total phenolic compounds (mg/l), and volatile compounds analysis (aroma) (Calín-Sánchez et al., 2011; Gimeno et al., 2009; Melgarejo et al., 2010; Navarro et al., 2010).

2.3.1. pH, TA, TSS, and MI

Juice pH was measured with a Crison MicropH 2001 pH meter. Titratable acidity (TA) was determined by acid-base pontentiometry (0.1 N NaOH up to 8.1). Total soluble solids (TSS) was measured with a digital refractometer DRB0-45nD. Maturity index (MI) was calculated as the relation between the total sugars and acids content.

2.3.2. Extraction and characterization of sugars and organic acids

A volume of 15 ml of leaked juice was centrifuged at 9500 rpm for 15 min. The supernatant was filtered through a cellulose nitrate membrane filter (0.45 μm pore size). The aqueous extracts were analyzed using a high performance liquid chromatography (HPLC, Hewlell Packard series 1100) containing a Supelcogel C-610H HPLC column (30 cm × 7.8 mm i.d.), connected in series to a Supelcogel™ carbohydrate precolumn (5 cm × 4.6 mm) and with a stationary phase of sulfonated polystyrene divinilbenzene. The isocratic separation of sugars and organic acids was realized at temperature of 30 °C, using a mobile phase of 0.1% of phosphoric acid adjusted to a flow rate of 0.5 ml/min. The quantification of sugars was carried out by the refractive index detector (RID); and the organic acids were quantified using a diode detector ultra-violet (UV) at a wavelength of 210 nm (DAD). The characterization and quantification of the sugars and organic acids in the samples was possible by comparison of retention times and the areas of the peaks with standards. Sugar and organic acid standards were supplied by Supelco analysis (Bellefonte, PA, USA).

2.3.3. Mineral content

A volume of 15 ml of leaked juice was centrifuged at a 9500 rpm for 15 min. The supernatant was caught and passed through a filter of 0.45 μm. Determination of Ca, K, Mg, P, S, Na, Cu and Zn was carried out using inductively coupled plasma-emission optical spectrometry (Iris Intrepid II, Thermo Electron Corporation, Franklin, USA).

2.3.4. Total antioxidant activity (TAA)

For each sample, 5 ml of mandarin juice was homogenized in 5 ml of 50 mM phosphate buffer pH 7.8 and 3 ml of ethyl acetate, then centrifuged at 10,000 × g for 15 min at 4 °C. The upper fraction was used for total antioxidant activity due to lipophilic compounds (L-TAA) and the lower for total antioxidant activity due to hydrophilic compounds (H-TAA). TAA was determined in each extract (quadruplicate) using the enzymatic system composed of the chromophore 2,2′-azino-bis-(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS), the horseradish peroxidase enzyme (HRP) and its oxidants substrate (hydrogen peroxide), in which $ABTS^+$ radicals are generated and monitored at 730 nm. A calibration curve was performed with Trolox ((*R*)-(+)-6-hydroxy-2,5,7,8-tetramethyl-croman-2-carboxylic acid).

2.3.5. Total phenolic compounds

The samples were diluted 1:10 with methanol at 80%. They were shaken for 30 min and after that time, centrifuged at about 6000 rpm for 10 min. In glass tubes, we added 500 μl of the previous extraction and added 2.5 ml of reagent Følling 10% and 2 ml of Na_2CO_3 (75 g/l). Returned to shake (it was realized by triplicate). Prepared the straight pattern using Gallic acid (0.1 g/l). The glass tubes were introduced in a bath to 50 °C for 5 min. After that time, was proceeded to measure the absorbance in a spectrophotometer model Hitachi U-2000 at 760 nm.

2.3.6. Extraction procedure of volatile aroma compounds

The steps that were carried out were the followings: (1) Extraction of the sample. The leaked juice samples were taken and were diluted 1:5 with ultrapure water. It was added 10 μl of the internal standard 3-Hexanol at a concentration of 10,000 ppm. (2) Absorption of volatile compounds by fiber. It was putted the sample with the fiber (50/30 μm divinylbenzene/carboxen/feature) in a water bath at 50 °C for 1 h. (3) The GC–GC/MS analysis. The isolation, identification and quantification of volatile compounds were performed on a gas chromatograph Shimadzu GC-17A (Shimadzu Corp., Kyoto, Japan), coupled with a Shimadzu mass spectrometer detector GC–MS QP-5050A. The GC/MS system was equipped with a TRACSIL Meta.X5 column, 95% dimethyl-polysiloxane and 5% diphenil-polysiloxane (Teknokroma S. Coop. C. LTD, Barcelona, Spain; 30 m × 0.25 mm, 0.25 μm of film thickness).

2.4. Statistical analysis

The results were analyzed using the SPSS Statistics 17.0 program. The differences between cultivars ($p < 0.05$) in the different parameters studied were evaluated by analysis of variance (ANOVA) followed by applying Duncan's test of comparison of means.