

CORRELATING SENSORY ATTRIBUTES, TEXTURAL PARAMETERS AND VOLATILE ORGANIC COMPOUNDS FOR THE ASSESSMENT OF DISTINCTIVE QUALITY TRAITS OF MELON AND PEACH FRUIT CULTIVARS

Tiago Luís Cardoso Ferreira Pinhanços de Bianchi

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DOCTORAL THESIS

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TEXTURAL PARAMETERS AND VOLATILE
ORGANIC COMPOUNDS FOR THE ASSESSMENT
OF DISTINCTIVE QUALITY TRAITS OF MELON
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FOR THE ASSESSMENT OF DISTINCTIVE QUALITY
TRAITS OF MELON AND PEACH FRUIT CULTIVARS

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DOCTORAL PROGRAMME IN TECHNOLOGY

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DECLAREM:

Que el treball titulat “Correlating sensory attributes, textural parameters and volatile organic compounds for the assessment of distinctive quality traits of melon and peach fruit cultivars”, que presenta Tiago Luís Cardoso Ferreira Pinhaños de Bianchi per a l'obtenció del títol de doctor, ha estat realitzat sota la meva direcció i que compleix els requisits per poder optar a Menció Internacional.

I, perquè així consti i tingui els efectes oportuns, signo aquest document.

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Dra. Marta Gratacós-Cubarsí

Girona, 28 de gener de 2020

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List of publications

This doctoral thesis is presented in the form of a compendium of the following research articles:

Publication 1:

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List of abbreviations

AATs	Alcohol acyl transferases
ADHs	Alcohol dehydrogenases
AOS	Allene oxide synthase
ANOVA	Analysis of Variance
B€	Billion Euros
°Brix	Brix degrees
CA	Cluster Analysis
CU	chilling units
DA	Discriminant Analysis
GC-MS	Gas Chromatography-Mass Spectrometry
HPLs	Hydroperoxide lyases
ICBN	International Code of Botanical Nomenclature
ICNCP	Code of Nomenclature for Cultivated Plants
ISO	International Organization for Standardization
Kt	Thousand tons
LOX	Lipoxygenase
MEP	Methylerythritol phosphate
MVA	Mevalonic acid
Mt	Million tons
NaCl	Salt
PCA	Principal Component Analysis
PCR	Principal Component Regression
PCs	Principal components
PLS	Partial least squares
ppt	parts per trillion
pptv	parts per trillion by volume
PTR-MS	Proton Transfer Reaction-Mass Spectrometry
PTR-ToF-MS	Proton Transfer Reaction-Time-of-Flight -Mass Spectrometry
SSC	Soluble solids content
TPSs	Terpene synthases
TPA	Texture Profile Analysis
TA	Titrateable acidity
vis/NIR	Visible/near infrared
VOCs	Volatile organic compounds

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Resum

El meló (*Cucumis melo* L.) i el préssec (*Prunus persica* (L.) Batsch) són dues espècies fruiteres d'interès econòmic a la Unió Europea. Totes dues fruites integren la dieta mediterrània i són molt apreciades pel seu flavor i sucositat. La millora en la qualitat de varietats de meló i préssec és fonamental per a mantenir i incrementar la seva acceptació i consum. També és un factor clau per a una ingesta adequada de fruites i verdures, amb la condició de complir amb les recomanacions de l'Organització Mundial de la Salut. En aquest context, l'objectiu central d'aquesta tesi va ser investigar els principals paràmetres de qualitat de diferents cultivars de meló i préssec mitjançant la correlació d'anàlisis sensorials i instrumentals. El desenvolupament d'aquesta recerca va conduir a tres objectius específics.

El primer objectiu es va centrar en l'estudi de la variabilitat de les característiques de textura de la fruita de meló. Es van avaluar fruits de les cultivars *cantalupensis*, *conomon*, *dudaim*, *inodorus* i *momordica*, en conjunt amb varietats comercials de referència de *cantalupensis* i *inodorus*. Els resultats obtinguts van mostrar una major correlació entre els paràmetres de textura instrumental i els atributs sensorials de duresa, masticabilitat i cruixença, que els de fibrositat, farinositat i sucositat. Els atributs sensorials, sòlids solubles i pH van mostrar una major capacitat discriminant entre els diferents tipus de meló que els paràmetres de textura instrumental. Les cultivars 'Iraq' i 'Calcuta' es van discriminar per la seva farinositat i 'Songwhan charmi' per la seva cruixença, però no es va discriminar l'accessió 'T111' de la varietat comercial de Piel de Sapo o la cultivar 'Dulce' de 'Védrantais'. Les varietats comercials (Galia, Cantaloupe, Amarillo, i Piel de Sapo) van reflectir l'èmfasi dels programes de millora en els paràmetres de duresa i sòlids solubles.

El segon objectiu va consistir en l'avaluació de la relació entre els atributs sensorials d'aroma i flavor i els compostos orgànics volàtils de la mateixa població de

fruits de meló. Les cultivars *cantalupensis* i *inodorus* van exhibir un patró oposat per a diferents paràmetres, d'acord amb els seus respectius patrons de respiració climatèrica i no climatèrica. La cultivar 'Iraq' va mostrar característiques més similars a les dels fruits de les cultivars *cantalupensis*, mentre 'Songwhan charmi' i 'Calcuta' van mostrar característiques intermèdies entre *inodorus* i *cantalupensis*. Els atributs d'intensitat d'olor i flavor, olor de fruita madura i olor i flavor fermentat es van correlacionar positivament amb diferents èsters, alcohols i aldehids. Així mateix, aquests atributs es van correlacionar negativament amb els aldehids de 9 àtoms de carboni i el mateix tipus de correlació es va observar entre la dolçor i els volàtils de fulles verdes de 6 àtoms de carboni.

El tercer objectiu es va centrar en la recerca de l'aroma de cultivars comercials de fruits de préssec mitjançant anàlisi sensorial i de compostos orgànics volàtils. Els resultats van evidenciar diferents perfils associats a cadascuna de les tipologies de fruit de préssec, nectarina, préssec pla, i pavia, mentre els dos últims van exhibir els trets més distintius. Els compostos amb major impacte positiu sobre els atributs d'intensitat d'aroma, aroma a fruita madura, intensitat de flavor i persistència de flavor van ser γ -hexalactona, γ -octalactona, hotrienol, àcid acètic i acetat d'etil, mentre que aquells amb major impacte negatiu sobre aquests atributs van ser benzeacetaldehid, trimetilbenzè i acetaldehid.

La correlació de mètodes sensorials i instrumentals va permetre identificar aquells paràmetres amb impacte positiu o negatiu sobre la percepció sensorial de fruits de meló i préssec, bé directament o mitjançant interacció amb altres trets de qualitat. La combinació d'aquestes metodologies va proporcionar informació important per a una millor avaluació de la qualitat i la seva aplicació permetrà la millora en la qualitat de fruits de meló i préssec sense comprometre altres trets de qualitat d'interès.

Resumen

El melón (*Cucumis melo* L.) y el melocotón (*Prunus persica* (L.) Batsch) son dos especies frutales de interés económico en la Unión Europea. Ambas frutas integran la dieta mediterránea y son muy apreciadas por su flavor y jugosidad. La mejora en la calidad de variedades de melón y melocotón es fundamental para mantener e incrementar su aceptación y consumo. También es un factor clave para una ingesta adecuada de frutas y verduras, con tal de cumplir con las recomendaciones de la Organización Mundial de la Salud. En este contexto, el objetivo central de esta tesis fue investigar los principales parámetros de calidad de diferentes cultivares de melón y melocotón mediante la correlación de análisis sensoriales e instrumentales. El desarrollo de esta investigación condujo a tres objetivos específicos.

El primer objetivo se centró en el estudio de la variabilidad de las características de textura de la fruta de melón. Se evaluaron frutos de los cultivares *cantalupensis*, *conomon*, *dudaim*, *inodorus* y *momordica*, en conjunto con variedades comerciales de referencia de *cantalupensis* e *inodorus*. Los resultados obtenidos mostraron una mayor correlación entre los parámetros de textura instrumental y los atributos sensoriales de dureza, masticabilidad y crujencia, que los de fibrosidad, harinosidad y jugosidad. Los atributos sensoriales, sólidos solubles y pH mostraron una mayor capacidad discriminante entre los diferentes tipos de melón que los parámetros de textura instrumental. Los cultivares 'Irak' y 'Calcuta' se discriminaron por su harinosidad y 'Songwhan charmi' por su crujencia, pero no se discriminó la accesión 'T111' de la variedad comercial de Piel de Sapo o el cultivar 'Dulce' del 'Védrantais'. Las variedades comerciales (Galia, Cantaloupe, Amarillo, y Piel de Sapo) reflejaron el énfasis de los programas de mejora en los parámetros de dureza y sólidos solubles.

El segundo objetivo consistió en evaluar la relación entre los atributos sensoriales de aroma y flavor y los compuestos orgánicos volátiles de la misma

población de frutos de melón. Los cultivares *cantalupensis* e *inodorus* exhibieron un patrón opuesto para diferentes parámetros, de acuerdo con sus respectivos patrones de respiración climatérica y no climatérica. El cultivar 'Irak' mostró características más similares a las de los frutos del cultivar *cantalupensis*, mientras 'Songwhan charmi' y 'Calcuta' mostraron características intermedias entre *inodorus* y *cantalupensis*. Los atributos de intensidad de olor y flavor, olor a fruta madura y olor y flavor fermentado se correlacionaron positivamente con diferentes ésteres, alcoholes y aldehídos. Asimismo, estos atributos se correlacionaron negativamente con los aldehídos de 9 átomos de carbono y el mismo tipo de correlación se observó entre el dulzor y los volátiles de hojas verdes de 6 átomos de carbono.

El tercer objetivo se centró en la investigación del aroma de cultivares comerciales de frutos de melocotón mediante análisis sensorial y de compuestos orgánicos volátiles. Los resultados evidenciaron diferentes perfiles asociados a cada una de las tipologías de fruto de melocotón, nectarina, paraguay, y pavía, mientras los dos últimos exhibieron los rasgos más distintivos. Los compuestos con mayor impacto positivo sobre los atributos de intensidad de aroma, aroma a fruta madura, intensidad de flavor y persistencia de flavor fueron γ -hexalactona, γ -octalactona, hotrienol, ácido acético y acetato de etilo, mientras que aquellos con mayor impacto negativo sobre estos atributos fueron bencenoacetaldehído, trimetilbenceno y acetaldehído.

La correlación de métodos sensoriales e instrumentales permitió identificar aquellos parámetros con impacto positivo o negativo sobre la percepción sensorial de frutos de melón y melocotón, bien directamente o mediante interacción con otros rasgos de calidad. La combinación de estas metodologías proporcionó información importante para una mejor evaluación de la calidad y su aplicación permitirá la mejora en la calidad de frutos de melón y melocotón sin comprometer otros rasgos de calidad de interés.

Abstract

Melons (*Cucumis melo* L.) and peaches (*Prunus persica* (L.) Batsch) are two commercially important fruit species in the European Union. Both fruits are part of the Mediterranean diet and highly valued for their flavorful and juicy flesh. The quality improvement of melon and peach cultivars is determinant to maintain and increase their acceptance and consumption. It is also a key factor for an adequate intake of fruit and vegetables, in order to meet the recommendations of the World Health Organization. In this context, the main objective of this thesis was to investigate key quality attributes of melon and peach fruit cultivars through the correlation of sensory and instrumental methodologies. The development of this investigation led to three individual objectives.

The former individual objective was to study melon fruit variation regarding its textural properties. Fruits from the *cantalupensis*, *conomon*, *dudaim*, *inodorus*, and *momordica* cultivar groups, together with *cantalupensis* and *inodorus* commercial reference varieties, were analyzed. The results obtained showed higher correlations between instrumental texture measurements and the sensory attributes of hardness, chewiness, and crunchiness, than the ones of fibrousness, mealiness, and juiciness. Sensory attributes, soluble solids content, and pH showed a higher ability to discriminate between melon types than instrumental texture parameters. 'Irak' and 'Calcuta' cultivars were discriminated for mealiness, 'Songwhan charmi' for crunchiness, but no discrimination was observed between 'T111' accession and commercial Piel de Sapo or 'Dulce' and 'Védrantais' cultivars. The commercial varieties (Galia, Cantaloupe, Amarillo, and Piel de Sapo) reflected the focus of fruit breeders over hardness and soluble solids content.

The second objective was to evaluate the relationship between the aroma and flavor sensory attributes and the volatile organic compounds of the same melon fruit types. Fruits of the *cantalupensis* and *inodorus* cultivars showed opposite patterns for

several parameters, in agreement with their respective climacteric and non-climacteric respiration patterns. Fruits of the 'Irak' cultivar had characteristics more similar to the ones of the *cantalupensis* cultivar, while 'Songwhan charmi' and 'Calcuta' showed an intermediate behavior between *inodorus* and *cantalupensis*. Positive correlations were found between the attributes of odor and flavor intensity, ripe fruit odor, and fermentative odor and flavor with several esters, alcohols, and aldehydes. Negative correlations were observed between the same attributes and C₉ aldehydes, as well as between sweetness and C₆ green leaf volatiles.

The third objective was to investigate the aroma of commercial peach cultivars through the analysis of sensory attributes and volatile organic compounds. The results highlighted the different profiles associated with each of the fruit typologies of peaches, nectarines, flat peaches, and canning peaches ('pavías'), while the latter two showed the most distinctive traits. A positive contribution to the attributes of aroma intensity, ripe fruit aroma, flavor intensity, and flavor persistence was observed from γ -hexalactone, γ -octalactone, hotrienol, acetic acid, and ethyl acetate, while a negative contribution for these attributes was observed from benzeneacetaldehyde, trimethylbenzene, and acetaldehyde.

The correlation of sensory and instrumental methods allowed to identify specific parameters with a positive or negative contribution to the sensory perception of melon and peach fruits, either directly or by their interaction with other quality traits. The combination of these methodologies provided important information for a comprehensive assessment of quality and their application can improve melon and peach fruit quality without compromising other valuable quality traits.

Presentation of the doctoral thesis

The present thesis was developed under the scope of a research project entitled "Genetic approach to the study of the aroma and the antioxidant compounds profile in different melon and peach varieties (MELOMICS)", funded by the National Institute for Agricultural and Food Research and Technology (INIA). The project was coordinated by the Food Industries center of the Institute of Agrifood Research and Technology (IRTA) and involved the participation of the Center for Research in Agricultural Genomics (CRAG) and Mas Badia research experimental station. This project intended to contribute to the existing knowledge on the quality parameters of melon and peach fruit species by providing complementary information to be considered in the selection and development of fruit cultivars with enhanced quality traits. The compromise between the productive quality criteria and the improvement of the sensory quality of melon and peach fruits is driven by economical and health motivations. This will allow the increase of their acceptance and consumption, as well as the marketability and competitive advantage of the fruit cultivars produced in Spain.

Adequate fruit and vegetable consumption is an important determinant of health. The World Health Organization (WHO) recommends the daily consumption of 5 portions of fresh fruit and vegetables (the equivalent to 400 g). However, according to the latest data available, the percentage of the population who meet this recommendation across the European Union (EU) is around 14% for fruits and 19% for vegetables, while 36% do not consume fruit or vegetable on a daily basis (EUROSTAT, 2017). The monitoring and promotion of the consumption of fresh fruit and vegetables is a target objective of numerous initiatives and policies all over the world. Among these initiatives, the WHO European Food and Nutrition Action Plan 2015-2020 was adopted with the objective to reduce the burden of preventable diet-related diseases, such as malnutrition (including undernutrition and micronutrient deficiencies),

overweight and obesity, and non-communicable diseases resulting from unhealthy diets, still prevalent in the WHO European Region (WHO, 2014). These initiatives promote equitable access to a healthy and varied diet to all the social groups, particularly the most vulnerable ones. But further than available, accessible and affordable fruit and vegetables, are also focused on quality improvement as one of the key factors to increase their consumption. Diversify the production, protect and preserve the desired quality, or improve and select cultivars by targeting attributes that influence acceptance are aspects that need to be considered to improve the quality of fruit and vegetables and, thus, their consumption (FAO/WHO, 2005; FAO, 2015).

Melons (*Cucumis melo* L.) and peaches (*Prunus persica* (L.) Batsch) are two of the most commercially important fruit species in the EU, holding the 8th and the 4th position of the most produced fruits during 2017. Spain is the main EU producing country of melon and peach fruits, with more than 37% and 41% of the EU production, and the leading exporter country worldwide (FAOSTAT, 2017). Both fruit species are common to the Mediterranean diet, highly appreciated for their flavorful and juicy flesh, and widely consumed from mid-spring and throughout the summer. As new melon and peach cultivars are being developed, the efforts to improve and select fruits with better and consistent quality are determinant to maintain and increase their consumption. Likewise, the focus of the efforts to improve fruit quality was shifted from a narrow approach based on productive or market-oriented criteria to an integrated approach able to consider the attributes that influence consumer acceptance. Today, further than appearance, shelf-life, or maturity related attributes (such as size, flesh firmness, sugar content, or the balance between sugars and acids), these efforts are focused on the improvement and selection of cultivars with desirable aroma, flavor, and texture. However, to achieve a comprehensive assessment of fruit quality it is important to investigate the relationships between the sensory and physicochemical quality traits. In

this context, the present thesis proposes to investigate the distinctive quality attributes of melon and peach fruit cultivars from a combined sensory and instrumental perspective. The development of this investigation led to the following research articles:

Bianchi, T., Guerrero, L., Gratacós-Cubarsí, M., Claret, A., Argyris, J., Garcia-Mas, J., & Hortós, M. (2016). Textural properties of different melon (*Cucumis melo* L.) fruit types: sensory and physical-chemical evaluation. *Scientia Horticulturae*, 201, 46–56.

Impact factor: 1.624 Quartile 1

Bianchi, T., Guerrero, L., Weesepeel, Y., Argyris, J., Koot, A., Gratacós-Cubarsí, M., Garcia-Mas, J., van Ruth, S., & Hortós, M. (2020). Linking sensory and proton transfer reaction-mass spectrometry analyses for the assessment of melon fruit (*Cucumis melo* L.) quality traits. *European Food Research and Technology*, 246, 1439–1457.

Impact factor: 2.056 Quartile: 2

Bianchi, T., Weesepeel, Y., Koot, A., Iglesias, I., Eduardo, I., Gratacós-Cubarsí, M., Guerrero, L., Hortós, M., & van Ruth, S. (2017). Investigation of the aroma of commercial peach (*Prunus persica* L. Batsch) types by Proton Transfer Reaction-Mass Spectrometry (PTR-MS) and sensory analysis. *Food Research International*, 99, 133–146.

Impact factor: 3.520 Quartile 1

1. Introduction

1.1 The origin and classification of horticultural species

The origin of fruit species has long been controversial. For a long period of time some species were assumed to be originated in places where these were actually diffused into. Extensive investigations of literature and historical records, archaeological evidence, together with genetic analyses, allowed their true origins to be known. A good example is an assumption that the botanical name of peach (*Prunus persica*) was a reference to its country of origin, Persia (actual Iran), that lasted until the 19th century. Of no less complexity is the taxonomy of fruit-producing species. There are two codes of plant nomenclature, the International Code of Nomenclature for Cultivated Plants (ICNCP) and the International Code of Botanical Nomenclature (ICBN), but these are not always compatible. Briefly, the former is used for cultivated species whereas the latter for wild ones. Detailed comparisons between both codes can be found elsewhere (Spooner, Hetterscheid, van den Berg & Brandenburg, 2003; Ochsmann, 2004). Furthermore, the enormous intraspecific variation existent within the plant species, and to a larger extent within cultivated than wild ones, has led to the development of several other formal and informal intraspecific classifications (Hanelt & Hammer, 1995).

Fruit and vegetables are often classified according to different purposes such as gastronomic, nutritional, or international trade. Peaches and nectarines, for example, are often classified as fruits but, in some cases, also grouped as stone fruits together with other species. In the case of melons, these are often included in the group of vegetables (fruit-bearing vegetables) because they are temporary crops and fruits are permanent crops (FAO, 2013), while in other classifications melons are also grouped with watermelons. Additionally, fruit and vegetables are often grouped together for dietary

guideline purposes as they comprise high-value foods of plant origin with similar nutritional composition and health benefits.

1.1.1 The origin and classification of melon (*Cucumis melo* L.)

It has been assumed that melon has African origin, although recent works suggest that it was originated in Asia (Sebastian, Schaefer, Telford & Renner, 2010). The former domestication events took place in the Middle East while the more extensive domestication of melon occurred in Asia (Luan, Delannay & Staub, 2008). From the Middle East, it was introduced in Europe during the Roman and Greek periods, possibly through eastern (Bulgaria, Hungary, and Russia), south-eastern (Albania, Greece, and Romania), and southern (Italy) borders quite simultaneously (Pitrat, Chauvet & Foury, 1999). However, it was not until the late 15th century that the sweet melon varieties were introduced in most of the European countries (Paris, Amar & Lev, 2012).

The melon species belongs to the *Cucurbitaceae* family and the *Cucumis* genus. This family encompasses around 100 genera and other economically important belonging species are cucumber (*Cucumis sativus*), courgette, pumpkin and squash (*Cucurbita pepo*), or watermelon (*Citrullus lanatus*). Nearly 66 species are known to be part of the *Cucumis* genus (Sebastian *et al.*, 2010). The fruit of melon is a kind of berry called pepo, with a firm rind (exocarp), fleshy mesocarp, and an inner cavity filled with several flattened seeds. Numerous intraspecific classifications have been used to divide melon fruits into different groups. One of these classifications defined 16 groups, 5 assigned to the subspecies *agrestis* and 11 to the subspecies *melo* (Pitrat, Hanelt & Hammer, 2000; Burger, Paris, Cohen, Katzir, Tadmor & Lewinsohn, 2010). This was later redefined and the number of groups reduced to 15, with 5 assigned to the subspecies *agrestis* (*acidulus*, *chinensis*, *conomon*, *makuwa*, and *momordica*) and 10 to

the subspecies *melo* (*adana*, *ameri*, *cantalupensis*, *chandalak*, *chate*, *dudaim*, *flexuosus*, *inodorus*, *reticulatus*, and *tibish*) (Pitrat, 2008). However, due to numerous similarities and name confusion, a simplified group combining *cantalupensis* and *reticulatus* into a single *cantalupensis* group has also been proposed (Table 1). The *cantalupensis* fruits were originally described as rough warty, sutured, and smooth, with salmon to orange sweet flesh, and were known as rockmelons or cantaloupes mainly in Europe. The *reticulatus* group comprised netted, plain, or almost smooth fruits, with orange, greenish or white flesh, and a musky odor, called 'nutmeg' melons, muskmelons, or cantaloupes in the United States. Additionally, several cultivars from crosses between the *cantalupensis* and *reticulatus* have been produced giving rise to nomenclature issues (Fernández-Trujillo, Picó, Garcia-Mas, Álvarez & Monforte, 2011; Perkins-Veazie, Beaulieu & Siddiq, 2012).

Table 1. Intraspecific classification of melon (*Cucumis melo* L.)¹

Subspecies	Cultivar group	Ripening behavior	External quality	Internal quality	Example
<i>agrestis</i>	<i>acidulus</i>		Oval, smooth, green or orange	White, firm and crisp, non-sweet, non-aromatic	
	<i>chinensis</i>	Climacteric/ non-climacteric	Piriform, light or dark green	Green or orange, medium sweet, little or no aroma	PI 161375
	<i>conomon</i>	Non-climacteric	Elongated, smooth	White, firm, non-sweet, non-aromatic	Songwhan charmi (PI 161375)
	<i>makuwa</i>	Climacteric	Oblate or piriform, smooth, white, yellow or light green	White, sweet, slightly aromatic	Chamoe, Ginsen Makuwa
	<i>momordica</i>	Climacteric	Flat, round or elongated	White, mealy, non-sweet, mild aroma	Calcuta (PI 124112)
<i>melo</i>	<i>adana</i>	Climacteric	Round to oval, slightly netted	Orange or white, mealy, non-sweet	Graydanka
	<i>ameri</i>	Climacteric	Long oval, slightly netted, yellow or light green	White or orange, juicy, sweet, less aromatic	PI 385966, Khatoni
	<i>cantalupensis</i>	Climacteric	Round to oval, ribbed, netted, warted or smooth	Green, light green or orange, sweet, aromatic	Dulce, Ogen, Védrantais
	<i>chandalak</i>	Climacteric	Oblate to round, slightly netted, green or yellow	White or green, sweet, less aromatic	Arka jeet
	<i>chate</i>	Climacteric	Elongated, smooth or wrinkled, light to dark green	White to light orange, non-sweet, non-aromatic	Carosello Barese
	<i>dudaim</i>	Climacteric	Round to slightly oval, stripped orange	White, non-sweet, highly aromatic	Queen Anne's pocket melon, Irak (C 1012)
	<i>flexuosus</i>	Climacteric	Long to very long, light green	White, non-sweet	Arya, Faqus
	<i>inodorus</i>	Non-climacteric	Round to oval, white, yellow or dark green	White, sweet, less aromatic	Amarillo, Piel de Sapo
	<i>tibish</i>		Small oval, stripped green	White, firm, non-sweet, non-aromatic	Tibish, Seinat

¹Adapted from: Pitrat, 2008; Burger *et al.*, 2010; Choudhary & Pandey, 2016.

1.1.2 The origin and classification of peach (*Prunus persica* (L.) Batsch)

Peach is native from Asia, western China, where it was originated more than 3000 years ago. It was initially assumed to be originated in Persia, to which its botanical name refers to, but it was not until around the 2nd or the 1st century before the Christian era that it was actually introduced in Persia (Faust & Timon, 1995). It was further obtained by the Romans and reached Europe through Italy, although a simultaneous arrival in France through the Balkan route is also considered (Bassi & Monet, 2008). Around the XVI century the peach was introduced into the Central and South America by the Lusitanian and Spaniard explorers, and then spread through North America by the natives (Hancock, Scorza & Lobos, 2008).

The peach species belongs to the *Rosaceae* family, the *Prunoideae* subfamily, and the *Prunus* genus. Almonds (*Prunus dulcis*), apricots (*Prunus armeniaca*), cherries (*Prunus avium*), or plums (*Prunus domestica*) are also among the nearly 98 species that comprise this genus. There are five main peach species, *Prunus persica* (L.) Batsch, *Prunus davidiana* (Carr.) Franch., *Prunus ferganensis* (Kost. and Rjab), *Prunus kansuensis* Redh., and *Prunus mira* Koehne. The commercial peach cultivars belong to the former one, while the other four are wild species valued for the development of rootstocks or their disease resistance but whose fruits lack eating quality. The peach fruit is a drupe, with a fleshy and non-split mesocarp surrounding a stony and deeply pitted endocarp that contains the seed. Several traits are used to characterize its cultivars: fruit shape (oblong, round or flat), skin type (fuzzy/velvety or glabrous/smooth), flesh color (white, yellow or red 'blood'), texture (melting, non-melting or 'stony-hard'), flesh adherence to the stone (freestone or clingstone), flavor (low-acid or high-acid), among others (Bassi & Monet, 2008; Byrne, Raseira, Bassi, Piagnani, Gasic, Reighard, Moreno & Pérez, 2012).

Table 2. Characteristics of commercial peach fruit varieties (*Prunus persica* (L.) Batsch)¹

Fruit type	Variety	External quality	Internal quality
Peach	<i>persica</i>	Round to oblong shape, variable color, fuzzy skin	Variable color, texture and flesh-stone adherence
Canning peach ("pavía")	<i>persica</i>	Round to oblong shape, mostly yellow, fuzzy skin	Yellow, clingstone, non-melting
Nectarine	<i>nectarina</i> (Aiton) Maxim	Round to oblong, variable color, non-fuzzy skin	Variable color and texture, freestone
Nectarine	<i>nucipersica</i> (Borkh.)	Round to oblong, variable color, non-fuzzy skin	Variable color and texture, clingstone
Flat peach or nectarine	<i>platycarpa</i> L.H. Bailey	Flat shape, variable color and skin	Variable color, texture and flesh-stone adherence

¹Adapted from: Bassi & Monet, 2008; Byrne *et al.*, 2012.

These traits are often used to classify peach fruits according to their botanical variety into peaches, canning peaches, nectarines, and flat peaches or nectarines (Table 2). Peaches (*P. persica* (L.) Batsch var. *persica*) are the fruits with fuzzy or velvety skin type, regardless the color or the texture of the flesh. Within this variety, the clingstone and non-melting fruits are named canning peaches (or “Pavía”) as they are usually intended for the canning industry. Nectarines are the fruits with non-fuzzy or smoother skin, any of the observed flesh colors, and either clingstone (var. *nucipersica* (Borkh.)) or freestone (var. *nectarina* (Aiton) Maxim). Flat peaches (var. *platycarpa* L.H. Bailey) are the flat shaped fruits with any of the skin types, flesh colors, or textures.

1.2 The cultivation of fruit-bearing species

The cultivation of fruit-bearing plants involves a series of techniques comprising the selection of the species, germplasm development, cultivation and management, and the application of specific practices more or less unique for each species. These include plant propagation (e.g. sowing, grafting, pollination), fertilization, irrigation, pruning,

thinning and girdling, harvesting, but also disease and pest control or postharvest handling and storage, among others.

Fruit development can be divided into several stages: cell division, cell expansion, maturation, ripening, and senescence. Cell division and expansion are characterized by an exponential enlargement of the fruit. At the maturation stage, the fruit is considered to be fully developed in size, but it is not until ripening that it will achieve the suitable aroma, flavor or texture to be consumed. Senescence takes place when the fruits become over-ripe and their characteristics deteriorate. The duration of these processes varies with the species and their ripening behavior. Fruits are generally classified into two broad groups based on the role of ethylene in the regulation of their ripening process: climacteric, those with a sharp rise in the respiration rate and ethylene production at the onset of ripening, and non-climacteric, those with little or no ethylene production (Lelièvre, Latchè, Jones, Bouzayen & Pech, 1997). Melon comprises both climacteric and non-climacteric cultivars within a single species, while peaches are climacteric fruit.

1.2.1 The cultivation of melon (*Cucumis melo* L.)

The melon is a diploid species ($2n = 2x = 24$ chromosomes) whose plants are annual, herbaceous, frost-sensitive vines, highly dependent on the temperature and light for growth and production. They are primarily grown in temperate and tropical regions, in fields and gardens, or greenhouses when climate conditions are less favorable. The optimum temperature ranges are between 28-32 °C for germination, 22-23 °C for flowering, and 25-30 °C for plant development. Melon growth performance is greater on deep, well-drained, and loamy soils within a pH range of 6-7.5 (Robinson & Decker-Walters, 1997). It has a low tolerance for acid soils as well as for waterlogged ones. High humidity has a growth reduction effect, compromises fruit quality, and favors the

development of leaf diseases. The fertilization requirements depend on the management practices, variety to be grown, type of soil, and nutrient status of the soil. The application of an NPK fertilizer is recommended before sowing. Melon is generally direct seeded using 2 or 3 seeds per hole with 2 to 4 cm deep, although seedling can also be performed in polyethylene pots or soil blocks. Mulching, i.e., covering the soil with a black or transparent polyethylene sheet, is a common practice in the melon growth as it allows the control of weeds, increases the temperature of the soil and conserves moisture (van der Vossen, El Tahir & Oluoch, 2004). Drip irrigation is considered to be the most adequate irrigation method. Plants have a high demand for water during the fruit growth and maturity, while the irrigation frequency and amount may affect yield and fruit quality traits. A higher water amount was observed to increase yields but decrease soluble solids content (SSC) and pH values (Sensoy, Ertek, Gedik & Kucukyumuk, 2007). Irregular irrigation and high humidity are also among the factors thought to promote fruit cracking (skin fracture), although some cultivars are more susceptible than others (Fernández-Trujillo, Lester, Dos-Santos, Martínez, Esteva, Jifon & Varó, 2013).

According to their ripening behavior, melon fruits can take from 70-75 days after sowing to mature, as the early cultivars of the *cantalupensis* group, to 90-120 days, as the cultivars of the *inodorus* group. A good indicator of full ripeness and harvest time is the partial or complete separation at the abscission zone. The degree of separation of the fruit from the vine is called "slip". Fruits intended for local markets are harvested at 3/4 slip to full slip, while fruits for shipping may be harvested between 1/2 slip and 3/4 slip (Beaulieu, Ingram, Lea & Bett-Garber, 2004). Other maturity indicators used for the harvest of the different melon fruits are the SSC and the change of the rind color. The fruits can reach a size from very small (<100 g), small (100-400 g), medium (400 g to 1 kg), large (1-5 kg), and up to very large (>5 kg and up to 10 kg), and can be round

to slightly ovoid, oblong or long shaped. The rind may be comprised of a primary background color (white, yellow, orange, green, or shades thereof) and a secondary color, i.e., the color of the spots, speckles, wrinkles, warts, stripes, or sutures (e.g. grey, yellow, green). The latter features also define the pattern of the skin (smooth or rough) (Stepansky, Kovalski & Perl-Treves, 1999; Fernández-Trujillo *et al.*, 2011; Monforte, Diaz, Caño-Delgado & Van Der Knaap, 2014). Fruits from the *inodorus* cv. group such as the 'Piel de Sapo' or 'Amarillo' are elliptical shaped and medium to large size. The former has a green background color and is slightly netted while the latter is completely yellow. On the other hand, fruits from the *cantalupensis* cv. group are small to medium-sized and round to ovoid-shaped. These can present a creamy background color and an intensely netted grey pattern like the 'Galia' fruits, or pale grey color with darker green ribs from the stem to the blossom end like the 'Cantaloupe' ones.

1.2.2 The cultivation of peach (*Prunus persica* (L.) Batsch)

The peach is a diploid species ($2n = 2x = 16$ chromosomes) with a deciduous, vigorous and medium height tree. The tree can live for 20 to 30 years, although the commercial plantings are limited to a maximum duration of 12–15 years, due to productivity decrease or cultivar obsolescence. Fruit production begins from the second or third year. Tree performance is enhanced in coarse to medium texture and well-drained soils, with pH values above 6.0, while pH below 5.5 is deleterious for tree growth, longevity, and productivity. However, several cultivars are well adapted or tolerate a different range of soils and challenging conditions. The tree tends to have high water requirements, although it is also very sensitive to waterlogged and anaerobic soil conditions. Irrigation is a standard practice, especially in drier growing areas. Water stress can have negative effects over fruit quality traits such as size, astringency, and lack of red color (Johnson, 2008; Byrne *et al.*, 2012). The temperature requirements are

essential for fruit production and vary with the cultivar. An amount of low winter temperatures is needed (chill-hour accumulation) for the flower buds to break dormancy and start their growth and development during spring when the temperatures are warmer. This is measured in chilling units (CU), i.e., 1 chilling unit equals to 1 hour below 7 °C and may vary from less than 100 CU to over 1000 CU, depending on the cultivar. Most commercial cultivars range between 650-900 CU (Bassi & Monet, 2008). Similarly, an amount of heat is also needed after dormancy to achieve organ development from blooming and leafing to fruit maturation. Fruitlet thinning (removal of the excess of fruitlets) is among the common canopy management practices performed in most cultivars to avoid over-cropping and increase fruit size. Pruning and leaf removal around the fruit, or girdling (bark removal) are also performed and can increase fruit color or size, respectively (Crisosto, Johnson, De Jong & Day, 1997).

The peach harvest season is very wide and can range from mid-April to mid-November in the temperate zone as the fruit development period of the commercial cultivars, from full bloom to the onset of ripening, may range from 55-60 days (very early-ripening cultivars) to 270 days (very late-ripening cultivars) (Bassi & Monet, 2008; Llácer, Alonso, Rubio-Cabetas, Batlle, Iglesias, Vargas, García-Brunton & Badenes, 2009). The fruit maturity varies with the cultivar, market, and use. Fruits for short-distance markets or processing are harvested at more advanced maturity (tree-ripe) and will have a short postharvest life. Fruits for long-distance markets are often harvested at lower maturity to avoid damage during harvest and postharvest management, but this may compromise their ability to ripen and achieve the typical aroma, flavor or textural characteristics (Crisosto, Mitchell & Johnson, 1995). Fruit size, skin and flesh color, firmness, SSC, titratable acidity (TA), or the ratio SSC/TA are common indices used to determine the maturity of peach cultivars. The peach fruit is generally round or slightly oval-shaped whereas flat fruits are flattened in lateral view.

The size of the commercial fruits varies between a diameter of 51 mm to >90 mm and a weight range of 65 g to >300 g (Commission Implementing Regulation (EU) No 543/2011). The skin color of peaches and nectarines can present a variable degree of red over a bright yellow whereas canning peaches ('pavías') are yellow. Flat fruits have a diameter between 55 mm to over 80 mm and a weight range of 85 g to over 120 g. These may be white-cream colored with 70% to 85% of marbled or shaded red over color, like the 'UFO' series, or even 70% to 100% red color, like the 'Mésembrine' cultivar (Nicotra, Conte, Moser & Fantechi, 2002; Pascal, Iglesias, Blanc & Pitiot, 2009; Reig, Iglesias & Echeverría, 2012).

1.3 Considerations about the fruit and vegetable sector

Globalization has been a major driver of the constant evolution of the food chains. The fruit and vegetable chain is no exception. The technological development and innovation of the whole chain, from production to post-harvest handling, storage, distribution, shelf-life extension, or safety and quality enhancement, allowed the trade of fresh fruit and vegetables all over the world. This global trade model was favored by diverse agreements, policies, and incentives leading to more efficient and competitive supply chains (Hawkes, 2009). Nowadays, the fruit and vegetable chain is able to provide the markets with exotic, out-of-season, and available year-round fruit and vegetables. These new supply conditions are shaping the consumer preferences, while the changes in the consumer's demands are also affecting the horticultural chain (Clay, Galvez-Nogales & Wall, 2005; Byrne, 2012).

The global agricultural production reached over 866 million tons (Mt) of fruit and nearly 1.1 billion tons of vegetables during 2017. Almost 9% of the fruit and 9% of vegetables in the world were produced in the EU, which together represented over 50 billion Euros (B€), 16 B€, and 34 B€ respectively. Spain is the 1st fruit (18 Mt) and

vegetable (13 Mt) producing country in the EU. Together with Italy, both Mediterranean countries are in charge of more than 54% of the fruits and 40% of the vegetables produced in the EU (EUROSTAT, 2017; FAOSTAT, 2017). As fruit and vegetables are one of the keys of the agricultural production in the EU, several measures are being developed to improve the sector and the consumption of its produce. Some examples are the regulations and policies addressing the common market organization, financial support, and rural development, market standards concerning the quality expectations of producers and consumers, or promotion campaigns and quality schemes aiming to raise consumer awareness and product marketability (Rossi, 2019).

1.3.1 The economical importance of melon (*Cucumis melo* L.)

Melon is a commercially important horticultural crop throughout the world. In 2017 the melon production reached nearly 32 Mt. China was by far the largest producing country with more than 17 Mt. Among the five main producing countries were also Turkey (1.8 Mt), Iran (1.6 Mt), Egypt (1.1 Mt), and India (1.0 Mt). Spain was among the ten most producing countries right after Kazakhstan and USA, holding the 8th position with nearly 656 thousand tons (Kt) and followed by Morocco and Guatemala. Regarding European Union figures, Spain was the leading country with 37% of the nearly 1.8 Mt of melons produced in 2017 (Figure 1). It was closely followed by Italy, which produced 34% of the EU melons (605 Kt), while France was in charge of 15% (262 Kt). The three countries have been holding their positions as the former European producers of melon during the 2007 – 2017 decade. Spain is also the leading exporter of melon worldwide and, according to the latest available data, more than 65% of the Spanish melon production was intended for export during 2016. Countries such as France, The Netherlands, and Germany are among the main European melon importers (FAOSTAT, 2017).

Melon is the 5th most consumed fruit species in Spain, after orange, banana, apple, and watermelon, and the 2nd most consumed fruit right after watermelon during the period between July and August. In 2017 the nearly 656 Kt of melon produced in Spain represented over 216 M€. The 85% of the production was grown in only three out of the seventeen autonomic communities, the Region of Murcia (33%), Castilla-La Mancha (31%) and Andalusia (22%) (MAPA, 2018).

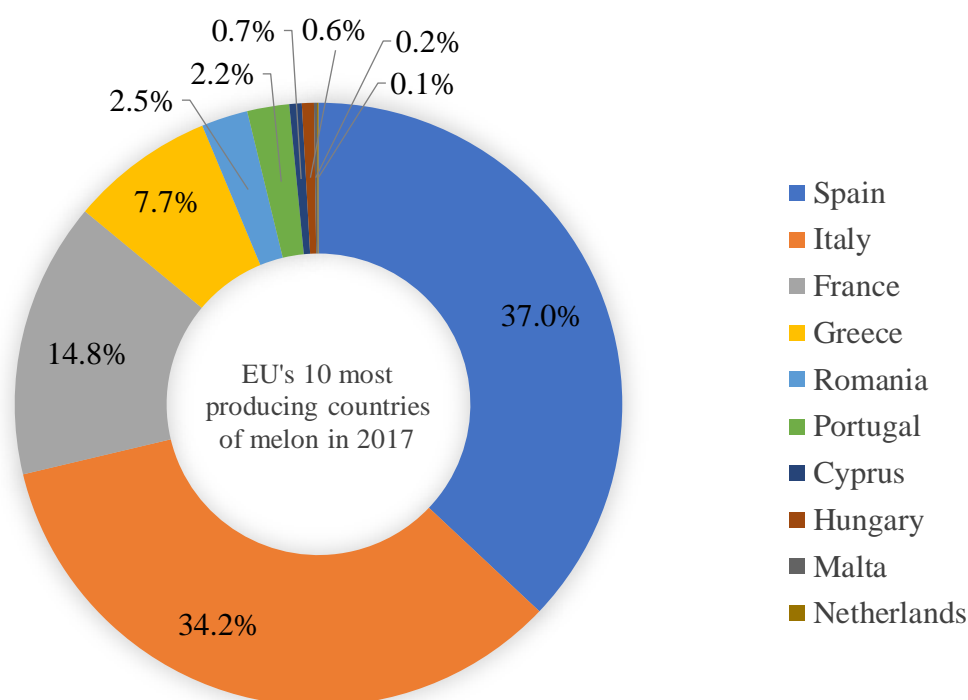


Figure 1. The top 10 of the most producing countries of melon fruit in the EU during 2017 (Source: FAOSTAT 2019).

1.3.2 The economical importance of peach (*Prunus persica* (L.) Batsch)

Peaches and nectarines are the most produced stone fruits in the world and in 2017 their production was higher than 24 Mt. China was, once again, the largest producing country with over 14 Mt, nearly 58% of the global production. Spain was in the 2nd position with almost 1.8 Mt and was closely followed by Italy with 1.3 Mt. Together with 938 Kt from Greece, the three countries were in charge of over 16% of the global peach and nectarine production and 92% of the EU production (4.3 Mt).

These countries held their positions as the three former peach and nectarine producers in the EU during all the 2007 – 2017 decade (Figure 2). Spain is the former EU exporter of peaches and nectarines and, during 2016, more than 45% of the Spanish peaches and nectarines were intended for export. Countries like Germany, France, and Poland are among the former European importers of these fruit types (FAOSTAT, 2017).

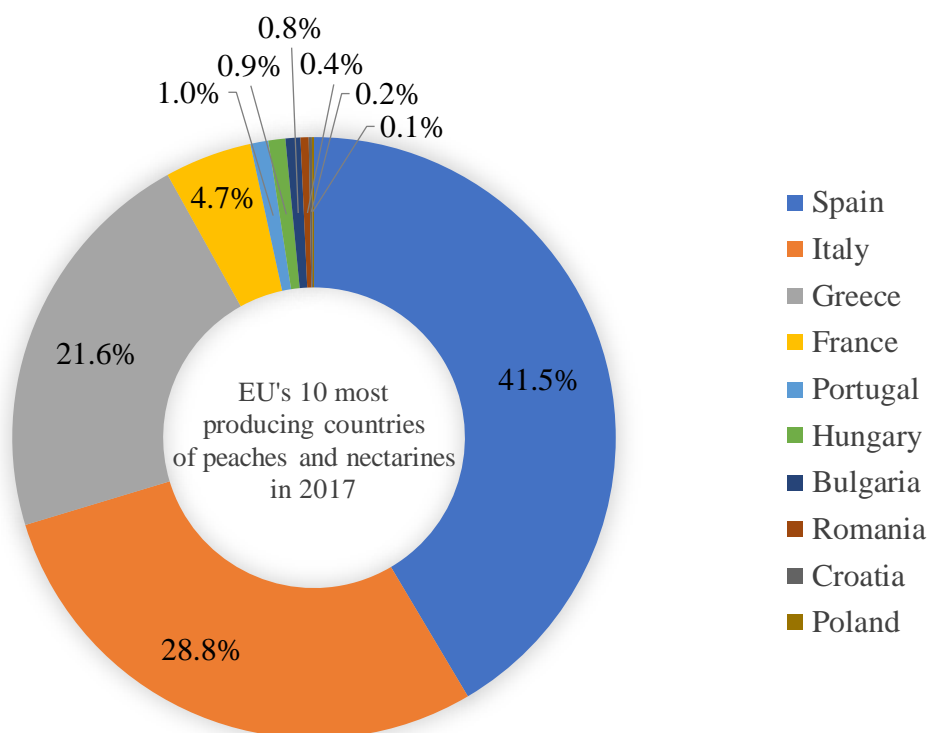


Figure 2. The top 10 of the most producing countries of peach and nectarine fruits in the EU during 2017 (Source: FAOSTAT, 2019).

Peaches and nectarines are the 7th most consumed fruit species in Spain, especially during the period between July and September. The nearly 1.8 Mt of peaches and nectarines produced in Spain in 2017 correspond to over 1 Mt of peaches (including the flat and the canning varieties) and 719 Kt of nectarines. This represented approximately 407 M€ and 401 M€, respectively. The production of more than the 80% of the peaches and 78% of the nectarines was led by Catalonia (29% and 35%, respectively), Aragon (28% and 27%) and the Region of Murcia (23% and 16%) (MAPA, 2018).

1.4 Considerations about the consumption of fruit and vegetables

The insufficient consumption of fruit and vegetables is among the major risk factors attributable to the global disease burden, together with high blood pressure, high blood glucose, overweight and obesity, and high cholesterol. According to the WHO, an inadequate fruit and vegetable intake was estimated to cause about 31% of ischemic heart disease, 19% of gastrointestinal cancer, and 11% of stroke worldwide (WHO, 2002; 2003). This has led to the creation of several strategies with the aim to promote the increase in consumption of fruit and vegetables worldwide, such as the Joint WHO/FAO Fruit and Vegetable Initiative launched in 2003. By that time, the joint WHO/FAO expert consultation on diet, nutrition and the prevention of chronic diseases recommended a minimum individual intake of 400 g per day, the equivalent to five servings of 80 g each, of fresh and varied fruit and vegetables. This recommendation is still up to date as part of a healthy diet low in fats, sugars, and sodium. Despite this recommendation, there are several countries and regions where the population shows a huge gap between the recommended intake and consumption. According to a survey among the EU countries, nearly 36% of the populations did not eat fruit and vegetables on a daily basis, while the percentage of the population who consumed fruit or vegetables at least once a day was 37% and 40%, respectively (EUROSTAT, 2017).

The fruit and vegetable intake is known to vary considerably among countries and population groups as a reflex of economic, cultural, and agricultural environments, but its accurate measurement is complex. There is a lack of agreement in the definition and classification of these food groups concerning the inclusion or exclusion of specific products. Potatoes, starchy roots/tubers, and legumes are often not considered as vegetables in many dietary guidelines, while nuts, dried fruits, olives, and avocados are not considered as fruits. Similarly, the estimations on food intake may be excluding composite foods that contain fruit or vegetables as ingredients leading to underestimated

values (Agudo, 2005). According to the latter author the different methods of dietary assessment, as well as their inherent measurement scales or sources and types of error, should also be considered. Since estimations from food balance sheets or household surveys provide different outcomes, cautious interpretations and comparisons are also advised.

1.4.1 Factors influencing the consumption of fruit and vegetables

The factors that influence food consumption can be divided, according to how these relate to consumer response or behavior, into consumer factors (such as expectations), environment factors (such as socio-economic), and food factors (such as sensory characteristics). Although this section will focus on the latter, it is important to consider that the behavior of consumers is complex and can be affected by interactions between multiple factors (Meiselman, 2007). For example, the place of origin may have an indirect influence over the sensory quality expectations for certain fruit and vegetables (Brueckner, 2014). Some of the consumer- and environment-related factors that most influence fruit and vegetable consumption are related to health, socio-economic, and convenience considerations. Fruit and vegetables are closely linked to a healthy lifestyle due to their high nutritional value. Their consumption is part of any dietary guideline and can be influenced by personal beliefs, attitudes, and claims, as many of them, including melons and peaches, have been investigated for numerous health benefits. Socio-economic factors such as gender, culture, education level, or income-cost relationship also have to be considered. Additionally, convenience comprises year-round availability, extended shelf-life, easiness and readiness to eat, and suitability for different types of meals. In this regard, fruits such as bananas or apples are generally more able to fit these considerations than fruits like melons and peaches (Jaeger, 2006).

Sensory factors reflect the quality and play a significant role in the consumers' choices before the eating process, on the pleasure and enjoyment experienced while eating and on the fulfillment of quality expectations. This sensory interaction between food and consumer is the basis of food acceptance (Costell, Tárrega & Bayarri, 2010). Appearance traits such as color, shape, finish or gloss, absence of imperfections, and hand-perceived firmness are assessed before the consumption and determine the attractiveness and purchase intention of fruit and vegetables (Barrett, Beaulieu & Shewfelt, 2010). Consumers generally use these traits to infer the degree of maturity, freshness, and flavor-related factors that might create expectations of overall quality, which will not always be fulfilled. For certain fruits, the color, size, shape or finish are useful to distinguish between individual varieties or fruit typologies. This is the case of peaches, nectarines, and flat peaches, or *cantalupensis* and *inodorus* melon varieties. The discrimination of produce based on size or shape will depend on the final use as these aspects influence the easiness to peel or bite, while the presence of appearance defects might be acceptable depending on the culinary use. Likewise, hand-perceived firmness may allow a quick measure of differences in overall firmness between fruits of certain species (Kays, 1999). Flavor (aroma and taste) or textural parameters influence consumer's acceptance during and after consumption, reflecting their behavior with regard to future decisions. Although taste or flavor are generally thought to be the most important aspects influencing consumption, their interaction with texture is more likely to cause rejection among fruit and vegetables (Harker, Gunson & Jaeger, 2003). Consumers have particular expectations for fresh produce. Juicy, flavorful, and with good overall texture fruits are more likely to be preferred than mealy, bland, and excessively firm ones. Similarly, the presence of off-flavors or losses of textural properties, such as firmness and crunchiness, are associated with a lack of freshness and lead to negative consumer responses. Additionally, different consumer segments can

have different preferences for a single fruit species. These can be due to the preference of different varieties or cultivars within a species or to the preference of different maturity stages of a specific variety or cultivar. Some consumer segments prefer crisp and sweeter fruits and others prefer juicy and more acidic ones. For certain cultivars, mature fruits have softer flesh, low acidity, and a fruitier flavor, while less mature ones have a firmer, high acidic flesh with a grassy/green flavor (Harker *et al.*, 2003; Iglesias & Echeverría, 2009; Shewfelt, 2014).

1.4.1.1 Sensory factors influencing the consumption of melon

Unlike other fruit species, the purchase intention of melon fruits is not often related to appearance traits. Consumers cannot use external color, size, shape, or hand-perceived firmness to infer the overall quality of melon fruits (Khatri, Wei & Wei, 2008). Yet, it was suggested that size and shape might influence fruit preference of *inodorus* fruits (Lester & Shellie, 1992; Pardo, Alvarruiz, Varón & Gómez, 2000). As fruit appearance can be extremely different, traits such as shape allow consumers to easily distinguish between fruits belonging to *cantalupensis* (round to ovoid-shaped) and *inodorus* (elliptical-shaped) cultivar groups, while skin pattern and external color between varieties within the same cultivar group (e.g. Galia and Cataloupe, Piel de Sapo and Amarillo).

The major factors reported to affect consumer preference of melons are related to flavor or texture traits. The sweetness was observed to be determinant for melon acceptance, as it is associated with high flavor intensity. Some authors have also suggested that a moderate acidity might be able to drive consumer's liking of certain cultivars (Albuquerque, Lidon & Barreiro, 2006; Escribano, Sánchez & Lázaro, 2010), although commercially available varieties lack acid taste (Burger, Sa'ar, Paris, Lewinsohn, Katzir, Tadmor & Schaffer, 2006). Flesh color, fruity aroma intensity,

firmness, and juiciness are other traits that influence consumer preference. Globally, the sweeter and juiciest melons are preferred by consumers, while fruits perceived as too firm or too fruity might be rejected (Pardo *et al.*, 2000; Escribano *et al.*, 2010) as these might be associated with unripe or overripe traits, respectively. Juiciness was observed to be the main factor influencing consumer's acceptance among non-climacteric cultivars (Lázaro & de Lorenzo, 2015). The latter authors identified consumer segments according to the combination of different textural traits, one main segment of consumers who preferred high juicy, medium-firm, and medium-high fibrous fruits, another formed by consumers who preferred less-firm fruits, and the third one of consumers who preferred less fibrous fruits.

1.4.1.2 Sensory factors influencing the consumption of peach

Traditionally, peach consumers have based their purchase intention on traits such as skin color, size, or firmness. Today, there is a numerous variety of peach cultivars and these traits are available in as many variations as consumer preferences. These appearance traits are still determinant drivers of preference for a high number of consumers (Zhou, Yue, Zhao, Gallardo, McCracken, Luby & McFerson, 2018), although there are also consumer segments more receptive to small-sized fruits (Olmstead, Gilbert, Colquhoun, Clark, Kluson & Moskowitz, 2015). Similarly, while an almost solid red skin color is preferred among European and American consumers, a mainly or even total yellow color has a good acceptance among the Spanish ones (Byrne *et al.*, 2012). Other appearance factors that influence purchase intention are the presence of speckles or lenticels over the skin of nectarines, or the sensitivity to fruit cracking of both nectarines and flat varieties, which may limit their acceptance.

Regarding the traits assessed during and after consumption, sweetness has been consistently reported as the main driver of liking of peach fruit. However, the

interaction between sweetness and acidity is thought to be more important for consumer acceptance than sweetness alone (Crisosto, Crisosto, Echeverria & Puy, 2006). Flesh color, aroma and flavor intensity, and texture are also among the main drivers of liking. Globally, consumers prefer yellow-fleshed, sweet, flavorful, smooth or slightly soft, and juicy peaches, while too firm, mealy, pasty and dry fruits are rejected (Kelley, Primrose, Crassweller, Hayes & Marini, 2015; Olmstead *et al.*, 2015; Zhou *et al.*, 2018). Due to the availability of cultivars with different combinations of these traits (e.g. low or high acidity, melting or non-melting flesh), different consumer segments have been identified. While certain consumer segments prefer sweeter and melting-texture varieties, others prefer crisp and non-melting fruits with high flavor intensity (Olmstead *et al.*, 2015). Segments formed by consumers with an opposed preference for high-acid cultivars, or the preference for grassy/green and pit (woody) aromas were also observed (Delgado, Crisosto, Heymann & Crisosto, 2013). Another trait reported to drive the overall liking of some cultivars is astringency, possibly through the indirect effect of its interaction with acidity and sweetness (Predieri, Ragazzini & Rondelli, 2006).

Additionally, consumers use appearance traits to choose between peaches, canning peaches, nectarines, or flat fruits but are unable to distinguish the diversity of cultivars with different sensory profiles and similar appearance. As this is thought to influence buying intention and acceptance, it has been suggested that a classification based on the internal fruit traits is needed (Iglesias & Echeverría, 2009; Byrne, 2012).

1.5 Fruit quality

Fruit quality is a multidisciplinary concept that relies on the biochemical changes occurring during the development, maturation and ripening processes, on the pre-, at- and post-harvest management conditions, on the storage and shelf-life performance, but also the pest and disease resistance, or the environmental conditions,

among others (Kader, 2008). The different biochemical processes that take place during ripening result in changes in the external and internal fruit traits that determine the sensory, physicochemical, and nutritional quality of fruit.

The fruit quality is also a common objective of the breeding programs. In the past, the breeders were focused on the appearance, firmness, and improvement of handling, storage and shelf-life performance as these are important traits to meet the market quality requirements (Byrne *et al.*, 2012). This has led to the trade of several fruit cultivars with poor sensory quality and, ultimately, to consumer dissatisfaction. More recently, several fruit species were bred for higher SSC and their quality based on the determination thereof, or the ratio between this and TA. However, this approach did not consider the role of the individual sugars, organic acids, or volatile organic compounds (VOCs) on the flavor perception (Colaric, Veberic, Stampar & Hudina, 2005). Today, many breeding programs consider the antioxidant and nutritional compounds, volatile and non-volatile constituents, and sensory attributes in order to achieve the production of fruits with consistent quality and promote fruit consumption (Kader, 2008; Reig, Iglesias, Gatus & Alegre, 2013).

1.5.1 Sensory quality

The sensory quality of fruit, as of any other food product, concerns the sensory properties that are perceived through the human senses of vision (sight), audition (hearing), gustation (taste), olfaction (smell), somesthesia (touch), and kinesthesia (movement). The assessment of the sensations within the attributes of appearance, aroma, taste, flavor, or texture, together with differences in their magnitude (intensity) and duration (persistence), is the basis of the sensory science. Through the processing of this perceptual information, it is possible to determine the acceptance of food (Cardello, 1996; Lawless & Heymann, 2010).

1.5.1.1 Appearance

The appearance of food is characterized by color, size, shape, gloss (shine), visual surface texture, among other properties determined by the sense of vision. The perception of appearance occurs as light is reflected from an object and enters the eye to reach the retina, where the visual receptors generate neural impulses that will travel through the optical nerve and get into the brain to be interpreted (Kemp, Hollowood & Hort, 2009). Appearance attributes are related to the degree under which the light is transmitted, absorbed, or reflected when it hits a food product. Among these attributes, color plays a significant role in food appearance as it is the visual attribute that most influences food acceptance. The interaction of color with other sensory attributes such as aroma or flavor might influence attribute recognition, discrimination, or intensity measurements (Cardello, 1996).

1.5.1.2 Texture

The texture is the sensory and functional manifestation of the structural, mechanical, and surface properties of foods detected through the senses of vision, hearing, touch, and kinesthetics. As a multi-parameter attribute, texture comprises the perception of three main types of characteristics: mechanical, those related to the responses of foods to applied forces (such as firmness, chewiness or cohesiveness); geometrical, those related to size, shape or orientation of food (such as smooth, grainy, flaky or fibrous); and moisture or fat-related, those related to the water and/or fat content of food (e.g. juiciness, oiliness, dryness). These parameters are perceived once the food gets inside the mouth and during chewing, when the food interacts with teeth, tongue, saliva, the muscles and joints of the jaw, and the somesthetic and kinesthetic receptors in the oral cavity (Cardello, 1996; Szczesniak, 2002). This reflects the complexity of the oral processes occurring in the mouth, known to affect the breakdown

of the physicochemical structure of the food. Additionally, further than its direct contribution to consumer acceptance, texture has an important role as a modulator of flavor release. The release of taste and aroma compounds is strongly dependent on the mechanisms under which the food structure breaks down in the mouth and, thus, on the initial texture of food and its change during mastication (Kilcast, 2004; Wilkinson, Dijksterhuis & Minekus, 2010; de Lavergne, van de Velde & Stieger, 2017).

1.5.1.3 Aroma

Aroma perception is characterized as the odor of a food product when volatile compounds stimulate the olfactory receptors by two different routes: via the nose by smelling (orthonasal olfaction), or via the mouth as these reach the nasopharynx by eating and drinking (retronasal olfaction). This duality confers the olfactory system with the ability to perceive and evaluate food in two different ways, in the outside and the inside of the body. Although smelling refers to the perception of food outside the mouth and tasting to its perception inside the mouth during consumption, the existence of complex interactions between the senses of smell and taste (at a flavor level) has been the object of several studies. These studies have focused on the misconception of attributing taste qualities to the sense of olfaction, such as those using "sweet" or "sour" terms to describe odors; on the extent to which odor and taste components form an appropriate combination in a food product (congruency); on the ability of odors to modify taste qualities, such as the sweetness enhancement and suppression effects; and on the detection of subthreshold concentrations of different taste-odor pairs, among others (Rozin, 1982; Schifferstein & Verlegh, 1996; Delwiche, 2004; Auvray & Spence, 2008). Moreover, other studies have focused on the mechanisms involving the interactions between the different stimuli, i.e., whether these can occur at a physicochemical, physiological, or psychological level. The former occurs between

different compounds at the level of the food matrix composition, whereas the latter occur between individual stimuli at the level of specific olfactory and oral receptors, and at a cognitive level once the signals are transmitted by the receptors to the brain (van Ruth & Roozen, 2002; Keast & Breslin, 2002; Poinot, Arvisenet, Ledauphin, Gaillard & Prost, 2013; Arvisenet, Guichard & Ballester, 2016; Thomas-Danguin, Barba, Salles & Guichard, 2016).

1.5.1.4 Taste

Taste involves the gustatory perception of four classical taste quality attributes: sweet, sour, salty, and bitter, by the taste receptors located on the tongue and mouth surfaces. Other qualities that have been proposed to join this category are umami (savory), metallic and astringent tastes. Umami is an oral sensation stimulated by salts of glutamic or aspartic acids, while metallic is occasionally used to describe the side tastes of sweeteners such as acesulfame-K and is a sensation experienced in certain taste disorders. The perception of astringency is complex and extensively reviewed in the literature but there is a lack of consensus about its definition further than being a sensation elicited by both mechanical (tactile) and chemical stimulation (Lawless, Horne & Giasi, 1996; Lawless & Heymann, 2010). The interaction between taste compounds has also been the object of numerous studies. When multiple taste stimuli are presented together, different effects are possible including the perceptual enhancement or suppression, the unmasking of a taste not initially perceived, or even the chemical synthesis of a new taste (Keast & Breslin, 2002; Thomas-Danguin *et al.*, 2016).

1.5.1.5 Flavor

The flavor relies on the complex combination of aroma and taste modalities inside the mouth. However, other senses affect the overall perception of flavor such as somesthetic (touch, temperature, and pressure), kinesthetic (position and movement), trigeminal (chemical sensitivity or irritation), visual, and auditory, for which reason flavor is considered a multisensory perceptual system. Though the chemical irritation sensations (e.g. burning, cooling, pungent) are perceived in the oral and nasal cavities as well as in the external skin, they are not mediated by taste and odor receptors but by somesthetic receptors as they reflect tactile and thermal sensations. Others can also stimulate the trigeminal nerve without burning or painful sensations. Examples of chemical irritative sensations are the ones from spices, onions, menthol, certain compounds like butyl acetate (with a fruity odor), and even from salt (NaCl) or citric acid at moderate to high concentrations. Astringency and metallic taste are sometimes grouped here. The role of visual cues over flavor perception has to do with the association of certain flavors with specific colors. The flavor identification decreases when the foods are miscolored, and the flavor intensity increases as the color level increases. The influence of audition on the perception of flavor has been mainly focused on textural properties (crunchy, crispy, brittle). The pitch and loudness of the sound produced during chewing contribute to the overall sensory impression and allow the assessment of the freshness or staleness of food. The temperature has also been shown to influence flavor perception. While temperature itself was observed to elicit taste perception, higher temperatures increase the release of VOCs from a food sample and, thus, odors become more intense (Delwiche, 2004; Auvray & Spence, 2008, Spence, 2016).

1.5.1.6 Methods of sensory evaluation

The classical methods used to perform sensory analyses are classified into three different types based on their primary purpose. The affective tests aim to quantify the degree of liking or disliking of a product (e.g. 9-point hedonic scale). These tests involve the selection of untrained panelists who represent the target market or are regular consumers of a product to understand their opinion or preference about that product. Affective tests require an appropriate panel size, formed of about 100 consumers, and may be useful to have an overview over consumer segments with preferences for different product characteristics. The discrimination or difference tests aim to determine whether two or more samples are perceptibly different (e.g. triangle test, duo-trio test, paired comparison test). These tests are performed by a panel made of either untrained or trained panelists, generally selected for their ability to detect product differences. Difference tests are generally used for quality control purposes and require a simple data analysis based on the proportion of correct answers. The descriptive analysis tests quantify the perceived intensities of the sensory attributes of a product to provide the most complete sensory profile of that product (e.g. Flavor Profile® method, Texture Profile® method, or Quantitative Descriptive Analysis®). These tests are used in different contexts such as quality control and assurance, comparison of prototypes to evaluate the effect of different ingredients or processes during product development and improvement, the study of product changes over time for shelf-life estimation, understand consumer acceptance, and investigate the relationships between sensory and instrumental measurements (Kemp *et al.*, 2009; Lawless & Heymann, 2010; Murray, Delahunty & Baxter, 2001).

The descriptive analysis tests can be adapted or combined in different ways to be used as a "generic descriptive analysis" and allow the use of different methods according to the needs of a project or research question. The common phases in

descriptive analysis include the selection and training of the panelists, the evaluation of their repeatability and reproducibility, and the sensory evaluation of the samples. The panel is formed by a minimum of 8 panelists selected by their sensory ability and trained to understand the attributes and their intensity within a product category. During the training phase, the panelists are exposed to a subset of samples representative of the product category as well as reference standards to exemplify the perception of a particular attribute. Panelists will generate specific attributes that describe the similarities and differences within the product category and discuss their meaning and evaluation protocol, i.e., the order of attribute assessment, the way in which the samples need to be assessed, and how the senses will be cleansed between samples. Then they are trained in the use of the scale to rate the intensity of the selected attributes for the particular sample set. Once the training is completed, panelists must be evaluated, both individually and the panel as a whole, for their performance: panelist discriminating ability, panelist reproducibility, panelist agreement with the panel as a whole, panel discriminating ability, and panel reproducibility (Kemp *et al.*, 2009; Lawless & Heymann, 2010). This can be achieved by providing the panelists with a subset of samples for evaluation, in triplicate, and use the data to perform the appropriate univariate or multivariate statistical methods. The individual panelists and panel performance can be easily assessed by calculating the mean and standard deviations (or the coefficient of variation) for each attribute across all the samples and replicates. One-way Analysis of Variance (ANOVA) can be used to assess the differences between panelists when they evaluate the same sample and the ability of the individual panelists to discriminate between samples. Three-way ANOVA, considering sample, panelist or replicate as main effects, and 'panelist x sample', 'panelist x replicate' or 'sample x replicate' as interactions, will allow the assessment of the panelist performance with regard to the panel as a whole. A principal component analysis (PCA), or PCA-based

methods such as the Tucker-1 method, performed on each attribute will allow a visual evaluation of the agreement of the panelists for that attribute. Panel and/or panelist performance can also be visually evaluated through different plots such as the Manhattan plot, correlation plots, profile plots, and eggshell plots, among others (Næs, Brockhoff & Tomić, 2010). Lastly, the experimental samples are assessed under standard sensory practices (e.g. ISO regulations) and according to the experimental design previously defined, concerning the randomization, the sample presentation method (monadic or simultaneous), replication, and the size of the panel.

1.5.2 Physicochemical quality

The physicochemical quality of fruit comprises the external and internal (compositional) parameters measured through physicochemical determinations. These may include size, color, SSC, acidity, textural properties, and VOCs, among others. Many of these parameters allow the definition of the appropriate ripening and harvest times and are used as common indices to achieve ideal quality standards. The physicochemical parameters of fruit can be determined or monitored using destructive and/or non-destructive methods. Some of these parameters, such as SSC or flesh firmness, may be assessed using common destructive methods using a hand refractometer or a penetrometer, respectively. Others, such as VOCs, soluble sugars or organic acids, require more elaborated laboratory equipment like chromatography or mass analysis devices. On the other hand, parameters such as color or SSC can be assessed through non-destructive methods using a colorimeter or visible/near-infrared (vis/NIR) spectroscopy devices (Costa, Fiori, Noferini & Ziosi, 2006; Nicolai, Defraeye, De Ketelaere, Herremans, Hertog, Saeys, Torricelli, Vandendriessche & Verboven, 2014). Despite the advances in the development of non-destructive methods, the assessment of several fruit quality parameters still relies on the simplicity of the

destructive ones. Today, both kinds of methods lead to real-time information and even if, arguably, non-destructive methods can be performed over all the fruits of a harvest, time and cost constraints may be still limiting their extensive usage.

1.5.2.1 Textural properties

The textural properties of fruit depend on the composition and structure of their cell walls, the turgor pressure, and the changes arising from the different biochemical and physiological processes that take place during ripening. The measurement of some of these properties is often used by fruit producers as a maturity index to assure and enhance quality throughout the whole chain. Also, several textural properties of fruit are key for its acceptance as these are not only perceived by the consumers as a synonym of quality, but also as a synonym of freshness and wholesomeness (Fillion & Kilcast, 2002).

The definition of texture is a sensory consideration (ISO 5492: 1992). Although from a physical approach, it belongs under the group of mechanical or rheological properties of food. Rather than a single property, texture represents a group of physical properties that are mainly perceived inside the mouth by the senses of touch, derive from the structure of food, and can be measured instrumentally (Bourne, 2002). The methods for the instrumental measurement of textural properties can be classified into fundamental, empirical, or imitative tests. Fundamental tests measure properties such as viscosity or elasticity and some examples are ultimate strength, Poisson's ratio or Young's modulus; empirical tests measure parameters generally related to textural quality such as firmness or tenderness, using a penetrometer (e.g. the Magness-Taylor test) or a shear device (e.g. the Warner-Bratzler shear); and imitative tests imitate the conditions to which a food product is subjected inside the mouth during eating and can be performed with a tenderometer or a texturometer (Szczesniak, 1973). The application

of fundamental tests in a food science context is rather limited, due to their assumption of sample homogeneity and uniformity, which is rarely the case of food samples. The empirical tests are the most used today as these are easy to perform, fast and affordable, although these are more suitable for quality control while imitative tests allow a higher extent of correlation with sensory methods (Bourne, 2002).

Among the empirical tests, puncture testing is a widely used method for the measurement of fruit firmness, either using a hand penetrometer or a probe coupled to a motorized testing machine (e.g. a texturometer). Both systems measure the force needed for the plunger or probe to penetrate into a fruit sample, at a constant distance. In the former, the firmness value can be directly read in the device, while the latter draws a force-deformation curve providing the parameters: slope (modulus of elasticity), F_{max} (the maximum puncture force), and the area under the curve (energy required to penetrate the sample). Additionally, it is possible to determine the relative proportions of compression and shear of a puncture force if two probes of different diameters are used, i.e., it can be determined whether a sample failure is dominated by a compression strength, a shear strength or a combination of both (Bourne, 1966). Among the imitative tests, the Texture Profile Analysis (TPA) is the method that allows the higher correlations with sensory analysis, as it was designed to imitate the behavior of food while being chewed. Initially, the method was developed in parallel with the General Foods Texturometer, although it was adapted to other testing machines (e.g. Instron or Stable Micro System's). It is based on the double compression of a bite-size food sample by a flat cylindrical probe, at predetermined speed and compression. The result is a force-time curve that allows multiple textural parameters to be quantified: fracturability (force at which the sample breaks during the first compression cycle), hardness (height of the force peak on the first cycle), cohesiveness (ratio of the positive areas under the second and the first compression), adhesiveness (negative area of the first cycle),

springiness (height that food recovers during the period of time between the end of the first cycle and the beginning of the second), gumminess (the product of hardness and cohesiveness), and chewiness (the product of hardness, cohesiveness, and springiness) (Szczesniak, Brandt & Friedman, 1963; Bourne, 1978). Note that gumminess should be reported for semi-solid foods and chewiness for solid ones since the same product cannot exhibit both properties, and even if as a solid it could become semi-solid during mastication, this transition cannot be measured through a TPA test (Szczesniak, 1995).

1.5.2.2 Soluble solids content

The determination of the SSC is essential for the assessment of internal fruit quality. The soluble solids comprise the amounts of sugars, organic and amino acids, as well as small amounts of dissolved polysaccharides, proteins, pigments, phenolic compounds, vitamins, and minerals. In many fruits, sugars (sucrose, glucose, and fructose) and sugar alcohols (such as sorbitol or mannitol) may constitute up to 85% of the total soluble solids and for this reason SSC is generally used to estimate sugar content and sweetness (Magwaza & Opara, 2015). The SSC is also widely used as a maturity index to determine the appropriate harvest time of numerous fruit species, as sugar accumulation increases with maturity and sweetness is one of the determinant parameters for consumer acceptance.

The SSC can be measured using a simple hand refractometer and the results are expressed in Brix degrees (°Brix), or through non-destructive methods such as vis/NIR spectroscopy and hyperspectral imaging. In the past years, the use of vis/NIR spectroscopy for the prediction of SSC has been extensively investigated and the improvements on the accuracy of the predictions have led to its successful application to several fruit species (Nicolai *et al.*, 2014).

1.5.2.3 Acidity

The acidity of fruit can be measured by pH and/or TA. pH represents the acidity due to the activity of free hydrogen ions (H^+), while TA measures the amount of weakly bound H^+ released from the organic acids present in fruit (e.g. citric, malic, quinic, tartaric) (Lobit, Soing, Génard & Habib, 2002). The determination of pH can be performed using a pH-meter and TA is generally done by titration of a known volume of fruit juice with a NaOH (0.1 M) solution up to an endpoint of pH near 8.0, through manual or automatic titration. TA results can be expressed in g of the major acid/L, although other units are accepted.

In many fruits, an increase in pH values occurs in parallel with a decrease of TA and both parameters may be inversely correlated, but this is not observed for all the fruits. TA is generally used along with the SSC (SSC/TA ratio) as a maturity index to determine the harvest time of several fruits. The relevance of the TA or SSC/TA ratio as quality indices depends on the type of fruit being evaluated. TA has shown to be a good quality index of fruits showing significant acidity changes during maturity. For these fruits, the balance between sugars and acids influences consumer acceptance, as observed for citrus (Lado, Rodrigo & Zacarías, 2014) or peaches (Crisosto *et al.*, 2006). But for fruits showing small acidity changes during maturity, the TA is less relevant in comparison to SSC alone, as previously reported for melons (Beaulieu, Lea, Eggleston & Peralta-Inga, 2003).

1.5.2.4 Volatile organic compounds

The majority of fruits produce a wide range of VOCs during ripening. The differences in the combination of VOCs, their concentration, and the perception threshold of each individual compound are the key to the distinctive aroma of a specific fruit species or cultivar. The VOCs of fruits are synthesized through different metabolic

pathways and can be classified according to their precursors as lipid-derived compounds, amino acid-derived compounds, phenolic derivatives, and mono and sesquiterpenes (Schwab, Davidovich-Rikanati & Lewinsohn, 2008; El Hadi, Zhang, Wu, Zhou & Tao, 2013). Some volatiles may also arise from the interaction of more than one pathway or from enzymatic modifications that will lead to the biosynthesis of new VOCs. The volatile profile of fruit is influenced by factors like cultivar, ripening stage, harvest conditions, storage, as well as the different analytical methodologies used for their determination. Regardless of the biosynthetic pathway of VOCs formation, it depends on the availability of precursor substrates and the activity of the specific enzymes involved in each pathway, although some of the processes are still not fully understood (Defilippi, Manríquez, Luengwilai & González-Agüero, 2009).

Fatty acid-derived volatile compounds are formed by three main oxidative processes, α -oxidation, β -oxidation, and the lipoxygenase (LOX) pathway. The α - and β -oxidation involve the enzymatic degradation of free fatty acids and the generation of short- and intermediate-chain length fatty acids. Further β -oxidation results in the successive removal of C_2 units (acetyl CoA), leading to short- and medium-chain linear carboxylic acids. Alcohols, esters, and aldehydes are generated as further volatile metabolites by the action of alcohol dehydrogenases (ADHs) or alcohol acyl transferases (AATs). AATs can synthesize a wide range of esters by combining the appropriate alcohols and acyl CoAs, while ADHs reversibly metabolize aldehydes into alcohols and provide the substrate for ester formation (Schwab *et al.*, 2008; Wüst, 2017). The LOX pathway involves the oxidation of C_{18} unsaturated fatty acids to form the green leaf volatiles, i.e. saturated and unsaturated C_6 and C_9 aldehydes and alcohols. Fatty acids, such as linoleic and linolenic acids, undergo dioxygenation in a reaction catalyzed by LOXs, leading to the formation of hydroperoxides. These are further metabolized by hydroperoxide lyases (HPLs) and allene oxide synthase (AOS), among

other enzymes, to generate VOCs. HPLs cleave the LOX products leading to the formation of C₆ and C₉ aldehydes, which are further metabolized to form the corresponding alcohols by ADHs. The AOS catalyzes the reactions of the LOX pathway that give rise to the formation of jasmonic acid (Dudareva, Negre, Nagegowda & Orlova, 2006). The biosynthesis of lactones is also fatty acid related as it combines both β -oxidation and the LOX pathways. Although lactones have their origin in the corresponding carboxylic acids, these may be formed through different routes, reduction of oxo acids, reduction of hydroperoxides, hydration of unsaturated fatty acids, and epoxidation of unsaturated fatty acids (Schöttler & Boland, 1996).

The metabolism of amino acids generates a wide diversity of volatiles. The initial steps in the biosynthesis of amino acid-derived volatiles involve deamination or transamination to form α -ketoacids. It follows decarboxylation to aldehydes and further reductions, oxidations or esterifications lead to the formation of alcohols, acids, and esters. These processes comprise the enzymatic activity of aminotransferases, decarboxylases, and ADHs. Branched-chain volatile alcohols, aldehydes and esters arise from the branched-chain amino acids valine, leucine, and isoleucine (Dudareva *et al.*, 2006; Pérez & Sanz, 2008). Benzenoid and phenylpropanoid compounds originate from phenylalanine, previously converted to cinnamic acid. Further hydroxylation and methylation reactions lead to the formation of hydroxycinnamic acids, aldehydes, and alcohols, while the synthesis of benzenoids occurs via a β -oxidative pathway, a non-oxidative pathway or a combination of both (Schwab *et al.*, 2008; Dudareva, Klempien, Muhlemann & Kaplan, 2013). Other important amino acid-derived compounds are the sulfur-containing or nitrogen-containing volatiles, as well as the cyanogenic glycosides. The latter are precursors of volatile ketones or aldehydes through the cyanogenesis of valine, isoleucine, or phenylalanine (Vetter, 2000). Sulfur-containing volatiles, such as volatile thiols or sulfur esters originate from methionine and cysteine, under the

enzymatic action of methionine γ -lyase and aminotransferase (Gonda, Lev, Bar, Sikron, Portnoy, Davidovich-Rikanati, Burger, Schaffer, Tadmor, Giovannonni, Huang, Fei, Katzir, Fait & Lewinsohn, 2013). Nitrogen-containing compounds such as glucosinolates are intermediates of volatile isothiocyanates, thiocyanates, and nitriles that are formed as a result of glycoside hydrolysis, while pyrazines are originated from valine, leucine or isoleucine but their biosynthesis is not fully understood (Rizzi, 2002; Wüst, 2017).

Two classes of compounds originate directly from the mevalonic acid (MVA) and the methylerythritol phosphate (MEP) pathways. The former leads to the formation of sesquiterpenes, and the latter to hemiterpenes, monoterpenes, and diterpenes. These are all derived from the common building units, isopentenyl diphosphate and dimethylallyl diphosphate, under several enzymatic actions, including the ones of terpene synthases (TPSs) and prenyltransferases. Other terpene volatiles may be formed through the transformation of the TPSs products by hydroxylation, dehydrogenation, and acylation, among other reactions. Additionally, carotenoids are also precursors of volatile norisoprenes (apocarotenoids) by an oxidative cleavage followed by enzymatic and non-enzymatic transformations (Schwab *et al.*, 2008; Dudareva *et al.*, 2013). The biosynthesis of furanones is still not well understood. One of the hypotheses is based on the conversion of fructose to form furaneol, the key metabolite of the pathway, leading to the subsequent formation of mesifurane and furaneol glucoside. This would occur through a series of unknown reactions involving hydrogen transfer, dehydration, and enzymatic methylation, initially catalyzed by an enone oxyreductase (Pérez & Sanz, 2008).

Gas chromatography-mass spectrometry (GC-MS) is the most used technique for the assessment of VOCs in fruits. It is based on the separation of compounds according to their volatility, as these elute through a column kept under controlled temperature,

and their ionization once they reach the MS detector. This is preceded by sample extraction methods such as liquid extraction, solid phase extraction, solid phase microextraction, or stir-bar sorptive extraction. The latter two are the most used nowadays due to the low sample amounts needed or the simplicity in use (Lubes & Goodarzi, 2017), although caution is required as the adsorbents applied in these methods may deteriorate over time and use, changing the isolated VOC profile (Reineccius, 2006). Another well-established technique for volatile assessment is proton transfer reaction-mass spectrometry (PTR-MS). This technique, which does not require any previous sample treatment or concentration, is based on a non-dissociative proton transfer from H_3O^+ ions to VOCs producing VOCH^+ and H_2O without reacting with any component of the ambient air (Lindinger, Hansel & Jordan, 1998). The choice of the appropriate technique will depend on the final objective of the analysis. GC-MS is a highly sensitive technique with detection limits in the range of ppt (parts per trillion) and improved compound identification, but it has a moderate time resolution and most of its sample preparation methods require high temperatures or conditions that may lead to the presence of artifacts (Derail, Hofmann & Schieberle, 1999; Beaulieu & Grimm, 2001). PTR-MS is also highly sensitive (pptv, parts per trillion by volume detection) and has a time resolution of less than 1 min. The major limitation of this technique is the unambiguous identification of compounds based on their m/z values, for which it is generally coupled with a time-of-flight detector (PTR-ToF-MS). The higher mass accuracy and precision provided by PTR-ToF-MS allow the determination of the sum-formulas and, thus, link the mass peaks in PTR-MS to the candidate chemical compounds. However, although this is one step closer to an unambiguous compound identification, this assignment has still to be considered a tentative identification (Yeretzian, Hansel & Lindinger, 2003; Graus, Müller & Hansel, 2010; Biasioli, Yeretzian, Märk, Dewulf & Van Langenhove, 2011).

1.6 Correlation between sensory and physicochemical quality

The relationship between sensory and instrumental methods for a complementary assessment of the quality of food has long been investigated. Sensory analysis allows the identification of the relevant attributes for the quality of a particular good, which will ultimately reflect consumer satisfaction and acceptance. On the other hand, several instrumental methods have been developed to measure the physicochemical parameters of food. When selected appropriately, these methods provide results that can help to understand or even predict the sensory characteristics of a product. However, a definition of quality exclusively based on instrumental results may lack significance (Shewfelt, 2014), since no instrument is able to fully mimic the human perception. In other words, sensory information represents a multidimensional integration of the information from all the senses, while instrumental information is mainly one dimensional (Sidel & Stone, 2006). The correlation between both methodologies has its application within different contexts and objectives. It allows the investigation of the causal relationships behind the formation and changes in time of specific sensory responses; to understand how the physical properties of food influence the release and perception of the aroma and flavor; or to study the effect that compositional parameters have over the sensory perception of food (Martens, Risvik & Martens, 1994; Langridge, 2004). When correlating sensory and instrumental analysis, there are several factors that shall be previously considered, such as the selection of the appropriate sensory and instrumental procedures, the parameters obtained thereof, or the methods of statistical analysis used to determine the relationships between both types of measurements (Kilcast, 2013).

Among the different types of methods of sensory analysis, affective, discrimination, or descriptive tests, only the latter provide a qualitative and quantitative definition of the sensory traits of a food product. For this reason, descriptive analysis is

considered to be the most comprehensive and informative sensory tool (Lawless & Heymann, 2010). Moreover, the quantitative descriptive data can be related to instrumental measurements, through the application of the appropriate statistical methods. These relationships will allow the understanding of the influence of physicochemical parameters over the sensory attributes of a product and which are the key attributes prone to influence its acceptance (Murray *et al.*, 2001; Kemp *et al.*, 2009).

The measurement of common quality indices, such as SSC, TA, pH, or SSC/TA, and their relationship with the perception of sweetness and acidity has been well established for several fruit species. However, a lack of correlation between both types of measurements was also observed among other species for which sweetness and acidity estimation are thought to be much more complex than the single determination of such parameters (e.g. Saftner, Polashock, Ehlenfeldt & Vinyard, 2008). Other approaches consider the determination of the total and individual contents of soluble sugars and organic acids, but these do not take into account the possible interactions between metabolites and, thus, have shown to be less correlated with sweetness or acidity than SSC, TA or pH (Harker, Marsh, Young, Murray, Gunson & Walker, 2002; Aprea, Charles, Endrizzi, Corollaro, Betta, Biasioli & Gasperi, 2017). Additionally, as investigated in both studies, the influence of sugar alcohols (sorbitol) on the perception of sweetness may also be evaluated, although only the latter authors have found it to be a good predictor of sweetness, yet similar to the prediction provided by SSC.

Among the instrumental methods for the measurement of textural properties of food, the selection of the most appropriate one to correlate with sensory attributes will mostly rely on the nature of the textural parameters to be studied. While fundamental tests are not generally able to provide a satisfactory extent of correlation with sensory methods, the opposite occurs with empirical and imitative tests (Bourne, 2002). However, empirical tests (such as puncture tests) may provide information of only a

part of the whole spectrum that comprises the textural properties of a product, while imitative tests (such as TPA) are able to provide the most complete measurement of texture up to date. The great advantage of the imitative tests is that the interpretation of the measurement curves is already sensory oriented, i.e., the classification system is designed to interpret the mechanical parameters in terms of sensory attributes (Szczeniak, 1973). High correlations between sensory and instrumental texture parameters, as measured through puncture tests or TPA, have been frequently reported in the literature for a wide variety of food products including dried and fresh fruits (Meullenet, Lyon, Carpenter & Lyon, 1998; Harker *et al.*, 2002; Chauvin, Ross, Pitts, Kupferman & Swanson, 2010).

The considerations on the selection of a suitable method for the instrumental analysis of aroma are deeply reviewed by Reineccius (2006). The choice of the appropriate method for the assessment of the VOCs profile is highly dependent on the sample characteristics (such as composition and aroma compounds concentrations), the volatiles of interest, the analysis time, and the objective of the study. A different approach is required whether the aim is to obtain a qualitative VOCs profile or a qualitative and quantitative one, and whether an extensive VOCs profile combining several methods or a profile of the key aroma compounds of a product. In the case of the correlations between the sensory and instrumental aroma profiles of a product, the most representative VOCs profile is needed. Once the compounds are identified and quantified, the focus may be placed on a subset of the ones with major sensory significance since not all the VOCs present are thought to contribute to human perception. Though all the analytical methods used for the selection of a subset of representative compounds have limitations, some may be overcome through the use of different statistical methods (Reineccius, 2006). The instrumental assessment of aroma through PTR-MS and its suitability as a tool to evaluate the relationship with sensory

analysis has been demonstrated in previous studies with different food products such as apples (Ting, Soukoulis, Silcock, Cappellin, Romano, Aprea, Bremer, Märk, Gasperi & Biasioli, 2012; Ting, Romano, Soukoulis, Silcock, Bremer, Cappellin & Biasioli, 2016), bread (Heenan, Dufour, Hamid, Harvey & Delahunty, 2009), cheese (Biasioli, Gasperi, Aprea, Endrizzi, Framondino, Marini, Mott & Märk, 2006) or wine (Arvisenet, Ballester, Ayed, Sémon, Andriot, Le Quere & Guichard, 2019). While being a technique with high sensitivity, speed, and reproducibility, PTR-MS allows the headspace VOCs to be collected at room temperature (25 °C), which reproduces the closest conditions of human perception at the moment of fruit consumption.

1.6.1 Statistical methods

There are several methods of statistical analysis available to investigate the relationships between sensory and physicochemical data. Some of these methods are generally sequentially applied as they allow a complementary understanding of the link between both types of data. As a first step, before even starting the statistical analysis, it is recommended to investigate the structure of the raw data. A visual evaluation of the sensory and instrumental datasets is helpful to avoid possible inconsistencies or detect main tendencies. This can be easily performed by representing the results through tables or plots using the mean values along with the variance or the standard deviation, especially for small datasets (Kilcast, 2013). The former evaluation of both datasets, separately, is also highly recommended. It will allow to detect the presence of outliers, to assess the performance of the panelists and the panel as a whole, regarding the sensory dataset, and to assess the extent of the relationship between variables of the same dataset which may indicate the presence of multicollinearity, especially among the instrumental dataset (Qannari & Schlich, 2006). Other authors suggest the use of pre-processing methods, also indistinctly referred to in the literature as pre-treatment

methods or variable transformations. These methods improve the comparability between the different types of measurements by correcting data aspects considered irrelevant to a specific research question, such as offset or scale effects, skewness of the data, or unequal variances (heteroscedasticity). Examples on how to use the different pre-processing methods on sensory and instrumental datasets can be found elsewhere (van den Berg, Hoefsloot, Westerhuis, Smilde & van der Werf, 2006; Romano, Brockhoff, Hersleth, Tomic & Næs, 2008).

One of the primary methods of statistical analysis applied after the inspection of the raw data is the ANOVA. This method is used to determine which factors or sources of variation of a dataset are important for the study. The sources of variation may be related to the samples, the panelists, the measured parameters, and replicates, as well as possible interactions between them. ANOVA calculates the F-ratio of each source of variation to identify which are significant, while further multiple comparison tests (or post hoc tests) will determine the levels of the significant differences (Kemp *et al.*, 2009). Different ANOVA models can be performed depending on the structure of the dataset: one-way ANOVA, when the variation is due to only one factor and all the other factors remain constant; two-way ANOVA, when the variation is due to two factors; multi-way ANOVA, when the variation is due to multiple factors and interactions between them; among other models used for specific experimental designs (O'Mahony, 1986). As a result, it is possible to identify which of the sensory and instrumental parameters are significantly different and allow the samples to be distinguished from each other. Subsequently, multivariate analysis methods are applied to explore the relationship between the measured parameters. These methods have been developed to deal with the complexity of multidimensional datasets, as in the case of sensory and instrumental relationships. One of the most commonly used multivariate methods is PCA. It reduces the dimensionality of the dataset, transforming a large number of

interrelated variables into a smaller number of linear combinations while keeping as much of the variation present in the dataset as possible. PCA sequentially identifies the linear combinations, or principal components (PCs), through which the maximum variation occurs and, in a way, that each new PC is uncorrelated to the previous. The PCs describe most of the variation present in the original variables, whose contribution for each PC is measured by their coefficient or loading values (Jolliffe, 2002). By projecting large datasets into two-dimensional or three-dimensional plots, PCA facilitates the understanding and interpretation of underlying patterns in the data. Additionally, it can also be used as a preliminary method before applying other classification, discrimination, or prediction methods since the PCs are uncorrelated and, thus, multicollinearity issues are avoided. Both uses of PCA are commonly applied to explore the relationships between sensory and instrumental datasets. Please refer to Næs *et al.* (2010) and Jolliffe (2002) for illustrative examples applied to sensory and instrumental datasets, respectively.

Once PCA is performed, the low dimensional data can be used to carry out other multivariate methods, depending on the nature of the datasets and the research question to be answered. As already mentioned, in the context of sensory and instrumental relationships there may be issues of multicollinearity, for which methods such as principal component regression (PCR) or partial least squares (PLS) regression can be used, as an alternative to multiple linear regression, to predict and interpret a relationship between the two sets of variables. The PCR consists of a previous PCA on the instrumental variables and subsequently investigates how the selected PCs relate to the sensory variables. However, the selection of the instrumental PCs used in the model may not be relevant enough to explain the variation in the sensory data, while some of the discarded ones may contain important information. On the other hand, PLS regression considers the original structure of both the sensory and instrumental

variables. It seeks for linear combinations between both datasets using the covariance, obtaining components that are more relevant for the model than the PCs, and maximizing the level of explained variation of both datasets (Qannari & Schlich, 2006; Næs *et al.*, 2010). Discriminant analysis (DA) and cluster analysis (CA) are supervised and unsupervised methods, respectively, that deal with the classification of the samples or variables into different groups or categories. DA uses predefined information about the groups to which the samples belong to, in order to identify the differences between groups and estimate the group membership of a given sample. CA identifies groups or clusters formed by the samples with the highest degree of similarity in each group, without using any preliminary information about the groups. Both methods are frequently applied as a classification tool for the sensory and instrumental measurements of many food products (Bower, 2013). Another method generally applied is PLS-DA, which combines the features of PLS regression with the classification ability of DA. It seeks for components which maximize the variance between groups, using the covariance, while considering the group to which the samples belong to (Rossini, Verdun, Cariou, Qannari & Fogliatto, 2012). Several additional approaches to relate sensory and instrumental variables are possible using other methods, although concerns regarding the stability and robustness of the models, as well as the complexity of interpretation of the outcomes, shall be taken into account. It is also worth to mention that, regardless of the methods chosen, a residual level of variation will remain unexplained, which may or may not fall within the limits of what can be measured by sensory and instrumental methods (Martens *et al.*, 1994).

2. Hypotheses

The selection and development of fruit cultivars with better and consistent quality is essential for their acceptance and commercial success. However, the knowledge about individual quality traits is not sufficient to improve fruit quality. To achieve a comprehensive assessment of quality it is important to investigate the relationships between the sensory and physicochemical quality traits. In this context, the following hypotheses were explored:

1. The wide variation of melon fruits for traits such as firmness and juiciness is expected to be extensive to other valuable textural traits. It is hypothesized that the textural quality of melon fruit is defined by the combination of multiple traits and their impact over the perception of texture.
2. The interactions between volatile and non-volatile compounds can affect the overall quality of fruit. It is hypothesized that evaluating the correlations between sensory attributes, VOCs, pH, and SSC contributes to a better understanding of their role over melon fruit quality.
3. Peaches, nectarines, flat peaches, and canning peaches have distinctive quality traits. It is hypothesized that analyzing their sensory and VOCs profiles provides valuable information for the improvement of peach aroma while considering the individual quality of each fruit typology.

3. Objectives

The main objective of the present thesis was to investigate key quality attributes of melon and peach fruit cultivars through sensory and instrumental methodologies. To achieve this objective, the relationships between sensory attributes, textural properties, VOCs, and other quality parameters were determined on a collection of fruits selected to provide a wide variation within each species. The following individual objectives were developed:

1. Study the variation within melon fruit types of different ripening behavior to understand the role of multiple physicochemical properties on the perception of their textural attributes.
2. Evaluate the relationship between the perceived and the instrumentally determined aroma and flavor of different melon fruit types by assessing their sensory attributes, volatile organic compounds, and common quality indices.
3. Investigate the aroma of commercial peach fruits and highlight the different sensory and volatile profiles associated with each fruit typology: peaches, nectarines, flat peaches, and canning peaches.

4. Methodology

The steps followed to achieve the individual objectives in the origin of the publications that comprise this thesis are represented in Figure 3. A comprehensive description of the methodologies performed is given in the section of "Material and methods" of each publication (chapter 5).

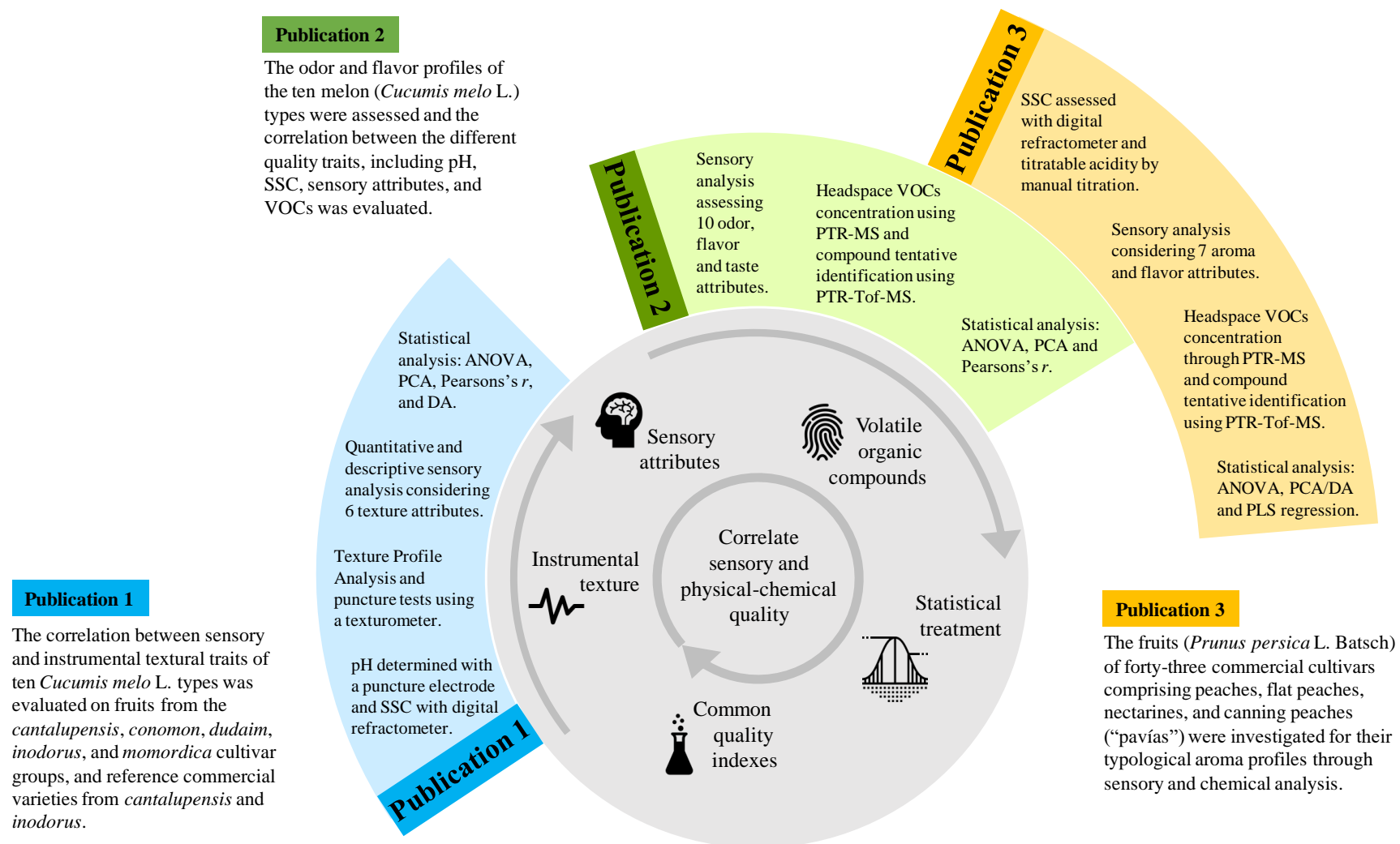


Figure 3. Schematic representation of the steps followed in each one of the publications that comprise the present thesis.

5. Compendium of publications

5.1 Publication 1: Correlation of sensory and instrumental texture of melon fruits

Bianchi, T., Guerrero, L., Gratacós-Cubarsí, M., Claret, A., Argyris, J., Garcia-Mas, J., & Hortós, M. (2016). Textural properties of different melon (*Cucumis melo* L.) fruit types: sensory and physical-chemical evaluation. *Scientia Horticulturae*, 201, 46–56.

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Quartile 1



Textural properties of different melon (*Cucumis melo* L.) fruit types: Sensory and physical-chemical evaluation



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ABSTRACT

Melon fruit properties are extremely different within the species and texture is one of the quality features that most influences its acceptance. The aim of this study was the comparison of melon textural traits, evaluating the linear correlations between both perceived and instrumentally determined texture of a distinctive group of genotypes representing wide species variability. Three landrace cultivars (the Korean 'Songwhan charmi PI-161375', the Indian 'Calcuta PI-124112', and the Iraqi 'Irak C-1012') and three elite cultivars (the Spanish 'Piel de Sapo T111', the French 'Védraçais', and the American 'Dulce'), grown under the same conditions in the same place, were analyzed, together with four Spanish major commercial varieties ('Piel de Sapo', 'Amarillo', 'Galia' and 'Cantaloupe'). Measurements of pH, Soluble Solids Content (SSC), weight losses, puncture tests (6 mm and 10 mm probes), texture profile analysis (TPA), and sensory analysis were performed in 38 fruits. Results showed wide parameter range depending on each particular type of melon. Significant differences were reported for five of six sensory descriptors: hardness (1.52–4.91), initial juiciness (1.77–7.45), crunchiness (0.29–4.58), mealiness (0.41–6.37) and chewiness (2.91–5.27); and for seven of nine physical-chemical parameters: hardness (921.3–4519.0), fracturability (587.4–4280.7), cohesiveness (0.027–0.061), adhesiveness (–15.7 to –105.0), pH (5.21–6.53), SSC (4.8–14.0) and weight losses (18.0–66.0). Puncture tests parameters were good predictors of sensory hardness, crunchiness and chewiness, while TPA gave further information about initial juiciness, fibrousness and mealiness. Discriminant analysis showed that initial juiciness and mealiness were the most discriminant variables while any instrumental parameter showed particular discriminate ability between samples. These results prove the usefulness of sensory analysis to reflect melon textural traits, when compared to single physical-chemical approach, and could be extended to the middle-late stages of variety development breeding programs.

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1. Introduction

Melon (*Cucumis melo* L.) is a diploid species with extensive phenotypic and genetic variation whose fruits have been divided into several different groups according to numerous intraspecific classifications. One of these classifications defines 16 groups, five assigned to subspecies *agrestis* and eleven to subspecies *melo* (Pitrat et al., 2000; Pitrat, 2008; Burger et al., 2009). It includes *inodorus* Spanish varieties with sweet white-flesh like 'Piel de Sapo' or 'Amarillo' melons; odor and flavor intense *cantalupensis* fruits, with green to orange-salmon flesh, like 'Cantaloupe', 'Védraçais', 'Dulce'

and 'Galia'; but also landraces, genetically distant from commercial melon, with exotic fruits like the Korean 'Songwhan charmi' of the *conomon* cultivar; Indian *momordica* cultivar fruits like 'Calcuta' with soft, little sweet and cream to orange flesh color; and *dudaim* cultivar fruits with smooth skin and aromatic flesh, like 'Irak'.

Melon is a commercially important horticultural crop throughout the world. Spain is the 7th largest melon producer (FAO, 2013) and the leading exporter worldwide (FAO, 2012). Melon is the 4th most consumed fruit in Spain (after orange, banana and apple) and in 2014 the consumption value was 387,914.38 kg that represented 340,499.01 € (Magrama, 2014).

Originally, the popularity of melon was due to its refreshing and tasty flesh and pleasant aroma. It was consumed mainly in the summer period as an appetizer, in cold soups or salads, and as a dessert. Increasing interest in melon consumption is associated

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with its potential human health benefits, in particular high antioxidant, and anti-inflammatory properties (Vouldoukis et al., 2004; Ismail et al., 2010), anti-diabetic benefits (Jayasooriya et al., 2000; Kenny et al., 2013), anti-ulcerogenic activity (Yesilada et al., 1999) antibacterial properties (Khan and Omoloso, 1998), and its use in folk medicine in various cultures (Subratty et al., 2005; Semiz and Sen 2007; Wu and Ng, 2008; Mahomoodally 2013).

Food quality is a multidimensional concept defined as a set of safety, nutritional and organoleptic characteristics of a product (Ismail et al., 2001). Fruit quality is a consequence of many biochemical processes that result in changes of its intrinsic properties such as color, texture, flavor and aroma, together with the exterior appearance (size, color and shape) and nutritional value. These properties exert a strong influence on producing commercially acceptable melons, and happen to be remarkably different depending on each particular melon cultivar, due to its morphological variability (Obando et al., 2008).

Texture represents one of the principal factors defining fruit quality (Bourne 2002) and in melon, as in fruits like tomato (Saladié et al., 2007), strawberry (Gunness et al., 2009), apple (Costa et al., 2011), blueberry (Giongo et al., 2013) or dates (Singh et al., 2013), textural characteristics are related to the cell walls' structure and their degradation during the ripening phase. To the consumer, there are two factors that most influence the mouth feel of a fruit or vegetable: hardness and juiciness (Toivonen and Brummell, 2008). Hardness is a decisive attribute for consumer acceptance (Hoehn et al., 2003; Harker et al., 2008), as hardness loss is perceived to be associated with quality loss. It is also a primary quality selection trait used by melon producers to enhance fruit shelf-life during transport and sale.

Texture definition is a sensory consideration (ISO 5492 1992), although it can be defined instrumentally. There are two ways to measure texture: sensory and instrumentally. Sensory measurement requires a previously trained panel, despite the existence of studies that employed consumer panels (Szczesniak et al., 1975); instrumental measurement uses fundamental, empirical or imitative methods. Fundamental tests, like ultimate strength, Poisson's ratio or Young's modulus, measure viscosity and elasticity; empirical tests, like puncture, shear, and extrusion, measure parameters found to be correlated with sensory texture; while imitative tests are those that imitate with instruments the way food products are subjected in the mouth, i.e., as TPA does (Szczesniak 1963).

With regard to melon fruit texture, little attention has been given to the complementary approach of sensory evaluation of melons and their physical characteristics. 'Songwhan charmi PI 161375', known for its resistance to 'Cucumber mosaic virus (CMV)', has been used in crosses with the Spanish Piel de Sapo T111 to study genetic control of quality traits, ripening behavior or post-harvest disorders (Eduardo et al., 2005; Fernández-Trujillo et al., 2008; Obando et al., 2008; Obando-Ulloa et al., 2008; Dos-Santos et al., 2013; Saladié et al., 2015). In these studies however, textural behavior beyond flesh firmness or juiciness was not evaluated. 'Calcuta PI 142112' melon, reported to have resistance to diseases like downy and powdery mildew, was previously used in crosses with Védrañtais (Percheviel et al., 2005), a susceptible cultivar, while 'Irak C-1012' was used to study gene content variations of melon wide phenotypic diversity (González et al., 2013). These landraces were also never evaluated from both a sensory and instrumental textural perspective. Dulce and Védrañtais are two genotypes representative of climacteric type that have been used to study melon ripening behavior. To our knowledge and with exception for flesh firmness (Saladié et al., 2015), no information on their sensory and physical texture characteristics have been published.

The combination of sensory and physical-chemical methodologies allows a closer understanding of melon fruit texture. The aim of this work was to compare melon fruit variability within a specific

group of genotypes, evaluating its quality parameters with emphasis on textural properties. Fruits were chosen concerning wide species variability: three landrace cultivars (the Korean 'Songwhan charmi PI-161375', the Indian 'Calcuta PI-124112', and the Iraqi 'Irak C-1012') and three elite cultivars (the Spanish 'Piel de Sapo T111', the French 'Védrañtais', and the American 'Dulce'), while four Spanish major commercial varieties were used as reference ('Piel de Sapo', 'Amarillo', 'Galia' and 'Cantaloupe'). Sensory analysis, Texture Profile Analysis (TPA), puncture tests with two probe sizes, pH, soluble solids content (SSC) and weight losses were measured in the fruits and the extent of linear correlation between them determined.

2. Materials and methods

2.1. Plant material

Ten different melon (*C. melo* L.) types, six melon cultivars and four commercial varieties, were sensory and physical-chemical analyzed (Table 1). Plants were grown during the summer of 2012 in a greenhouse in 'Torre Marimon' (Barcelona) in peat bags under 16 light hours minimum, constant temperature (20 °C) and drip irrigation. The lines were arranged in a completely randomized design. Flowers were hand pollinated and each plant was allowed to set a single fruit.

Maturity was defined by change in color and abscission of the fruits: 40–45 days after pollination (DAP) for Calcuta and Irak, 45 DAP for Védrañtais and 50 DAP for Dulce, while for Piel de Sapo T111 and Songwhan charmi maturity was considered to be the point at which fruits had high sucrose content, and thus optimal fruit quality. This was at, 55 and 50 DAP for Piel de Sapo T111 and Songwhan charmi, respectively, as determined in a previous study (Saladié et al., 2015). Commercial varieties were retrieved from a local market.

2.2. Melon samples

Fruits were transversally hand cut with a sharp knife into 2 cm slices, from which the stem and the blossom-ends were discarded. Central slice was used for physical-chemical determinations whereas contiguous ones were used for sensory evaluation. The slices to be used in sensory evaluation were wrapped in cling film and stored at 4 °C until the moment of the tasting. From the slices to be used for physical-chemical determinations, six cylindrical pieces of 2 × 1.5 cm were made by pressing a fruit corer of 1.5 cm diameter against the flesh. The cylinders were carefully placed into a tray that once wrapped in cling film was also stored at 4 °C for a maximum of two hours. All the analysis were performed at harvest.

2.3. Physical-Chemical Evaluation

The pH was determined in triplicate through the central slice flesh using a 5053-T puncture electrode pH-meter (Crison Instruments S.A., Barcelona, Spain) equipped with temperature probe.

Instrumental texture profile analysis (TPA) test described by Bourne (1978) and puncture tests (Bourne, 1979) with 6 and 10 mm diameter probes were performed in a Texture Analyzer TA-HD Plus (Anname, Spain) equipped with a 50 kg load-cell. Parameters achieved with both methods are listed and described in Table 2. TPA measurements were made in six cylindrical pieces of 2 × 1.5 cm per fruit, previously obtained with a corer. Samples were compressed twice to 75% of their original height at a crosshead speed of 1 mm/s. Three puncture measurements were done directly in the central section of the slices, between the core/seed cavity and the rind areas, at 1 mm/s speed with a 0.5 cm penetration of the probes.

Table 1
Melon fruit types used for the sensory and physical-chemical evaluation.

Samples	Accession	Subspecies	Cultivar group	Type	Origin	Replicates
Commercial varieties						
Cantaloupe	–	<i>melo</i>	<i>cantalupensis</i>	Commercial	Spain	3
Amarillo	–	<i>melo</i>	<i>inodorus</i>	Commercial	Spain	2
Galia	–	<i>melo</i>	<i>cantalupensis</i>	Commercial	Spain	4
Piel de Sapo	–	<i>melo</i>	<i>inodorus</i>	Commercial	Spain	7
Cultivars						
Piel de Sapo	T111	<i>melo</i>	<i>inodorus</i>	Elite	Spain	2
Songwhan charmi	PI-161375	<i>agrestis</i>	<i>conomon</i>	Landrace	Korea	6
Calcuta	PI-124112	<i>agrestis</i>	<i>momordica</i>	Landrace	India	3
Irak	C-1012	<i>melo</i>	<i>dudaim</i>	Landrace	Irak	4
Dulce	–	<i>melo</i>	<i>cantalupensis</i>	Elite	USA	4
Védrantais	–	<i>melo</i>	<i>cantalupensis</i>	Elite	France	3

Table 2
Physical parameters measured during instrumental texture analysis.

Parameters	Definition	Units
Texture profile analysis (adapted from Bourne 1978, 2002, 2004)		
Hardness	Highest value of force required to compress the sample during the first compression cycle	g
Fracturability	Force value at the first peak of the first compression cycle with which the sample breaks	g
Cohesiveness	Strength of the internal bonds in the sample calculated by dividing the areas of work of the first by the second compression cycles	Dimensionless
Adhesiveness	Energy required to overcome attractive forces between the sample and any surface in contact with it, calculated as the area of the negative curve during the first compression cycle	g sec
Springiness	Elastic recovery that occurs when the compressive force is removed obtained by dividing the distance of the height of the second by the first compression cycle	Dimensionless
Chewiness	Energy required to chew a solid food into a state ready for swallowing calculated by multiplying the values of hardness, cohesiveness and springiness	g
Puncture tests (adapted from Bourne 1966, 1979)		
Slope	Slope of the force-deformation curve when the probe penetrates the sample between 1 and 4 mm, providing the modulus of elasticity	g/sec
Fmax	Value of force in which the major sample failure leads to the force decrease	g
Area	Area under the force deformation curve, which indicates the energy required to penetrate the sample	g sec

The six fruit cylinders per sample were weighted before TPA analysis and weight losses were calculated from the weight differences before and after the run.

The soluble solids content (SSC) was measured with a Quick-Brick™ 90 (Mettler-Toledo, GmbH, Germany) digital handheld refractometer. A drop of juice released by smashing each cylinder of fruit during TPA test was carefully placed into the lens and values were expressed in °Brix degree as average results. Calibration was made with deionized water and the lens was rinsed between samples.

2.4. Sensory evaluation

The samples used for the sensory evaluation were obtained from the same fruits used for the physical-chemical evaluations. The two

Table 3
Melon texture sensory parameters as assessed by the trained panel.

Attributes	Score	Reference	Description
Hardness	1	White asparagus first section (head part) (adapted from Escribano et al., 2010)	Force required to bite completely through sample placed between molars
Initial juiciness	2	Carrot	Amount of juice released on the first two chews
	10	Granny Smith apple (adapted from Escribano et al., 2010)	
	9	Watermelon (adapted from Escribano et al., 2010)	
Crunchiness	0	White asparagus first section (head part)	Hard texture with a sound mainly described as being low in pitch
	10	Granny Smith apple	
Fibrousness	0	White asparagus first section (head part) (adapted from Escribano et al., 2010)	Amount of wet and soft fibrous structures detected during chewing
	9	White asparagus last section (bottom part) (adapted from Escribano et al., 2010)	
Mealiness	0	Granny Smith apple	Excess softness with lack of free juice
	9	Reinette apple	
Chewiness	0	White asparagus first section (head part)	Energy needed to masticate a food product until a state ready to swallow
	9	Carrot	

central slices of 2 cm thick from each melon were selected and the seeds were rejected. Each slice was cut in four portions of similar size and placed in an individual plastic dish coded with a three-digit random number.

Samples were assessed by a trained panel made up of eight panelists selected and trained according to ISO regulations (ISO 8586-1 1993 and ISO 8586-2 1994) and having extensive experience in descriptive and quantitative sensory analysis. The texture descriptors (Table 3) were previously chosen through open discussion between the panel members after tasting different melon commercial samples. Six specific training sessions, one for every descriptor, in which panelists evaluated and discussed different food products to build a reference scale per attribute were performed (Table 3). The attribute intensity on the scale was discussed with the same commercial samples. The panel performance was evaluated in two more sessions where panelists assessed six melon samples using the descriptors and reference scales previously obtained. All the assessors showed a good repeatability, reproducibility and discriminant ability according to Etaio et al. (2010). None of the interactions 'Panelist x Melon sample' was significant ($p < 0.05$), indicating a good agreement between the assessors (Lea et al., 1997).

A total of 38 fruits were evaluated in 8 tasting sessions (Table 4). In each session all the panelists assessed the same 4–5 melons in

Table 4
Sensory evaluation sessions composition.

Samples	Tasting session								Replicates
	1st	2nd	3rd	4th	5th	6th	7th	8th	
Commercial varieties									
CANT		x	x	x					3
AMA					x	x			2
GAL	x	x		x				x	4
PS	x	x	x	x		x	x	x	7
Cultivars									
T111			x				x		2
SC	x	x	x	x	x	x			6
CAL	x	x					x		3
IRK	x		x	x	x				4
DUL					x	x	x	x	4
VED					x	x		x	3
Replicates	5	5	5	5	5	5	4	4	TOTAL = 38

Melon types: CANT, Cantaloupe; AMA, Amarillo; GAL, Galia; PS, Piel de Sapo; T111, Piel de Sapo T111; SON, Songwhan charmi; CAL, Calcuta; IRK, Irak; DUL, Dulce; VED, Védtrantais.

Table 5
ANOVA results (means \pm standard deviations) of the attributes scored by the sensory panel.

Samples	Hardness	Initial juiciness	Crunchiness	Fibrousness	Mealiness	Chewiness
Commercial varieties						
CANT	4.91 \pm 1.72 ^a	5.83 \pm 0.69 ^b	3.47 \pm 1.00 ^{abc}	3.00 \pm 0.51	0.41 \pm 0.65 ^b	5.27 \pm 0.21 ^a
AMA	4.56 \pm 0.09 ^{ab}	5.67 \pm 0.53 ^b	3.30 \pm 0.09 ^{abc}	2.89 \pm 0.05	0.85 \pm 0.20 ^b	5.11 \pm 0.40 ^{ab}
GAL	4.41 \pm 0.87 ^{ab}	6.81 \pm 1.30 ^{ab}	2.81 \pm 1.16 ^{bc}	2.83 \pm 0.40	0.56 \pm 0.35 ^b	4.61 \pm 0.62 ^{ab}
PS	4.24 \pm 0.74 ^{ab}	7.31 \pm 0.57 ^a	3.69 \pm 0.63 ^{ab}	2.86 \pm 0.32	0.59 \pm 0.40 ^b	4.76 \pm 0.31 ^{ab}
Cultivars						
T111	3.57 \pm 0.36 ^{ab}	7.45 \pm 0.61 ^a	3.40 \pm 0.37 ^{abc}	2.42 \pm 0.64	0.97 \pm 0.35 ^b	4.46 \pm 0.15 ^{abc}
SC	4.38 \pm 0.55 ^{ab}	5.82 \pm 0.55 ^b	4.58 \pm 0.54 ^a	2.53 \pm 0.18	0.97 \pm 0.68 ^b	4.60 \pm 0.49 ^{ab}
CAL	3.49 \pm 1.66 ^b	1.77 \pm 1.03 ^c	2.03 \pm 1.58 ^{cd}	2.20 \pm 1.10	5.43 \pm 3.27 ^a	4.15 \pm 0.65 ^{abcd}
IRK	2.22 \pm 0.12 ^c	2.26 \pm 0.90 ^c	1.20 \pm 0.32 ^{de}	2.66 \pm 0.58	6.37 \pm 1.52 ^a	3.75 \pm 0.35 ^{bcd}
DUL	1.94 \pm 0.53 ^c	7.49 \pm 0.36 ^a	0.29 \pm 0.30 ^e	2.04 \pm 0.42	1.73 \pm 0.53 ^b	2.91 \pm 0.30 ^d
VED	1.52 \pm 0.20 ^c	6.68 \pm 0.60 ^{ab}	0.57 \pm 0.29 ^{de}	2.20 \pm 0.44	1.17 \pm 0.18 ^b	3.13 \pm 0.30 ^{cd}

Values with the same letter within column do not differ significantly by Tukey's HSD post hoc test ($p \leq 0.05$).

Melon types: CANT, Cantaloupe; AMA, Amarillo; GAL, Galia; PS, Piel de Sapo; T111, Piel de Sapo T111; SON, Songwhan charmi; CAL, Calcuta; IRK, Irak; DUL, Dulce; VED, Védtrantais.

different presentation orders to block the first-order and carry-over effects (Macfie et al., 1989).

Sensory evaluation was carried out in a test room designed following ISO guidelines (ISO 8589 2007). Samples were evaluated under white lighting (700 lux \pm 150 lux) using a non-structured 10 cm lineal scale, in which 0 meant low intensity of the descriptor and 10 meant high intensity of the descriptor. Mineral water was provided to panelists to rinse their mouth between samples.

2.5. Statistical analysis

Sensory data was analyzed using a three-way ANOVA including the type of melon, the assessor and the tasting session as fixed factors. The double interaction 'type of melon x assessor' was also included in the preliminary analysis but dropped later since it was not significant ($p > 0.05$) for any of the six texture descriptors assessed. Physical-chemical data was submitted to a one-way ANOVA (melon type as a fixed effect) over the mean values obtained for each experimental unit (each individual melon). In all cases a Tukey's HSD post hoc test ($p \leq 0.05$) was performed to test the existence of statistical differences between the different melon types.

A Pearson's correlation analysis and a Principal Component Analysis were carried out to monitor the relationship between all the variables measured over the same samples. The univariate and multivariate discriminate ability of the measured variables was evaluated through discriminant analysis. Different confusion matrices were also computed to verify the percentage of correctly

classified samples in their respective varieties/cultivars as a function of the selected descriptors.

All the analyses were carried out using XLSTAT 2014 software (Addinsoft, Paris, France).

3. Results and discussion

3.1. Sensory Evaluation

Panelists found significant differences for all sensory attributes except fibrousness (Table 5). Despite this fact, they related fibrousness with chewiness ($r=0.52$), hardness ($r=0.57$) and mealiness ($r=-0.61$). Possibly, higher fiber content of a food product requires a bigger chewy effort. Lee et al. (1999) found a significant linear correlation ($r=0.74$, $p < 0.01$) between chewiness and fibrousness of processed diced tomatoes and Lázaro and De Lorenzo (2015) between fibrousness and hardness ($r=0.47$, $p < 0.05$) of melon landraces. Other authors observed higher scores and significant differences for fibrousness in different Piel de Sapo, Galia and Amarillo melon types from *inodorus* and *cantalupensis* cultivars (Escribano et al., 2010; Escribano and Lázaro, 2012) and diverse Spanish landraces (Lázaro and De Lorenzo, 2015).

Three significantly different groups were reported for hardness. Commercial Cantaloupe was the hardest melon followed by Amarillo, and with Irak, Dulce and Védtrantais being the softest. Hardness was highly correlated with chewiness ($r=0.83$) indicating that it was a strong predictor of this sensory descriptor. Consistently, cantaloupe was also the chewiest type and Irak, Dulce and Védtrantais

the easiest to chew. Meullenet et al. (1998) determined a high linear correlation ($r=0.77$, $p<0.001$) between hardness and chewiness in a study with twenty one different food samples representing a wide texture spectrum, including fresh and dried fruits, cheeses, candies, breads or frankfurters, and Chauvin et al. (2010) ($r=0.64$, $p\leq 0.05$) between both attributes in apple. Chewiness derives from hardness, since it is the total amount of work necessary to reduce a sample to a ready for swallowing state (Amerine et al., 1965). It is evident that in the case of melon, the harder the product, the higher the work.

After Songwhan charmi cultivar, commercial Piel de Sapo was the crunchiest one along with the other commercial types and T111. Once again Irak, Dulce and Védraçais were the least crunchy, reflecting the linear correlation between crunchiness and hardness ($r=0.87$). Crunchiness is a positive attribute that contributes to food enjoyment (Szczesniak and Khan, 1984) and it is particularly important in fruits and vegetables since it is associated with freshness and wholesomeness (Fillion and Kilcast, 2002). It involves three components: the mastication activity, the food being chewed and the noise produced by grinding food between the teeth (Usunier and Sbizzera, 2013), explaining the high linear correlation ($r=0.80$) between crunchiness and chewiness.

The initial juiciness was scored highest in Dulce and Piel de Sapo melons, both the commercial type and T111 accession, followed by the rest of the *cantalupensis* cultivars, then by *S. charmi* and Amarillo. The driest samples were Calcuta and Irak. The latter two cultivars also showed a wider variation of juiciness when comparing to previous works (Escribano and Lázaro, 2012; Lázaro and De Lorenzo, 2015). No linear correlation was found between initial juiciness and chewiness, but the highest initial juiciness of Dulce melons could be explained by its lowest chewiness value. Harker et al. (2003) postulated that watermelon fruits tend to rapidly release all the juice from the tissue when little chewing is required. Juiciness was negatively correlated with mealiness ($r=-0.85$) as the driest fruits were also the mealier and significantly different from the others. Fernández-Trujillo et al. (2008) described Songwhan charmi fruits as mealier than and Piel de Sapo. Based on the parameter of extractable juice at harvest, these authors also reported Védraçais cultivar as mealier than both. The perception of mealiness consists in abnormal softness and lack of free juice, being one of the most undesirable characteristics in fruit (Barreiro et al., 1998; Crisosto and Labavitch, 2002; Nobile et al., 2011; Galmarini et al., 2013).

No significant differences for any attribute were found between Piel de Sapo melons, of which sensory homogeneity was previously reported by Escribano and Lázaro (2012). Considering hardness, crunchiness and chewiness, *cantalupensis* were divided into two clear groups, one formed by elite cultivars (Dulce and Védraçais) and another by Cantaloupe and Galia aligned with the commercial varieties. An opposite trend was observed for mealiness suggesting that, in this cultivar group, it was more hardness than juiciness dependent. Galia and elite cultivars were also higher scored than Cantaloupe for initial juiciness. These differences are possibly due to an improved storage and shelf-life of the commercial varieties.

Our results reflected the focus of melon breeders over hardness or juiciness, but provide new data in the subsequent impact on hardness related texture traits like crunchiness and chewiness. The extremely wide sensory behavior of these genotypes combined with genomic tools can be of great importance for variety development breeding programs.

3.2. Physical-chemical evaluation

The physical-chemical parameters (Table 6) showed significant differences between samples in seven of the nine parameters ana-

Table 6
ANOVA results (means \pm standard deviations) of the TPA test parameters and chemical parameters determined.

Samples	Hardness (g)	Fracturability (g)	Cohesiveness	Adhesiveness (g.s)	Springiness	Chewiness (g)	pH	SSC ($^{\circ}$ Brix)	Weight loss
Commercial varieties									
CANT	3316.5 \pm 1949.2 ^{ab}	2666.8 \pm 1696.0 ^{ab}	0.055 \pm 0.003 ^{ab}	-65.5 \pm 25.1 ^{ab}	0.18 \pm 0.08	38.8 \pm 29.8	6.53 \pm 0.1 ^a	14.0 \pm 2.9 ^a	59.0 \pm 15.6 ^a
AMA	4519.0 \pm 363.7 ^a	4280.7 \pm 4.5 ^a	0.039 \pm 0.006 ^{bc}	-56.9 \pm 54.5 ^{ab}	0.18 \pm 0.04	30.7 \pm 12.1	6.05 \pm 0.2 ^{abcd}	10.7 \pm 0.8 ^{abcd}	34.5 \pm 5.6 ^{ab}
GAL	941.0 \pm 582.4 ^b	587.4 \pm 432.8 ^b	0.061 \pm 0.008 ^a	-33.9 \pm 21.7 ^a	0.20 \pm 0.10	9.2 \pm 8.0	6.38 \pm 0.1 ^{ab}	12.1 \pm 2.6 ^{abc}	43.9 \pm 17.1 ^{ab}
PS	2794.8 \pm 836.4 ^{ab}	2190.0 \pm 437.8 ^{ab}	0.047 \pm 0.005 ^{ab}	-52.8 \pm 18.8 ^a	0.21 \pm 0.03	25.1 \pm 5.2	5.97 \pm 0.3 ^{bc}	12.6 \pm 1.0 ^{ab}	50.3 \pm 14.8 ^a
Cultivars									
T111	1249.1 \pm 525.3 ^{ab}	1153.5 \pm 193.5 ^{ab}	0.040 \pm 0.004 ^{bc}	-34.3 \pm 31.5 ^a	0.17 \pm 0.00	9.4 \pm 3.4	6.02 \pm 0.2 ^{abc}	10.2 \pm 1.6 ^{abcd}	66.0 \pm 5.6 ^a
SC	2687.0 \pm 781.9 ^{ab}	2275.0 \pm 1005.4 ^{ab}	0.054 \pm 0.012 ^{ab}	-34.1 \pm 12.9 ^a	0.24 \pm 0.02	38.4 \pm 12.8	5.65 \pm 0.1 ^{cd}	9.2 \pm 1.1 ^{bcd}	47.4 \pm 10.9 ^{ab}
CAL	2444.4 \pm 2028.5 ^{ab}	2304.8 \pm 2206.2 ^{ab}	0.039 \pm 0.008 ^{bc}	-61.0 \pm 9.2 ^{ab}	0.24 \pm 0.12	30.0 \pm 37.8	5.67 \pm 0.1 ^{cd}	8.4 \pm 6.6 ^{bcd}	18.0 \pm 5.8 ^b
IRK	937.5 \pm 291.5 ^b	764.9 \pm 166.3 ^b	0.027 \pm 0.002 ^c	-105.0 \pm 35.0 ^b	0.14 \pm 0.02	3.6 \pm 1.3	5.21 \pm 0.4 ^d	4.8 \pm 1.2 ^d	40.2 \pm 10.5 ^{ab}
DUL	921.3 \pm 687.2 ^b	735.2 \pm 549.8 ^b	0.042 \pm 0.001 ^{bc}	-42.6 \pm 25.1 ^a	0.12 \pm 0.01	5.0 \pm 3.8	6.13 \pm 0.2 ^{abc}	7.9 \pm 1.0 ^{cd}	59.6 \pm 8.4 ^a
VED	1840.2 \pm 1897.9 ^{ab}	1250.0 \pm 1363.1 ^{ab}	0.052 \pm 0.012 ^{ab}	-15.7 \pm 3.9 ^a	0.15 \pm 0.06	21.3 \pm 29.2	6.49 \pm 0.3 ^{ab}	9.5 \pm 0.9 ^{abcd}	53.7 \pm 9.6 ^a

Values with the same letter within column do not differ significantly by Tukey's HSD post hoc test ($p\leq 0.05$).

Melon types: CANT, Cantaloupe; AMA, Amarillo; GAL, Galia; PS, Piel de Sapo; T111, Piel de Sapo T111; SON, Songwhan charmi; CAL, Calcuta; IRK, Irak; DUL, Dulce; VED, Védraçais.

Table 7
ANOVA results (means ± standard deviations) of the puncture tests parameters and shear force result.

Samples	P 6 mm			P 10 mm			Shear (%)
	Slope (g/s)	F max (g)	Area (g.s)	Slope (g/s)	F max (g)	Area (g.s)	
	Commercial varieties						
CANT	312.9 ± 153.4 ^{ab}	690.8 ± 377.8 ^{ab}	2522.8 ± 1358.8 ^{ab}	669.4 ± 369.0 ^{ab}	1553.7 ± 999.5 ^{bc}	5366.0 ± 3347.4 ^{bc}	77.4 ± 16.5 ^{ab}
AMA	625.0 ± 156.4 ^a	1128.1 ± 57.9 ^a	4184.1 ± 5.2 ^a	1363.3 ± 338.2 ^a	3213.0 ± 105.7 ^a	9846.8 ± 1051.2 ^a	45.0 ± 4.34 ^b
GAL	185.2 ± 39.0 ^b	350.1 ± 97.1 ^{ab}	1311.3 ± 291.1 ^b	644.2 ± 377.5 ^{ab}	810.8 ± 317.5 ^c	3873.1 ± 2227.2 ^{bc}	88.1 ± 6.4 ^a
PS	385.9 ± 111.8 ^{ab}	801.4 ± 220.9 ^{ab}	2853.5 ± 744.2 ^{ab}	899.0 ± 296.4 ^{ab}	1761.3 ± 407.6 ^{abc}	6055.4 ± 1097.2 ^{abc}	74.9 ± 9.8 ^{ab}
Cultivars							
T111	404.3 ± 47.3 ^{ab}	431.3 ± 141.5 ^{ab}	1810.1 ± 525.0 ^{ab}	409.3 ± 2.8 ^b	795.2 ± 84.9 ^c	2937.7 ± 383.0 ^{bc}	90.7 ± 1.5 ^a
SC	517.4 ± 105.2 ^a	1097.7 ± 164.2 ^a	3701.9 ± 513.3 ^a	918.1 ± 151.9 ^{ab}	2226.9 ± 461.3 ^{ab}	6693.3 ± 1337.5 ^{ab}	70.4 ± 14.0 ^{ab}
CAL	432.9 ± 98.9 ^{ab}	726.5 ± 394.8 ^{ab}	2542.4 ± 1396.6 ^{ab}	849.9 ± 235.2 ^{ab}	1780.7 ± 951.2 ^{abc}	6388.8 ± 3265.4 ^{bc}	72.4 ± 14.8 ^a
IRK	243.6 ± 116.5 ^b	457.0 ± 166.5 ^{ab}	1560.9 ± 578.0 ^b	542.7 ± 202.0 ^b	723.8 ± 30.8 ^c	3169.5 ± 1084.8 ^{bc}	92.0 ± 4.0 ^a
DUL	206.1 ± 101.6 ^b	341.3 ± 215.9 ^b	1258.7 ± 774.9 ^b	325.7 ± 93.3 ^b	684.3 ± 386.2 ^c	2523.2 ± 1328.3 ^c	91.2 ± 4.89 ^a
VED	140.4 ± 37.7 ^b	511.0 ± 444.2 ^{ab}	1463.0 ± 881.8 ^b	504.7 ± 430.6 ^b	1186.3 ± 1036.4 ^{bc}	3459.7 ± 2480.5 ^{bc}	82.4 ± 16.2 ^a

Values with the same letter within column do not differ significantly by Tukey's HSD post hoc test ($p \leq 0.05$).

Melon types: CANT, cantaloupe; AMA, Amarillo; GAL, Galia; PS, piel de sapo; T111, Piel de Sapo T111; SON, Songwhan charmi; CAL, Calcuta; IRK, Irak; DUL, Dulce; VED, Védtrantais.

lyzed: hardness, fracturability, cohesiveness, adhesiveness, pH, SSC and weight losses.

Amarillo type were the hardest and most fracturable fruits ($r=0.96$). Galia, Irak and Dulce were the softest and least fracturable ones. Results were consistent with those from Pardo et al. (2000) and Escribano et al. (2010) which refer the Amarillo melon as harder than Piel de Sapo, but different from these last ones for Galia type. In our study, Amarillo and Piel de Sapo were harder than Galia, possibly due to fruit analysis at different stages of maturity.

The most cohesive melon was commercial Galia while the least one was Irak. A linear correlation between cohesiveness and hardness would be expected since weakening of cohesive forces directly influences hardness loss, as reported by Lázaro and De Lorenzo (2015). However, softness and cohesiveness loss increase with fruit ripening and in this study the determinations were performed at harvest. Cohesiveness is related to fruit microstructural properties and their changes during ripening. Solubilisation and depolymerization of polysaccharides are responsible for cell wall structure changes leading to a loss of a cohesive pectin matrix and intercellular rupture (Goulão and Oliveira, 2008). However, cell arrangement and packing, size of intercellular air space, water loss and turgor pressure (Harker and Sutherland, 1993; Toivonen and Brummell, 2008; Bordoloi et al., 2012) must also be considered. Fruits with the highest adhesive flesh were the Irak melons, while Védtrantais were the least adhesive. Lázaro and De Lorenzo (2015) found a small but significant linear correlation between adhesiveness and hardness ($r=0.27$) while in the present study it was only correlated with cohesiveness ($r=0.37$). Adhesiveness depends on a combined effect of adhesive and cohesive forces (Kilcast and Roberts 1998; Hoseney and Smewing, 1999) and differences may be due to the same reasons mentioned above for cohesiveness.

Springiness provides a measure of the viscoelastic properties of food. Compared to vegetable, fruit is mostly formed by extensible and somewhat elastic cell walls (Toivonen and Brummell, 2008) that determine springiness. No significant differences were found for springiness and chewiness but they were highly correlated ($r=0.80$). Irak and Dulce were the least chewy and springy while the chewiest fruits had higher springiness values. Since instrumental chewiness is calculated as the product of the values of hardness, cohesiveness and springiness, it was also correlated with cohesiveness ($r=0.49$) but especially with hardness ($r=0.89$).

Fruits of the *Cantaloupensis* group had the highest pH values and Irak the lowest. Results for Amarillo melon were similar to those at harvest from Pardo et al. (2000) but higher for Galia than the ones from Escribano et al. (2010). pH was correlated with cohesiveness ($r=0.49$), adhesiveness ($r=0.54$) and SSC ($r=0.56$). Changes in the intercellular ionic conditions, and therefore in pH, influence the dynamic changes in ripening fruit cell walls (Almeida and Huber 1999) affecting cohesiveness and adhesiveness. Regarding SSC, Galia and Piel de Sapo showed lower values than the ones found by Escribano et al. (2010), Védtrantais and Piel de Sapo T111 showed similar values to those at harvest from Fernández-Trujillo et al. (2008), and Songwhan charmi presented slightly higher values than the ones from the latter authors. Aguayo et al. (2007, 2008) did not found significant differences in SSC with time of storage for Amarillo melon but determined that glucose and fructose levels were higher after 3 ways of storage than at harvest, while sucrose level followed the opposite trend. SSC and hardness had no linear correlation, although negative linear correlations between SSC and instrumental hardness were found in melon fruit by Pardo et al. (2000) ($r=-0.27$, $p=0.05$) and Obando et al. (2008) ($r=-0.22$, $p \leq 0.01$). Differences may be attributed to different harvest times and SSC changes with time as showed in results 'at' and 'post' harvest from Hoberg et al. (2003); Fernández-Trujillo et al. (2008). Weight losses had only slight negative linear correlations with fracturability ($r=-0.33$) and springiness ($r=-0.42$). Moisture content

and springiness decrease in parallel with fracturability increase. With moisture loss, cellular turgor pressure decreases and tissues are less resistant to compression, becoming more deformable (Chiralt and Talens 2005; Mayor et al., 2007).

ANOVA of the puncture test data measured in each type of melon revealed significant differences both with the 6 mm or the 10 mm probe (Table 7). Commercial Amarillo melon showed the highest values of Slope, F max and Area with both probes. 10 mm punctures were in agreement with the results from the TPA test ($r=0.91$) showing that commercial Amarillo melon was significantly harder than the rest of fruits and reiterating the existence of a significantly different group with Galia, Irak and Dulce within the softest melons.

Other puncture tests have been performed in melon but with different size fruit sections or whole fruits and using different size probes, thereby limiting the comparison of results. However, considering commercial varieties, Amarillo and Piel de Sapo were harder than Galia and Cantaloupe, in agreement with the trend observed by Aguayo et al. (2004) in a whole fruit puncture test. The 10 mm probe results were also within the range of those of Dos-Santos et al. (2013), Silveira et al. (2011) and Saftner and Lester (2009) for the Piel de Sapo T111, Galia and Cantaloupe melons, respectively, while results with both probes were higher than the ones of Dos-Santos et al. (2011) for Songwhan charmi. No literature was found concerning puncture tests for the rest of the varieties.

By using two different punch diameters it is possible to determine whether the puncture test is measuring compression, shear or a combination of both (Bourne 1966, 1979). Samples in this study were mainly characterized for having a shear force component, with the exception of Amarillo melon that had mainly a compression force behavior. Since the puncture conditions were the same for all the samples, it is possible that Amarillo melon has different mechanical properties than the rest of the melon fruits. The highest hardness of Amarillo melon along with low weight losses, suggest stronger cellular structure. With limited juice release, breakage happens between the cells rather than in the cells (Vandenberghe and Claes 2011) and thus, tissue fracture occurs rather by compression.

The 10 mm puncture parameters were higher, and although the results of both probes had similar significance, it was more sensitive detecting differences than 6 mm probe. Perhaps the major contact area of the 10 mm probe compresses a higher measurable number of cells providing more consistent parameter values (Klatzky et al., 2003).

The present work confirms that both TPA and puncture tests allow the discrimination of melon fruit variability. However the methods point to different fruit properties and provide complementary information.

3.3. Linear correlation between sensory and physical-chemical determinations

Principal component analysis on the sensory and physical-chemical data (Fig. 1) showed that the first and second principal components explained 51.8% and 19.6% of the observed variation (71.5% in total). The majority of instrumental texture parameters, both TPA and puncture, along with sensory hardness, chewiness and crunchiness contributed to explain the variance of the principal component 1. The second factor was explained by chemical parameters, three sensory attributes and two instrumental parameters, which opposed pH and SSC, initial juiciness and fibrousness, cohesiveness and adhesiveness, in the positive side, to mealiness, in the negative side. TPA and puncture tests were strongly correlated and instrumental and sensory textural parameters were well related with each other. TPA gave further feedback on sensory parameters than puncture tests did.

Table 8 shows the linear correlation coefficients between sensory attributes, along the first row, and physical parameters, along the first column, starting with the slope, force (F max) and area measurements with 6 mm and 10 mm probes, TPA parameters and chemical determinations.

Both punctures and TPA parameters were positively correlated with sensory hardness, crunchiness and chewiness, while TPA gave further information on the initial juiciness, fibrousness and mealiness. Samples studied showed a shear force behavior which is exclusively measured in puncture tests (Bourne 1966, 1979) while TPA results depend on the comparison between the two successive compression cycle forces. Initial juiciness, fibrousness and mealiness are mainly compression related attributes and therefore correlated with TPA parameters.

Sensory hardness, crunchiness and chewiness were correlated with puncture parameters, instrumental hardness and fracturability. Vallone et al. (2013) found positive linear correlations with instrumental tests (Puncture and TPA) between hardness and sensory hardness and crunchiness with *reticulatus* cultivars. Sensory crunchiness was equally correlated with instrumental hardness, fracturability and springiness, suggesting the possibility of an approach including these three parameters to predict crunchiness.

Contrarily to the results of Lázaro and De Lorenzo (2015), no linear correlation was found between initial juiciness and instrumental hardness or chewiness. Initial juiciness was most highly correlated to weight loss ($r=0.67$) and based on results from Vandenberghe and Claes (2011) this could be a good predictor for instrumental juiciness in melon fruit. These authors found a significant linear correlation ($r=0.67$, $p=0.007$) between sensory and instrumental juiciness of strawberries, calculating juice release after TPA double compression and filter paper absorption.

Mealiness was most highly correlated to cohesiveness ($r=-0.60$), adhesiveness ($r=-0.59$) and pH ($r=-0.57$). Weakening of cohesive and adhesive forces during ripening is consistent with mealiness while pH correlation may be due to an indirect effect of its correlation with cohesiveness ($r=0.49$) and adhesiveness ($r=0.54$).

Sensory and instrumental chewiness were not very highly correlated ($r=0.58$). Instrumental definition of chewiness does not necessarily correspond to its sensory perception, as postulated by Meullenet et al. (1998). These authors pointed out that considering instrumental chewiness as the mathematical result of multiplying the values of hardness, cohesiveness and springiness is to assume that the three parameters contribute equally to chewiness incurring in an over simplification.

The only parameter with which all sensory attributes were correlated, although slightly, was SSC. Sensory parameters, along with SSC, depend on fruit maturity and the linear correlations found suggest that SSC can explain part of consumers preferences for melon fruits, as previously found for melons (Khatri et al., 2008), apples (Harker et al., 2008) and cherries (Crisosto et al., 2003), among others.

Sensory perception depends on the mechanical properties of plant tissue associated with their different compositional and structural levels (Waldrom et al., 1997; Chiralt and Talens 2005; Mayor et al., 2007). Results from Table 6 suggest a separation of sensory attributes into two groups. One formed by hardness, crunchiness and chewiness, associated with the macro-structural or physical properties of the fruits, and the second, formed by the initial juiciness, fibrousness and mealiness, related with the micro-structural or chemical properties of the fruits. However, Szczesniak (1963) developed a classification of the textural characteristics into three main types depending on the food product properties: mechanical, geometrical (size, shape and orientation of particles) and those related to fat and moisture content. While mechanical and geometrical characteristics are evaluated with standard rating

Table 8
Simple linear correlation coefficients between sensory attributes and physical-chemical parameters.

Parameters	Sensory attributes					
	Hardness	Initial juiciness	Crunchiness	Fibrousness	Mealiness	Chewiness
Puncture 6 mm						
Slope (g/s)	0.65	–	0.69	–	–	0.60
F max (g)	0.68	–	0.74	–	–	0.63
Area (g s)	0.75	–	0.77	–	–	0.70
Puncture 10 mm						
Slope (g/s)	0.61	–	0.60	–	–	0.64
F max (g)	0.68	–	0.69	–	–	0.67
Area (g s)	0.69	–	0.68	–	–	0.68
Texture Profile Analysis (TPA)						
Hardness (g)	0.74	–	0.66	–	–0.35	0.70
Fracturability (g)	0.74	–	0.66	–	–0.33	0.72
Cohesiveness	0.35	0.47	0.36	0.40	–0.60	–
Adhesiveness (g s)	–	0.44	–	–	–0.59	–
Springiness	0.64	–	0.66	–	–	0.54
Chewiness (g)	0.69	–	0.63	0.34	–0.35	0.58
Other parameters						
Weight loss	–	0.67	–	0.32	–0.44	–
Soluble solids content	0.48	0.53	0.41	0.36	–0.52	0.47
pH	–	0.51	–	0.36	–0.57	–

Only significant correlation coefficients are shown ($p \leq 0.05$).

scales, juiciness is a multidimensional trait that can be evaluated not only for the juice degree but also for its release rate during chewing (Brandt et al., 1963), force with which it squirts out of the product or flow properties of the expressed fluid (Szczesniak 2002). Consistently, these sensory attributes can actually be divided

in three groups, a first one formed by hardness, crunchiness and chewiness, a second formed by fibrousness and mealiness and the last one by initial juiciness. Nevertheless, initial juiciness had no linear correlation with chewiness, sensory or instrumental. As

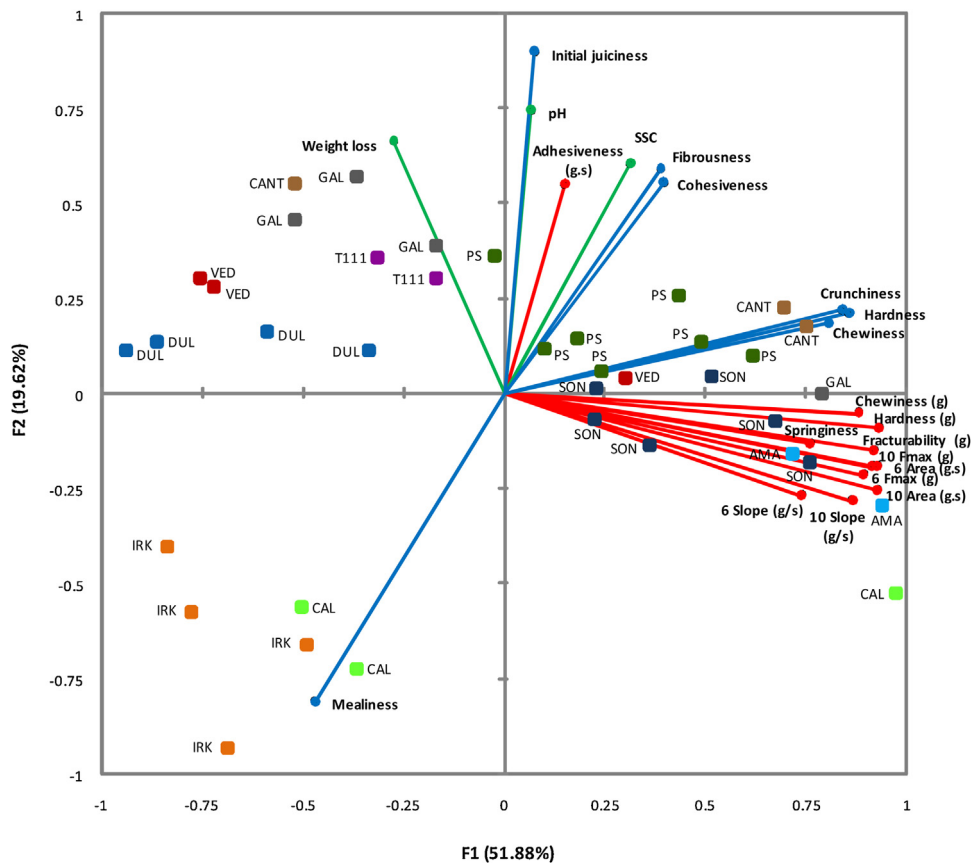


Fig. 1. Principal component analysis of sensory, physical and chemical data obtained on the melon fruit samples. Melon types: CANT, Cantaloupe; AMA, Amarillo; GAL, Galia; PS, Piel de Sapo; T111, Piel de Sapo T111; SON, Songwhan charmi; CAL, Calcuta; IRK, Irak; DUL, Dulce; VED, Védrañtais.

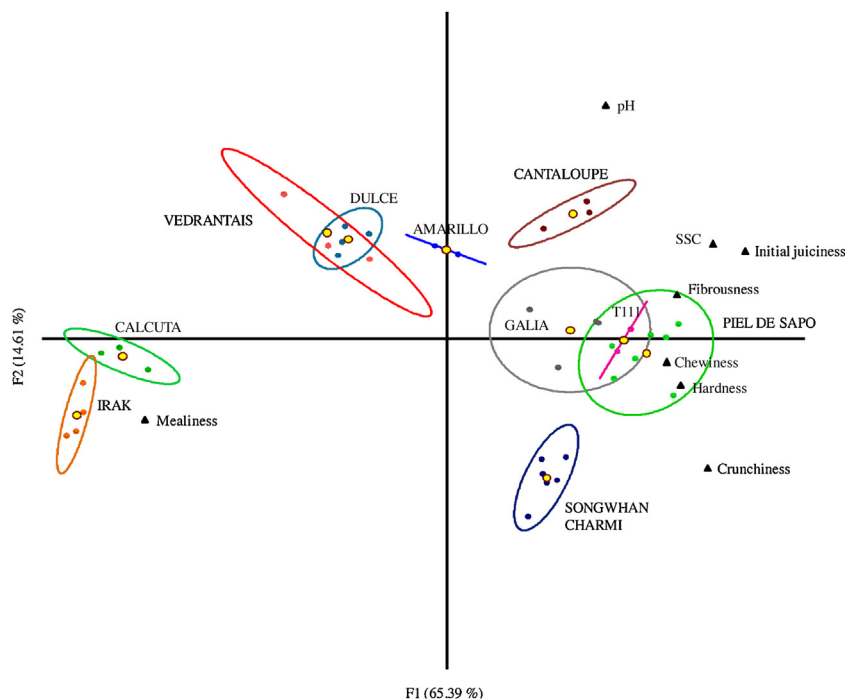


Fig. 2. Discriminant analysis of sensory, physical and chemical data obtained on the melon fruit samples. Only variables correlated higher than 0.6 with any of the first two axes are represented.

mentioned before, this would be due to the small number of chews needed to release all the juice from the tissue of a fruit like melon.

Fig. 2 represents melon sample location and the most discriminate variables in the first two dimensions of the discriminant analysis (correlation coefficient with any of the two axes higher than 0.6). Sensory attributes and chemical measurements were the most discriminate variables of this particular group of melon fruits. A clear overlapping of the different confidence ellipses (significance level of 5%) between elite cultivars (Dulce and Védtrantais) or Piel de Sapo melons (commercial and T111 cultivar) was observed. The opposed discrimination of both groups is more than likely due to their different ripening behavior: climacteric for *cantalupensis* and non-climacteric for *inodorus* fruits. A burst of ethylene production for Piel de Sapo and Sogwhan charmi was previously reported (Périn et al., 2002; Obando-Ulloa et al., 2008; Saladié et al., 2015), with subsequent impact on their textural characteristics. The rest of fruits were also visibly differentiated according to their texture properties. Irak melons were sensory and instrumentally very similar to elite cultivars but were discriminated along with Calcuta based on their mealiness, identifying this attribute as one of the strongest discriminate variables. Songwhan charmi melons were discriminated by their crunchiness while Cantaloupe by a combined effect of SSC and pH. Amarillo melon showed intermediate sensory properties in what refers to mealiness and initial juiciness.

Despite the overlapping mentioned, it is worth to mention that all the samples were correctly classified (100%) in their respective varieties, according to the confusion matrix provided by the discriminant analysis. The same percentage (100%) was obtained when performing the discriminant analysis for sensory attributes (6 descriptors), chemical measurements (pH and SSC) and weight losses, or instrumental texture (13 parameters), independently. However, when comparing the discriminate ability of puncture tests versus TPA, 100% and 92.1% of the samples were correctly classified in their corresponding varieties, respectively. In general, TPA

had lower discriminant ability than puncture test. This is in agreement with the results that determined melon samples as having a shear force behavior, a puncture test measurement, rather than compression, a TPA measurement.

Two sensory descriptors, initial juiciness and mealiness, were the most discriminate variables between samples, followed by crunchiness, pH, chewiness and the rest of the parameters (SSC, hardness and fibrousness) (Fig. 2). Lázaro and De Lorenzo (2015) also postulate juiciness as the most determinant textural trait for consumer acceptance of melon. Any instrumental parameter used to measure texture showed an important ability to discriminate between samples in the two first dimensions. These differences between sensory and instrumental measurements can be explained by the highest compression rates occurred in the mouth, the presence of saliva and the plasticity of the oral cavity compared to the stiffness of the texturometer (Voisey 1975; Bourne 2004). Similar trends have been observed in previous texture studies of fruit (Harker et al., 2002; Gunness et al., 2009; Chauvin et al., 2010) and other foodstuffs (Meullenet et al., 1998; Drake and Gerard 1999; Guerrero et al., 1999).

4. Conclusions

The combined approach of sensory and physical-chemical methods in the evaluation of distinct melon genotypes proves to be efficient, reflecting the wide textural variability within the species and exhibiting the differences in the ripening behavior or the improvement of commercial varieties.

Our results reflect the focus of melon breeders over decisive textural traits but provide new information in the ones not generally considered. These methodologies could potentially be extended to breeding programs in the middle to late stages of variety development to provide detailed textural information beyond the narrow focus on single traits like disease resistance or sugar content.

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5.1 Publication 2: Correlation of sensory and instrumental aroma and flavor of melon fruits

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Linking sensory and proton transfer reaction–mass spectrometry analyses for the assessment of melon fruit (*Cucumis melo* L.) quality traits

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Abstract

Sixty-seven samples of ten melon types (*Cucumis melo* L.) were evaluated to determine the relationship between their quality traits: sensory attributes, pH, soluble solids, and volatile organic compounds. Fruits from the *cantalupensis*, *conomon*, *dudaim*, *inodorus*, and *momordica* cultivar groups were analyzed. The sensory profiles were assessed using ten attributes covering odor, flavor, and taste characteristics, whereas the volatile profiles were derived by proton transfer reaction–mass spectrometry. Fruits from the *cantalupensis* and *inodorus* cultivars showed an opposite pattern for several quality traits. Fruits from the *dudaim* cultivar were more related to the *cantalupensis*, whereas *conomon* and *momordica* showed an intermediate behavior between *inodorus* and *cantalupensis*. The attributes of odor and flavor intensity, ripe fruit odor, fermentative odor, and fermentative flavor correlated positively to C₃–C₉ esters ($r=0.43$ – 0.73 ; $p \leq 0.01$). Positive correlations were also observed for several alcohols ($r=0.36$ – 0.82 ; $p \leq 0.05$), including methanol, ethanol, and diol alcohols, as well as for several aldehydes ($r=0.43$ – 0.85 ; $p \leq 0.01$), such as acetaldehyde, butanal, methyl butanal, heptanal, and decanal. The attributes mentioned above were negatively correlated with two C₉ aldehydes, 2,6-nonadienal and nonenal ($r=-0.45$ to -0.62 ; $p \leq 0.01$), whereas sweetness was negatively correlated with two C₆ green leaf volatiles, hexenal and 3-hexenol ($r=-0.50$; -0.67 ; $p \leq 0.001$). The melon fruits presented distinct differences in the quality traits evaluated. These results provide information for the development of new cultivars with characteristic taste combinations without compromising other desirable fruit quality traits.

Keywords Flavor · Melon fruit · Odor · PTR–MS · Sensory analysis · Volatile organic compounds

Introduction

Melon (*Cucumis melo* L.) is a species with high genetic variation, the fruits of which show a wide diversity in morphological, physical–chemical, and sensory traits. The sweet melons of the *inodorus* group or the highly aromatic melons of the *cantalupensis* one are generally consumed as fresh fruits. In contrast, while the exotic cultivars of the *conomon*, *dudaim*, or *momordica* groups are either inedible or consumed as fresh, cooked, or pickled vegetables [1, 2]. Melon has an exceptional ripening pattern as it comprises both climacteric and non-climacteric cultivars within a single species, i.e., cultivars with a rise in the respiration rate and ethylene production at the onset of fruit ripening (e.g., *cantalupensis*), and cultivars with little or no ethylene production (e.g., *inodorus*). However, it has also been reported that melon-ripening behavior follows a continuous spectrum between the climacteric and non-climacteric

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references rather than just two ripening patterns [3]. In addition, ethylene-dependent and ethylene-independent pathways can coexist during the ripening process of climacteric melon fruits [4–6]. However, the relationships between fruit quality traits and the biochemical pathways involved in ethylene-dependent and ethylene-independent ripening processes are not entirely understood [7]. The fruits of the *cantalupensis* cultivars are generally more aromatic but show a faster loss of firmness and a shorter shelf-life than the ones of *inodorus* cultivars [8]. These differences are reflected in the sensory attributes and consumer acceptance of commercial cultivars [9, 10], but little is known about the odor and flavor profiles of the *conomon*, *dudaim*, or *momordica* exotic cultivars.

Odor and flavor are among the properties that most influence the sensory perception of fruit. Melon odor perception depends on the presence and concentration of volatile organic compounds (VOCs), which comprise a profile typically associated with each cultivar [9, 11]. In addition, flavor perception relies not only on volatile but also non-volatile compounds such as soluble sugars and organic acids. Sweetness is considered a determinant attribute for the eating quality of melon fruit, but a moderate acidity is also able to drive consumers' liking of this fruit species [10]. Interactions between volatile and non-volatile compounds should also be considered as VOCs are known to enhance the perception of several flavor attributes [12–15].

Gas chromatography is the most common technique for the assessment of melon VOCs profile, which comprises esters, alcohols, aldehydes, some sulfur-containing compounds, and minor quantities of ketones, terpenes, and hydrocarbons [8, 11, 16–22]. An alternative is the use of proton transfer reaction–mass spectrometry (PTR–MS), which allows the headspace VOCs to be drawn from the samples at room temperature (25 °C), simulating the conditions of consumer perception of the fruits. Headspace

PTR–MS allows a highly sensitive, real-time volatile detection (pptv, parts per trillion by volume detection and less than 1 min for a complete spectrum acquisition) without any sample pretreatment. The method is based on a soft chemical ionization by protonated water molecules (H_3O^+), which perform a non-dissociative proton transfer to most of the common VOCs without reacting with any of the natural components of air [23, 24].

The aim of the present study was to assess the odor and flavor profiles of ten types of melon fruits and evaluate the correlation between their quality traits: i.e., between their sensory attributes, pH, soluble solids, and VOCs. Melon genotypes belonging to the *cantalupensis*, *conomon*, *dudaim*, *inodorus*, and *momordica* cultivar groups, together with commercial reference varieties from *cantalupensis* and *inodorus* cultivars, were selected to represent the variation within the species.

Materials and methods

Materials

Fruits of ten melon (*Cucumis melo* L.) types (Table 1), comprising genotypes from the subspecies *melo* and *agrestis*, together with commercial reference varieties, were analyzed ($N=67$). The commercial varieties were obtained from a local market, while the cultivars were grown at the 'IRTA-Torre Marimon' greenhouse (41°36'47.88" N 2°10'10.45" E, Barcelona, Spain) and harvested at physiological maturity. The fruits were harvested at 40–45 days after pollination (dap) for 'Iraq' and 'Calcuta' cultivars, 45 dap for 'Védrantais' and 50 dap for 'Dulce', which corresponded to the change in color and abscission of the fruits, or at 50 dap for 'Songwhan charmi' and 55 dap for 'Piel de Sapo-T111'

Table 1 Melon fruits used in this study ($N=67$)^a

Melon fruit (accession)	Subspecies	Cultivar group	Respiration pattern	Country of origin
Cultivars				
'Dulce'	<i>melo</i>	<i>cantalupensis</i>	Climacteric	USA
'Védrantais'	<i>melo</i>	<i>cantalupensis</i>	Climacteric	France
'Iraq' (C-1012)	<i>melo</i>	<i>dudaim</i>	Climacteric	Iraq
'Calcuta' (PI-124112)	<i>agrestis</i>	<i>momordica</i>	Climacteric	India
'Songwhan charmi' (PI-161375)	<i>agrestis</i>	<i>conomon</i>	Non-climacteric	Korea
'Piel de Sapo' (T111)	<i>melo</i>	<i>inodorus</i>	Non-climacteric	Spain
Commercial varieties				
Galia	<i>melo</i>	<i>cantalupensis</i>	Climacteric	Spain
Cantaloupe	<i>melo</i>	<i>cantalupensis</i>	Climacteric	Spain
Amarillo	<i>melo</i>	<i>inodorus</i>	Non-climacteric	Spain
Piel de Sapo	<i>melo</i>	<i>inodorus</i>	Non-climacteric	Spain

^aNumber of samples for each melon fruit type: Amarillo ($n=3$); Cantaloupe ($n=3$); Galia ($n=6$); Piel de Sapo ($n=7$); Calcuta ($n=10$); Dulce ($n=6$); Iraq ($n=10$); Songwhan charmi ($n=8$); Piel de Sapo-T111 ($n=6$); Védrantais ($n=8$)

as it was previously determined to be the point at which these cultivars had high sucrose content, and thus optimal fruit quality [3].

Fruits were transversally cut into 2 cm slices, and both stem and blossom ends discarded. The middle slice was used for pH and soluble solid content (SSC) determinations, while the two contiguous slices were covered with plastic wrap and stored at 4 °C until the sensory analysis. The flesh of the remaining slices was vacuum-packed in double-layer aluminum bags and stored at –80 °C for further analyses, after the removal of the skin plus 1 cm of underlying flesh and the placental tissue.

Methods

Common quality indices

The pH measurements were performed in the flesh of the middle slice of each fruit using a puncture electrode pH meter with temperature correction probe, model 5053-T (Crison Instruments, Barcelona, Spain). Flesh from the same slice was hand-squeezed, and the soluble solid content (SSC) was measured in the juice using a Quick-Brick™ 90 digital refractometer (Mettler-Toledo, GmbH, Germany). Both parameters were measured in triplicate, and the values were expressed as average results ($N=67$) (Table 6, Appendix).

Sensory analysis

The sensory analyses were performed by an eight-member panel with extensive experience in quantitative and descriptive methods, selected and trained following ISO 8586–1:1993 [25] and ISO 8586–2:1994 [26]. Ten descriptors of odor, flavor, and taste attributes (Table 2) were chosen during training sessions of open discussion between the panelists. Different commercial melon samples were

evaluated during these sessions to have a wide range of sensory characteristics frequent in melon fruits, following a procedure previously described [27].

A total of 38 samples obtained from the same fruits used for the chemical determinations were assessed at harvest. Two melon slices (2 cm) of each fruit sample were cut into eight pieces of similar size, placed in a plastic dish labeled with a random number of three digits, and given to each one of the eight assessors. All of them assessed the same number of samples per session in different presentation orders, following a Williams Latin square design to block first-order and carry-over effects. A non-structured 10 cm linear scale was used for the evaluation of each descriptor, in which 0 meant low intensity and 10 meant high intensity. Mineral water was used as a palate cleanser between samples. The analyses were performed in a test room designed following ISO 8589:2007 [28] and the samples evaluated under white lighting (700 lx ± 150 lx).

PTR–MS profiling of VOCs

The frozen flesh of each melon fruit was cut into pieces, immersed in liquid nitrogen, and immediately ground for 15 s at 10,000 rpm using a Grindomix GM 200 (Retsch, Düsseldorf, Germany). Ground samples were stored (–20 °C) and analyzed within 24 h. For each sample, 1.0 g of ground powder was weighted in screw cap glass flasks of 250 mL. Before the analyses, the flasks were equilibrated in a water bath at 25 °C for 30 min. The temperature was selected to match the volatile emission in the headspace of the flasks and the conditions of the consumer perception of the fruits. The flasks were attached to the inlet of the PTR–MS system (Ionicon GmbH, Innsbruck, Austria), and the headspace was extracted at a 60 mL/min flow rate. The temperature of both the inlet and the drift chamber was kept at 60 °C. Mass spectral data in a range between 20 and 160

Table 2 Sensory attributes and description used for sensory analysis

Attributes	Description
Odor	
Odor intensity	Strength of melon overall odor perceived during chewing
Ripe fruit	Typical fruity odor in a range from under to over-ripe
Fermentative	Presence of chemical or solvent-like odor
Cucumber	Presence of cucumber characteristic odor
Flavor	
Flavor intensity	Strength of melon overall flavors perceived during chewing
Fermentative	Presence of chemical or solvent-like flavor
Cucumber	Presence of cucumber characteristic flavor
Astringency	Drying out, roughness aftertaste felt in any mouth surface
Taste	
Acidity	Amount of acid perceived during chewing
Sweetness	Amount of sugar perceived during chewing

atomic mass units (amu) were collected with a dwell time of 200 ms. Blank measurements were run between samples to monitor background air, and these values were subtracted from the sample measurements. All values were corrected for transmission, converted to ppbv according to the procedure described by Lindinger et al. [24] and considering a reaction rate constant of $k_R = 2 \times 10^{-9} \text{ cm}^3/\text{s}$. All the analyses were carried out in independent triplicates, and the average mass spectra were calculated. The masses m/z 32 (O_2^+) and m/z 37 (water cluster ion) were removed from the dataset, and mass spectral data (m/z 20–160) of the 67 melon fruits were used for data analysis.

PTR–ToF–MS tentative identification of VOCs

Volatile organic compounds tentative identification was performed using a PTR–ToF–MS 8000 system (Ionicon GmbH, Innsbruck, Austria). A representative subset of samples ($n = 6$) was selected considering the variability observed in the PTR–MS results. The procedure was identical as in the previous section, except that only 0.25 g of the ground powder was used. The ionization conditions in the reaction chamber were maintained as follows: drift temperature 60 °C, drift voltage 421 V, and drift pressure 3.80 mbar. The instrument was operated at E/N value of 133 Townsend ($1\text{Td} = 10^{-17} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). A further description of PTR–ToF–MS is given elsewhere [23]. The sample measurements lasted 60 s with an acquisition rate of 1 spectrum/s. Baseline removal and spectra alignment by internal calibration of the ToF data were performed according to a procedure previously described [29]. The interfering ions (O_2^+ , NO^+ , and water clusters) and their isotopologues were excluded from the dataset. VOCs were tentatively identified based on the PTR–ToF–MS results and the existing literature.

Data analysis

The sensory data were evaluated using a one-way Analysis of Variance (ANOVA) on the mean values per melon across panelists, considering the type of melon as a fixed factor. A Tukey's HSD post hoc test ($p \leq 0.05$) was performed to examine significant statistical differences between the melon types. Due to the lack of normality, the PTR–MS data were evaluated using a non-parametric ANOVA (Kruskal–Wallis test), followed by Dunn's multiple comparison test and Bonferroni correction ($p \leq 0.05$).

The data of the sensory scores and headspace VOCs measured on the same samples were used to evaluate the relationship between both methods. Principal Component Analysis (PCA) and Pearson's correlation analysis were performed over the 10 sensory attributes and the 40 significantly different VOCs obtained from the ANOVA results.

The PCA was performed on the correlation matrix to normalize the different datasets. All the statistical analyses were performed with XLSTAT 2018 software (Addinsoft, Paris, France).

Results and discussion

Sensory characteristics

The significant differences observed for the ten sensory attributes among the melon types are shown in Table 3. 'Védrantais' and 'Dulce' cultivars showed higher scores for the intensity, ripe fruit, and fermentative odor attributes, whereas the lower were observed for the 'T111' line of the Piel de Sapo cultivar followed by the 'Calcuta'. The same was observed between the commercial *cantalupensis* (Cantaloupe and Galia) and *inodorus* (Amarillo and Piel de Sapo). Other authors observed higher fruity odor for climacteric fruits belonging to the *cantalupensis* cultivar group but smaller differences between these and non-climacteric *inodorus* ones [10]. The slight differences between 'Iraq', Cantaloupe, and Galia were consistent with the previous results for the odor scores of *dudaim* and *cantalupensis* fruits [30]. These authors also reported higher odor scores for fruits of both cultivar groups than *inodorus*. 'Védrantais', and 'Dulce' cultivars were also significantly higher scored for the intensity and fermentative flavor attributes. The lowest scores of these attributes were observed for 'Calcuta' and 'T111' fruits, respectively. The higher score for fermentative flavor of *cantalupensis* than *inodorus* fruits was consistent with the results of the odor attributes.

The sweeter fruits belonged to the commercial varieties and 'Védrantais' cultivar. These were followed by 'Dulce' and 'T111' cultivars, while 'Calcuta' was the least sweet. No sweetness differences between *inodorus* and *cantalupensis* fruits were previously observed [10], although changes may occur depending on the type of cultivar studied [11]. *Cantalupensis* fruits were observed to be sweeter than *inodorus*, and both sweeter than *dudaim* fruits [30]. This was consistent with our results for 'Iraq' cultivar. The highest acidity scores were observed for 'Védrantais' and 'Songwhan charmi' cultivars. Except for the lowest scores of Amarillo, no significant differences were observed for the rest of the fruits. Other authors reported minimal [10] or not significant acidity differences [11] between *inodorus* and *cantalupensis* cultivars. With the exception of 'Calcuta' and 'Iraq' melons, perceived acidity was substantially lower than sweetness. This reflects the predominance of sweet varieties among the fruits analyzed, as several melon types showed a high SSC level together with near-neutral pH values (Table 6, Appendix). The sweet/acid ratio is an important quality index for other fruit species, but the sweet melon varieties lack acid taste,

Table 3 Sensory panel scores of the odor, flavor, and taste attributes among melon fruit types: mean values and standard deviation in brackets ($n = 38$)^a

Attributes	Cultivars (cv. group)									
	Non-climacteric			Commercial varieties (cv. group)						
	Climacteric			Climacteric		Non-climacteric				
	'Dulce' ^b (<i>cantalupensis</i>)	'Védrantais' (<i>cantalupensis</i>)	'Iraq' (<i>dudaim</i>)	'Calcuta' (<i>momordica</i>)	'Songwhan charmi' (<i>conomon</i>)	Piel de Sapo 'T111' (<i>inodorus</i>)	Galia (<i>cantalupensis</i>)	Cantaloupe (<i>cantalupensis</i>)	Amarillo (<i>inodorus</i>)	Piel de Sapo (<i>inodorus</i>)
Odor										
Odor intensity	7.95 (0.33) ^{ab}	9.03 (0.06) ^a	6.00 (0.36) ^c	4.71 (0.62) ^{cd}	5.29 (0.67) ^c	3.31 (0.83) ^d	6.36 (1.02) ^{bc}	6.61 (1.05) ^{bc}	3.79 (0.06) ^d	3.95 (0.59) ^d
Ripe fruit	7.80 (0.38) ^{ab}	8.91 (0.36) ^a	5.11 (0.88) ^{cde}	3.76 (0.88) ^e	4.12 (0.66) ^{de}	3.33 (0.32) ^e	6.20 (1.38) ^{bc}	5.95 (0.90) ^{bcd}	3.83 (0.38) ^e	3.45 (0.74) ^e
Fermentative	4.23 (0.60) ^{ab}	6.50 (0.08) ^a	2.38 (0.19) ^{bc}	1.35 (0.78) ^{cd}	1.70 (0.65) ^{cd}	0.12 (0.07) ^d	3.85 (1.61) ^b	3.46 (1.21) ^{bc}	0.39 (0.06) ^{cd}	0.11 (0.14) ^d
Cucumber	0.60 (0.44) ^b	0.02 (0.10) ^b	0.73 (0.59) ^b	0.74 (0.62) ^b	3.10 (0.62) ^a	0.78 (0.50) ^b	0.41 (0.28) ^b	0.51 (0.41) ^b	1.53 (0.72) ^{ab}	0.89 (0.24) ^b
Flavor										
Flavor intensity	6.81 (0.55) ^{ab}	7.94 (0.39) ^a	5.28 (0.56) ^{cd}	3.86 (0.34) ^d	5.97 (0.41) ^{bc}	5.58 (0.29) ^{bcd}	6.86 (0.58) ^{ab}	7.11 (0.31) ^{ab}	6.03 (0.25) ^{bc}	6.63 (0.49) ^{ab}
Fermentative	3.41 (0.54) ^b	5.94 (0.39) ^a	2.46 (0.62) ^{bc}	0.99 (1.07) ^{cd}	1.08 (0.63) ^{cd}	0.20 (0.38) ^d	2.67 (0.39) ^b	3.23 (0.91) ^b	0.89 (0.11) ^{cd}	0.22 (0.27) ^d
Cucumber	0.59 (0.43) ^b	0.17 (0.31) ^b	1.53 (0.82) ^b	1.38 (1.17) ^b	4.05 (0.77) ^a	0.80 (0.04) ^b	0.59 (0.42) ^b	0.73 (0.64) ^b	0.49 (0.07) ^b	0.31 (0.18) ^b
Astringency	1.37 (0.26) ^{ab}	1.43 (0.55) ^{ab}	2.27 (0.63) ^a	1.84 (0.11) ^{ab}	1.65 (0.50) ^{ab}	0.99 (0.06) ^{ab}	1.22 (0.37) ^{ab}	1.29 (0.35) ^{ab}	0.87 (0.19) ^{ab}	0.77 (0.39) ^b
Taste										
Acidity	1.10 (0.22) ^{ab}	1.53 (0.03) ^a	1.19 (0.29) ^{ab}	1.22 (0.61) ^{ab}	1.46 (0.32) ^a	0.70 (0.24) ^{ab}	1.16 (0.31) ^{ab}	1.23 (0.23) ^{ab}	0.46 (0.05) ^b	0.67 (0.23) ^{ab}
Sweetness	4.26 (0.87) ^{ab}	5.22 (0.57) ^a	1.15 (0.50) ^{cd}	0.55 (0.12) ^d	2.56 (0.72) ^{bc}	4.17 (0.15) ^{ab}	5.77 (0.90) ^a	5.67 (0.33) ^a	5.48 (0.63) ^a	5.90 (0.68) ^a

^aValues with different letters in the same row indicate significant differences by Tukey's HSD post hoc test ($p \leq 0.05$)

^bNumber of samples of each melon type: 'Dulce' ($n=4$), 'Védrantais' ($n=3$), 'Iraq' ($n=4$), 'Calcuta' ($n=3$), 'Songwhan charmi' ($n=6$), Piel de Sapo 'T111' ($n=2$), Galia ($n=4$), Cantaloupe ($n=3$), Amarillo ($n=2$), Piel de Sapo ($n=7$)

and their eating quality is mainly determined by sweetness [2]. At these levels, the interaction between acid and sweet tastes has a suppressive effect of sweetness over acidity [31].

Small differences were observed for cucumber odor and flavor attributes. ‘Songwhan charmi’ fruits had higher cucumber odor, followed by Amarillo ones, while the rest of the fruits had lower scores for this attribute. This pattern was reflected in cucumber flavor perception for ‘Songwhan charmi’ fruits but not for Amarillo ones, possibly due to the high sweetness perception observed for Amarillo melons. Regarding astringency, the highest scores were observed for ‘Iraq’ cultivar, while for commercial Piel de Sapo the least. No differences were observed between the rest of the fruits, neither cultivars nor commercial varieties.

These results showed that panelists distinguished *cantalupensis* and *inodorus* fruits by their odor and flavor, but also perceived small differences between *cantalupensis* cultivars and their commercial relatives as well as unique traits of the exotic cultivars. Our results provide information for the quality-oriented programs with an aim to produce more aromatic and flavorful melon cultivars.

VOCs’ profile

The VOCs’ profile of melon fruit is influenced by cultivar, maturity stage, harvest conditions, or storage. Moreover, as the pathways involved in the formation of specific compounds (such as esters) are known to depend on the production of ethylene, the climacteric and non-climacteric melon fruits exhibit different volatile profiles. Among the key volatile compounds reported in melon, C₄–C₉ esters have the highest impact over the aroma of climacteric fruits, considered very aromatic, whereas C₆ and C₉ alcohols and aldehydes have the highest impact over the aroma of non-climacteric fruits, generally considered as less aromatic [4–8].

In the present study, significant differences were observed for 40 compounds among the ten melon fruit types (Table 4). The VOC profile consisted of 9 alcohols (including 3 alcohol fragments at *m/z* 29.037, 71.058 and 85.099), 9 aldehydes, 1 compound at *m/z* 143.143 tentatively identified as an alcohol/aldehyde (Nonanal/nonenol), 8 esters (including 1 ester fragment at *m/z* 67.054), 4 terpenes (including a monoterpene fragment at *m/z* 95.085 and a farnesene fragment at *m/z* 123.117), and 4 other volatiles or related compounds (acetone, acetic acid, and a nitrile compound at *m/z* 42.034). Some fragments of several possible origins (alcohols, aldehydes, esters, and terpenes) were also observed for *m/z* 41.038, 43.018/43.053, 55.054, 57.069, 81.070, and 83.086. The VOC profiles obtained for the different melon types showed that, among the climacteric fruits, the ones belonging to the *cantalupensis* cultivar group (‘Védrantais’, ‘Dulce’, Galia, and Cantaloupe) had a higher concentration of alcohols, aldehydes, and esters.

The opposite was observed for the non-climacteric fruits, especially those belonging to the *inodorus* cultivar group (Piel de Sapo ‘T111’, Amarillo and Piel de Sapo), which are reported to have a lower volatile concentration. Regarding the exotic cultivars, the fruits of the *dudaim* cultivar (‘Iraq’) showed several similarities with the VOC profile of the other *cantalupensis* fruits. In contrast, fruits of the *momordica* (‘Calcuta’) and *conomon* (‘Songwhan charmi’) cultivars showed an intermediate behavior between *cantalupensis* and *inodorus*. This was in agreement with the previous works reporting similarities between the VOC profile of several *dudaim*, *conomon*, and *momordica* fruits with either *cantalupensis* or *inodorus* regardless of their climacteric or non-climacteric classification [32].

Alcohols

The abundance of alcohols was significantly higher for ‘Védrantais’, mostly followed by ‘Dulce’ and ‘Iraq’ cultivars, and lower for ‘Calcuta’, ‘Songwhan charmi’, and ‘T111’. A similar alcohol profile was observed for the commercial *cantalupensis* (Cantaloupe and Galia) and the ‘Iraq’ cultivar. Methanol was the major alcohol observed for all the melon types followed by ethanol. It is a marker of pectin degradation involved in the regulation of ethanol production during ripening [33]. Ethanol is produced by the reduction of acetaldehyde, and the changes in the concentration of both compounds occur in a related pattern [16]. The ratio methanol/ethanol in melon fruit differs between cultivars, ripening stage, and processing [18, 33].

Aldehydes

Acetaldehyde was the major aldehyde for all the melon types. It was present at significantly higher concentrations in the headspace of the ‘Védrantais’ cultivar, while lower concentrations were observed for the ‘Calcuta’ cultivar and commercial *inodorus*. Other authors reported prominent levels of acetaldehyde among melon fruits [16, 34]. Hexenal was determined at significantly higher concentrations for ‘Iraq’ and ‘Calcuta’ cultivars in comparison with ‘Songwhan charmi’ and ‘T111’ cultivars. The lower concentrations of hexenal observed for *inodorus* fruits are consistent with the previous works [22, 35]. Heptanal was significantly higher for ‘Védrantais’ cultivar along with commercial *cantalupensis* and ‘Songwhan charmi’, while lower for *inodorus* fruits. Nonenal was significantly higher for ‘T111’ cultivar along with the commercial *inodorus* fruits. 2,6-nonadienal was significantly higher for ‘Iraq’ cultivar and Amarillo. Lower concentrations of both C₉ aldehydes were observed among the commercial *cantalupensis* fruits. Higher concentrations of nonenal and 2,6-nonadienal among *inodorus* than *cantalupensis* were previously reported [11, 36].

Table 4 Tentative identification by PTR–ToF–MS (three left-side columns) and concentration (ppbv) of the significantly different VOCs among melon fruit types ($N=67$) by PTR–MS (ten right side columns): mean values and standard deviations in brackets^a

Mass (m/z) Tentative identification ^b	Sum formula	References	Cultivars (cv.group)					Commercial varieties (cv. group)				
			Climacteric		Non-climacteric			Climacteric		Non-climacteric		
			'Dulce' ^c (<i>cantalupen- sis</i>)	'Védrantais' (<i>cantalupen- sis</i>)	'Iraq' (<i>dudaim</i>)	'Calcuta' (<i>momordica</i>)	'Songwhan charmi' (<i>conomon</i>)	Piel de Sapo 'T111' (<i>inodorus</i>)	Galia (<i>cantalupen- sis</i>)	Cantaloupe (<i>cantalupen- sis</i>)	Amarillo (<i>inodorus</i>)	Piel de Sapo (<i>inodorus</i>)
29.037 Fragment (alcohol)	$C_2H_5^+$		16.2 (7.0) ^{ab}	217.4 (112.8) ^a	10.1 (9.3) ^{ab}	3.3 (2.7) ^b	4.8 (4.8) ^b	9.2 (13.6) ^b	10.8 (10.2) ^{ab}	17.3 (0.9) ^{ab}	0.9 (1.1) ^b	2.4 (3.7) ^b
31.017 Formaldehyde	CH_3O^+	[37]	17.5 (5.3) ^{ab}	41.1 (9.0) ^a	10.1 (4.3) ^{ab}	6.4 (2.3) ^b	5.1 (2.6) ^b	5.7 (5.4) ^b	14.3 (6.1) ^{ab}	18.5 (6.9) ^{ab}	3.8 (0.9) ^b	4.2 (2.6) ^b
33.034 Methanol	CH_3O^+	[18, 33]	5385 (2068.8) ^{ab}	6106.8 (1245.3) ^a	1343.7 (579.3) ^{abc}	849.1 (357.1) ^c	564.8 (329.2) ^c	1074.4 (613.4) ^{abc}	5519.9 (2405.1) ^{ab}	5471.8 (3169.4) ^{ab}	1014.4 (498.9) ^{abc}	885.8 (425.5) ^b
41.038 Fragment (alcohol, ester)	$C_3H_5^+$	[37, 38]	72.1 (36.0) ^{abc}	127.8 (30.6) ^a	53.8 (22.9) ^{abc}	33.4 (12.2) ^{abc}	23.4 (11.5) ^{bc}	17 (12.2) ^c	122.3 (70.4) ^{ab}	89.9 (37.3) ^{abc}	8.8 (2.4) ^c	11.2 (3.7) ^c
42.034 Acetonitrile, nitrile frag- ment	$C_2H_4N^+$		16.9 (15.6) ^{ab}	36.3 (34.2) ^a	11.7 (7.3) ^{ab}	5.2 (3.4) ^b	14.5 (24.2) ^{ab}	6.5 (6.9) ^{ab}	12.4 (7.3) ^{ab}	8.9 (1.1) ^{ab}	6 (7.3) ^b	3.2 (2.6) ^b
43.018 Fragment (ester)	$C_2H_3O^+$	[37, 38]	416 (295.5) ^{ab}	1949.9 (1252.4) ^a	209.1 (143.3) ^{ab}	116 (49.1) ^b	302.7 (235.4) ^{ab}	242.3 (352.2) ^b	584.7 (699.9) ^{ab}	533.6 (443.6) ^{ab}	31.2 (12.3) ^b	38.8 (12.4) ^b
43.053 Fragment (alcohol, ester, acetate)	$C_3H_7^+$	[37, 38]										
45.033 Acetaldehyde	$C_2H_5O^+$	[4, 34]	3961.2 (1184.9) ^{ab}	12084.9 (4842.8) ^a	4163.5 (4136.2) ^{ab}	1511.3 (1055.5) ^b	5968.6 (3827.4) ^{ab}	3794 (1676.4) ^{ab}	4879.7 (1133.1) ^{ab}	8332.9 (2026.9) ^{ab}	1366.6 (670.8) ^b	2172.8 (757.8) ^b
47.049 Ethanol	$C_2H_7O^+$	[4, 34]	329.7 (117.6) ^{ab}	3737.5 (187.3) ^a	233.5 (164.2) ^{ab}	114.5 (62.3) ^b	146.9 (91.2) ^b	209.3 (241.4) ^b	230 (162.7) ^{ab}	367.9 (45.8) ^{ab}	71.6 (29.5) ^b	84.9 (75.7) ^b
55.054 Fragment	$C_4H_7^+$	[37]	28.5 (14.5) ^{ab}	19.7 (7.2) ^{ab}	38.4 (20.9) ^a	29.6 (9.1) ^a	13.3 (4.7) ^{ab}	6.5 (1.2) ^b	21 (12.8) ^{ab}	11.9 (4.8) ^{ab}	5.2 (1.0) ^b	5.4 (0.8) ^b
57.069 Fragment (alcohol, ester)	$C_4H_9^+$	[37, 38]	76.3 (43.2) ^{ab}	98.6 (47.3) ^a	35.6 (16.1) ^{abc}	23.8 (7.2) ^{abc}	21 (12.8) ^{abc}	11.3 (12.5) ^{bc}	143.7 (86.7) ^a	124.9 (60.2) ^a	3.5 (1.2) ^{bc}	3.1 (0.5) ^c

Table 4 (continued)

Mass (m/z) Tentative identification ^b	Sum formula	References	Cultivars (cv.group)						Commercial varieties (cv. group)			
			Climacteric			Non-climacteric			Climacteric		Non-climacteric	
			'Dulce' ^c (<i>cantalupensis</i>)	'Védraçais' (<i>cantalupensis</i>)	'Iraq' (<i>dudaim</i>)	'Calcuta' (<i>momordica</i>)	'Songwhan charmi' (<i>conomon</i>)	Piel de Sapo 'T111' (<i>inodorus</i>)	Galia (<i>cantalupensis</i>)	Cantaloupe (<i>cantalupensis</i>)	Amarillo (<i>inodorus</i>)	Piel de Sapo (<i>inodorus</i>)
59.049	$C_3H_7O^+$	[4, 17]	19.3 (3.0) ^{ab}	26.2 (6.7) ^{ab}	32 (8.7) ^a	25.4 (11.4) ^{ab}	26.6 (8.3) ^{ab}	14.8 (6.1) ^b	17.7 (5.1) ^{ab}	18.4 (3.7) ^{ab}	8.4 (1.0) ^b	22 (6.7) ^{ab}
61.028	$C_2H_5O_2^+$	[17, 35]	341.3 (287.2) ^{ab}	1539.3 (1324.8) ^a	114.3 (84.9) ^{abc}	72.7 (47.1) ^{bc}	257.3 (230.9) ^{ab}	211.9 (366.4) ^{abc}	496.8 (786.2) ^{abc}	443 (522.2) ^{ab}	3.8 (1.0) ^{bc}	4.2 (4.9) ^c
63.044	$C_2H_7O_2^+$		7.8 (2.1) ^{ab}	24.9 (11.7) ^a	7.2 (5.7) ^{ab}	3.8 (1.2) ^b	10 (5.8) ^{ab}	7 (4.2) ^{ab}	10.2 (3.3) ^{ab}	14 (2.2) ^{ab}	3.2 (1.0) ^b	4.1 (1.2) ^b
67.054	$C_3H_7^+$	[37]	1 (0.5) ^{ab}	0.8 (0.4) ^{ab}	1.9 (0.7) ^a	0.8 (0.3) ^{ab}	1.3 (0.5) ^{ab}	2.3 (0.7) ^a	0.5 (0.2) ^b	0.4 (0.1) ^b	2.3 (1.1) ^a	1.8 (0.5) ^{ab}
69.07	$C_3H_9^+$	[37]	2.7 (0.5) ^{ab}	5.5 (1.8) ^a	4.2 (1.1) ^a	3 (0.8) ^{ab}	4 (1.4) ^a	2.6 (0.5) ^{ab}	3.6 (1.6) ^{ab}	2.4 (0.3) ^{ab}	2.2 (0.9) ^{ab}	2 (0.5) ^b
71.085	$C_3H_{11}^+$	[38]	10.9 (7.2) ^{ab}	155.4 (174.2) ^a	11.6 (13.9) ^{ab}	3.9 (2.0) ^b	3.6 (3.2) ^b	1.8 (1.8) ^b	21.2 (12.4) ^{ab}	9.5 (5.3) ^{ab}	0.6 (0.1) ^b	0.6 (0.1) ^b
73.064	$C_4H_9O^+$	[22, 35]	3.9 (1.9) ^{ab}	18.2 (9.3) ^a	2.3 (0.8) ^b	1.6 (0.8) ^b	4.9 (3.7) ^{ab}	2.7 (3.5) ^b	5.4 (3.1) ^{ab}	4.5 (0.9) ^{ab}	1 (0.5) ^b	1.5 (1.1) ^b
75.044	$C_3H_7O_2^+$	[4, 35]	105.1 (73.4) ^{ab}	162.1 (122.5) ^a	24.3 (9.5) ^{abc}	14.7 (9.9) ^{bc}	9 (4.6) ^c	21.8 (38.0) ^{bc}	121.3 (97.0) ^{ab}	87.2 (90.4) ^{abc}	19.7 (14.5) ^{abc}	7.3 (9.2) ^c
77.059	$C_3H_9O_2^+$		0.6 (0.4) ^{ab}	1.2 (0.7) ^a	0.5 (0.2) ^{ab}	0.2 (0.1) ^{bc}	0.1 (0.1) ^{bc}	0.2 (0.2) ^{bc}	0.7 (0.5) ^{ab}	0.5 (0.4) ^{abc}	0.1 (0.1) ^{bc}	0.1 (0.1) ^c
81.07	$C_6H_9^+$	[37, 38]	8.3 (7.9) ^{ab}	1.9 (0.9) ^b	54.4 (26.4) ^a	49.5 (19.7) ^a	5.4 (8.6) ^b	4.2 (8.6) ^{ab}	4.1 (1.7) ^{ab}	1.2 (0.7) ^b	3.8 (1.8) ^{ab}	2.9 (0.7) ^b
83.086	$C_6H_{11}^+$	[37]	12.2 (7.9) ^{ab}	6.4 (2.3) ^{abc}	18.1 (11.6) ^a	13.7 (4.7) ^a	2.8 (3.1) ^{bc}	1.4 (3.1) ^{bc}	3.4 (1.5) ^{abc}	2.1 (0.6) ^{abc}	1.2 (0.3) ^{bc}	1.1 (0.3) ^c
85.099	$C_6H_{13}^+$	[37]	1.9 (1.3) ^{ab}	4.9 (1.5) ^a	3.7 (1.2) ^{ab}	3.1 (1.7) ^{ab}	0.9 (0.7) ^b	0.6 (0.2) ^b	3.5 (2.5) ^{ab}	1 (0.4) ^{ab}	0.5 (0.2) ^b	0.6 (0.3) ^b
87.08	$C_3H_{11}O^+$	[4, 34]	0.5	2.9	0.7	0.6	0.6	0.5	1.1	0.6	0.3	0.3

Table 4 (continued)

Mass (m/z) Tentative identification ^b	Sum formula	References	Cultivars (cv.group)						Commercial varieties (cv. group)					
			Climacteric			Non-climacteric			Climacteric		Non-climacteric			
			'Dulce' ^c (<i>cantalupensis</i>)	'Védramtais' (<i>cantalupensis</i>)	'Iraq' (<i>dudaim</i>)	'Calcuta' (<i>momordica</i>)	'Songwhan charmi' (<i>conomon</i>)	Piel de Sapo 'T111' (<i>inodorus</i>)	Galia (<i>cantalupensis</i>)	Cantaloupe (<i>cantalupensis</i>)	Amarillo (<i>inodorus</i>)	Piel de Sapo (<i>inodorus</i>)		
<i>Methyl butanal</i>			(0.2) ^b	(1.3) ^a	(0.2) ^{ab}	(0.2) ^b	(0.3) ^b	(0.3) ^b	(0.8) ^{ab}	(0.02) ^{ab}	(0.1) ^b	(0.1) ^b		
89.059	C ₄ H ₉ O ₂ ⁺	[4, 34]	63.5	354.1	16	7.3	33.3	30	80	57.7	0.7	0.6		
<i>Ethyl acetate/methyl propanoate</i>			(53.4) ^{ab}	(228.6) ^a	(16.1) ^{abc}	(6.5) ^{bc}	(31.3) ^{abc}	(52.1) ^{abc}	(107.8) ^{ab}	(66.6) ^{ab}	(0.3) ^{bc}	(0.5) ^c		
91.074	C ₄ H ₁₁ O ₂ ⁺		6.6	5.6	1.4	2.6	0.9	0.4	2.2	2.2	0.2	0.1		
<i>2,3-Butanediol</i>			(5.4) ^{ab}	(2.5) ^a	(0.7) ^{abc}	(1.3) ^{yab}	(0.5) ^{bc}	(0.4) ^{bc}	(1.5) ^{abc}	(1.3) ^{yabc}	(0.1) ^{bc}	(0.1) ^c		
95.085	C ₇ H ₁₁ ⁺	[37]	0.6	0.5	1.2	0.6	1.8	1	0.3	0.2	1.1	0.8		
<i>Fragment (monoterpene)</i>			(0.2) ^{abc}	(0.2) ^{bc}	(0.4) ^{ab}	(0.2) ^{bc}	(0.9) ^a	(0.3) ^{abc}	(0.1) ^c	(0.1) ^c	(0.4) ^{abc}	(0.2) ^{abc}		
99.08	C ₆ H ₁₁ O ⁺	[34, 35]	1.3	0.5	10.4	10	0.9	0.3	0.7	0.1	0.2	0.2		
<i>Hexenal</i>			(1.4) ^{ab}	(0.2) ^{ab}	(5.1) ^a	(3.9) ^a	(1.9) ^b	(0.3) ^b	(0.3) ^{ab}	(0.04) ^b	(0.1) ^b	(0.1) ^b		
101.095	C ₆ H ₁₃ O ⁺	[34, 36]	0.3	0.4	1	0.8	0.2	0.1	0.3	0.2	0.1	0.1		
<i>3-Hexenol</i>			(0.2) ^{ab}	(0.1) ^{ab}	(0.7) ^a	(0.3) ^a	(0.2) ^b	(0.1) ^b	(0.2) ^{ab}	(0.04) ^{ab}	(0.1) ^b	(0.1) ^b		
103.075	C ₅ H ₁₁ O ₂ ⁺	[34, 36]	14.5	13.1	1.6	1.1	0.5	1.5	12.5	3.8	0.1	0.05		
<i>Ester (Ethyl propanoate, Isopropyl acetate, Methyl butanoate, Methyl isobutyrate, Propyl acetate)</i>			(10.6) ^a	(9.2) ^a	(1.4) ^{abc}	(1.0) ^{abc}	(0.4) ^{bc}	(2.6) ^{abc}	(9.6) ^{ab}	(3.8) ^{abc}	(0.03) ^{bc}	(0.03) ^c		
115.111	C ₇ H ₁₅ O ⁺	[34–36]	0.3	2.1	0.2	0.2	0.4	0.1	0.4	0.9	0.1	0.04		
<i>Heptanal</i>			(0.2) ^{abc}	(2.8) ^a	(0.1) ^{abc}	(0.1) ^{abc}	(0.4) ^{ab}	(0.2) ^{bc}	(0.2) ^{ab}	(1.2) ^{yab}	(0.05) ^{bc}	(0.03) ^c		
117.091	C ₆ H ₁₃ O ₂ ⁺	[4, 36]	18.3	18.1	1.4	1.2	0.9	1	11.8	4.8	0.1	0.1		
<i>Ester (Butyl acetate, Ethyl butanoate, Isobutyl acetate, Methyl n-methyl butanoate)</i>			(19.0) ^{ab}	(14.7) ^a	(0.9) ^{abcd}	(0.9) ^{abcd}	(0.9) ^{abcd}	(0.9) ^{cd}	(9.1) ^{abc}	(5.2) ^{yabcd}	(0.1) ^{cd}	(0.1) ^d		
123.117	C ₉ H ₁₅ ⁺	[37]	0.9	0.5	1.1	0.4	1.4	2.8	0.5	0.4	2.8	2		
<i>Fragment (farnesene)</i>			(0.6) ^{yab}	(0.4) ^{ab}	(0.9) ^{ab}	(0.2) ^b	(0.6) ^{ab}	(0.8) ^a	(0.2) ^{ab}	(0.1) ^{ab}	(1.6) ^a	(0.5) ^a		
131.107	C ₇ H ₁₅ O ₂ ⁺	[34, 36]	2.5	13.4	0.7	0.2	0.3	0.6	3.4	1.5	0.04	0.02		
<i>Ester (Ethyl methylbutanoate, Ethyl pentanoate, Methyl hexanoate, Pentyl acetate)</i>			(1.9) ^{ab}	(9.1) ^a	(0.7) ^{ab}	(0.2) ^{bc}	(0.3) ^{bc}	(0.3) ^{bc}	(3.5) ^{yab}	(2.0) ^{yab}	(0.02) ^{bc}	(0.02) ^c		
137.132	C ₁₀ H ₁₇ ⁺	[11, 34]	0.9	0.4	0.2	0.3	0.1	0.1	0.2	0.4	0.1	0.1		
<i>Limonene</i>			(0.5) ^a	(0.2) ^a	(0.1) ^{abc}	(0.1) ^{yab}	(0.04) ^{bc}	(0.04) ^c	(0.2) ^{abc}	(0.5) ^{abc}	(0.06) ^{abc}	(0.02) ^{bc}		
139.112	C ₉ H ₁₅ O ⁺	[34, 36]	0.4	0.2	1	0.5	0.5	0.8	0.2	0.1	1.1	0.8		

Table 4 (continued)

Mass (m/z) Tentative identification ^b	Sum formula	References	Cultivars (cv. group)										
			Climacteric					Non-climacteric					
			Climacteric		Non-climacteric			Climacteric		Non-climacteric			
'Dulce' ^c (<i>cantalupensis</i>)	'Védrantais' (<i>cantalupensis</i>)	'Iraq' (<i>dudaim</i>)	'Calcuta' (<i>momordica</i>)	'Songwhan charmi' (<i>conomon</i>)	Piel de Sapo 'T111' (<i>inodorus</i>)	Galia (<i>cantalupensis</i>)	Cantaloupe (<i>cantalupensis</i>)	Amarillo (<i>inodorus</i>)	Piel de Sapo (<i>inodorus</i>)				
2,6-Nonadienol			(0.3) ^{ab}	(0.1) ^b	(0.4) ^a	(0.3) ^{ab}	(0.4) ^{ab}	(0.3) ^{ab}	(0.3) ^{ab}	(0.1) ^b	(0.04) ^b	(0.3) ^a	(0.3) ^{ab}
141.128	C ₉ H ₁₇ O ⁺	[34, 36]	0.5	0.4	0.6	0.3	0.8	1.2	0.2	0.1	0.1	1.7	1
Nonenal			(0.4) ^{ab}	(0.2) ^{ab}	(0.5) ^{ab}	(0.1) ^b	(0.4) ^{ab}	(0.4) ^a	(0.1) ^b	(0.02) ^b	(0.02) ^b	(1.1) ^a	(0.3) ^a
143.143	C ₉ H ₁₉ O ⁺	[34–36]	0.3	0.5	0.2	0.1	0.3	0.2	0.2	0.2	0.2	0.2	0.1
Nonanal/non-enol			(0.2) ^{ab}	(0.2) ^a	(0.1) ^{ab}	(0.06) ^b	(0.2) ^{ab}	(0.05) ^{ab}	(0.1) ^{ab}	(0.1) ^{ab}	(0.1) ^{ab}	(0.1) ^{ab}	(0.04) ^b
145.123	C ₈ H ₁₇ O ₂ ⁺	[34–36]	1	3.5	0.1	0.1	0.1	0.1	0.2	0.2	0.2	0.04	0.03
Hexyl acetate/Ethyl hexanoate			(0.9) ^{ab}	(3.5) ^a	(0.1) ^{abc}	(0.05) ^{abc}	(0.1) ^{bc}	(0.03) ^c	(0.2) ^{abc}	(0.2) ^{abc}	(0.2) ^{abc}	(0.02) ^{bc}	(0.02) ^c
157.159	C ₁₀ H ₂₁ O ⁺	[34–36]	0.1	0.4	0.1	0.1	0.07	0.06	0.1	0.1	0.1	0.1	0.06
Decanal			(0.03) ^{ab}	(0.2) ^a	(0.06) ^{ab}	(0.05) ^{ab}	(0.02) ^b	(0.05) ^b	(0.05) ^{ab}	(0.08) ^{ab}	(0.08) ^{ab}	(0.04) ^{ab}	(0.04) ^b
159.138	C ₉ H ₁₉ O ₂ ⁺	[34–36]	0.1	0.2	0.05	0.02	0.03	0.04	0.04	0.06	0.06	<0.01	0.02
Ester (Heptyl acetate, Hexyl propanoate, 2-Methylbutyl butanoate)			(0.06) ^{ab}	(0.1) ^a	(0.02) ^{ab}	(0.02) ^b	(0.04) ^b	(0.04) ^{ab}	(0.03) ^{ab}	(0.06) ^{ab}	(0.06) ^{ab}	(<0.01) ^b	(0.02) ^b

^aValues with different letters in the same row indicate significant differences by Kruskal–Wallis non-parametric test with Dunn's multiple comparison test and Bonferroni correction ($p \leq 0.05$)

^bTentative identification based on PTR–ToF–MS and the references in square brackets

^cNumber of samples of each melon type: 'Dulce' ($n=6$), 'Védrantais' ($n=8$), 'Iraq' ($n=10$), 'Calcuta' ($n=10$), 'Songwhan charmi' ($n=8$), 'Piel de Sapo 'T111' ($n=6$), Galia ($n=6$), Cantaloupe ($n=3$), Amarillo ($n=3$), and Piel de Sapo ($n=7$)

Esters

The higher headspace concentrations of esters were observed for the ‘Védrantais’ cultivar, followed by ‘Dulce’ and the commercial *cantalupensis*. Intermediate concentrations were observed for ‘Iraq’ and ‘Songwhan charmi’, whereas the ester pattern of ‘Calcuta’ and ‘T111’ cultivars was more similar to the one of commercial *inodorus*. Within the latter, Piel de Sapo had the lowest ester concentration and showed small differences when compared to the ‘T111’ cultivar. The C₃ and C₄ esters at m/z 75.044 and 89.059 were within the most abundant ester related masses, while lower concentrations were observed for C₅–C₉ esters. The differential ester profile of *cantalupensis* and *inodorus* fruits is well documented in the literature [11, 22, 32, 36].

Terpenes

Isoprene and a monoterpene fragment at m/z 95.085 were responsible for the higher terpene concentration determined for ‘Védrantais’, ‘Songwhan charmi’, and ‘Iraq’ cultivars. The lower terpene concentrations were observed for ‘Calcuta’ cultivar. A farnesene fragment at m/z 123.117 was present at significantly higher concentrations for ‘T111’ cultivar, along with the commercial *inodorus* fruits.

Other compounds

Acetic acid and a nitrile compound (m/z 42.034) were present at significantly higher concentrations in the headspace of ‘Védrantais’ cultivar and lower for ‘Calcuta’ and commercial *inodorus*. Acetone was determined at a significantly higher concentration for ‘Iraq’ in comparison to ‘T111’ cultivar and Amarillo fruits. No significant differences were observed for the rest of the fruits.

Globally, volatile emission was more pronounced for *cantalupensis* fruits. ‘Védrantais’ cultivar was different from the other *cantalupensis* fruits due to the higher concentrations of most of the VOCs, while the VOC profile of ‘Dulce’ cultivar was more related to the commercial *cantalupensis* fruits, Galia and Cantaloupe. The significantly higher concentrations of two C₉ aldehydes, 2,6-nonadienal and nonenal, the C₅, C₆, and C₈ esters, and limonene, found for ‘Dulce’ cultivar, or the higher concentrations of a fragment at m/z 57.069 and methyl butanal found for Galia and Cantaloupe, were on the basis of the differences between the VOC profiles of these melon types. The lower volatile emission was observed for *inodorus* fruits, although some differences were detected between ‘T111’ cultivar and the commercial *inodorus* fruits, Amarillo and Piel de Sapo. The ‘T111’ and Amarillo fruits showed significantly higher concentrations of methanol, 1,2-propanediol, acetic acid, isoprene, methyl acetate, and C₅–C₇ esters than Piel de Sapo. In contrast, higher concentrations of acetaldehyde, a nitrile

compound, 1,2-ethanediol, and ethyl acetate/methyl propanoate, were found for ‘T111’ than the other *inodorus* fruits. Regarding the exotic cultivars, the VOCs’ pattern of the ‘Iraq’ cultivar was more similar to that of ‘Dulce’ and the commercial *cantalupensis* fruits for several alcohols, aldehydes, esters, and terpenes, except for methanol, butanal, hexenal, 2,6-nonadienal, C₄–C₅ esters, isoprene, and acetone. The VOC profile of ‘Calcuta’ and ‘Songwhan charmi’ cultivars showed intermediate profiles between the ones of *cantalupensis* and *inodorus* fruits. Additionally, both exotic cultivars had significantly lower concentrations of methanol, whereas ‘Calcuta’ showed a higher concentration of 3-hexenol and hexenal, two C₆ green leaf volatiles. These results are consistent with the intermediate ripening expression between the climacteric and the non-climacteric patterns previously observed for several exotic melon cultivars [3, 32].

Correlation between sensory and PTR–MS analyses

Principal component analysis

A PCA was performed on the sensory scores and headspace VOCs measured on the same samples, to which the SSC and pH were added as supplementary variables (Fig. 1). The first three principal components (PCs) explained 68% of the variance (46%, 13%, and 9%, respectively). Three main groups can be observed, in the clockwise direction from the third to the fourth quadrants. One of *inodorus* fruits, formed by the ‘T111’ cultivar along with Amarillo and Piel de Sapo commercial fruits, a second one formed by the exotic cultivars (‘Calcuta’, ‘Iraq’, and ‘Songwhan charmi’), and another of *cantalupensis* fruits, formed by the ‘Védrantais’ and ‘Dulce’ cultivars along with Cantaloupe and Galia commercial fruits. The higher positive loadings of the majority of VOCs and odor intensity, ripe fruit odor, and fermentative odor and flavor attributes contributed to the opposed projection of *inodorus* and *cantalupensis* fruits along with the PC 1. ‘Védrantais’ exhibited a clear differentiation, not only from the rest of the melon types but also from the other *cantalupensis* fruits. The separation of ‘Calcuta’ and ‘Iraq’ from the other melon fruits was mainly due to the high positive loadings of the fragments at m/z 81.070 and 83.086, hexenal, and astringency, together with high negative loadings of nonenal, flavor intensity, and sweetness. ‘Songwhan charmi’ melons had intermediate characteristics between *inodorus*, exotic, and *cantalupensis*. Cantaloupe, ‘Dulce’ and Galia were further separated from the rest of the fruits along with PC 3 due to the high positive loadings of an ester (m/z 67.054) and monoterpene (m/z 95.085) fragments, as well as high negative loadings of cucumber odor and flavor attributes.

Pearson’s correlation analysis

The significant correlations found between sensory attributes and VOCs are shown in Table 5. Most of the volatiles showed

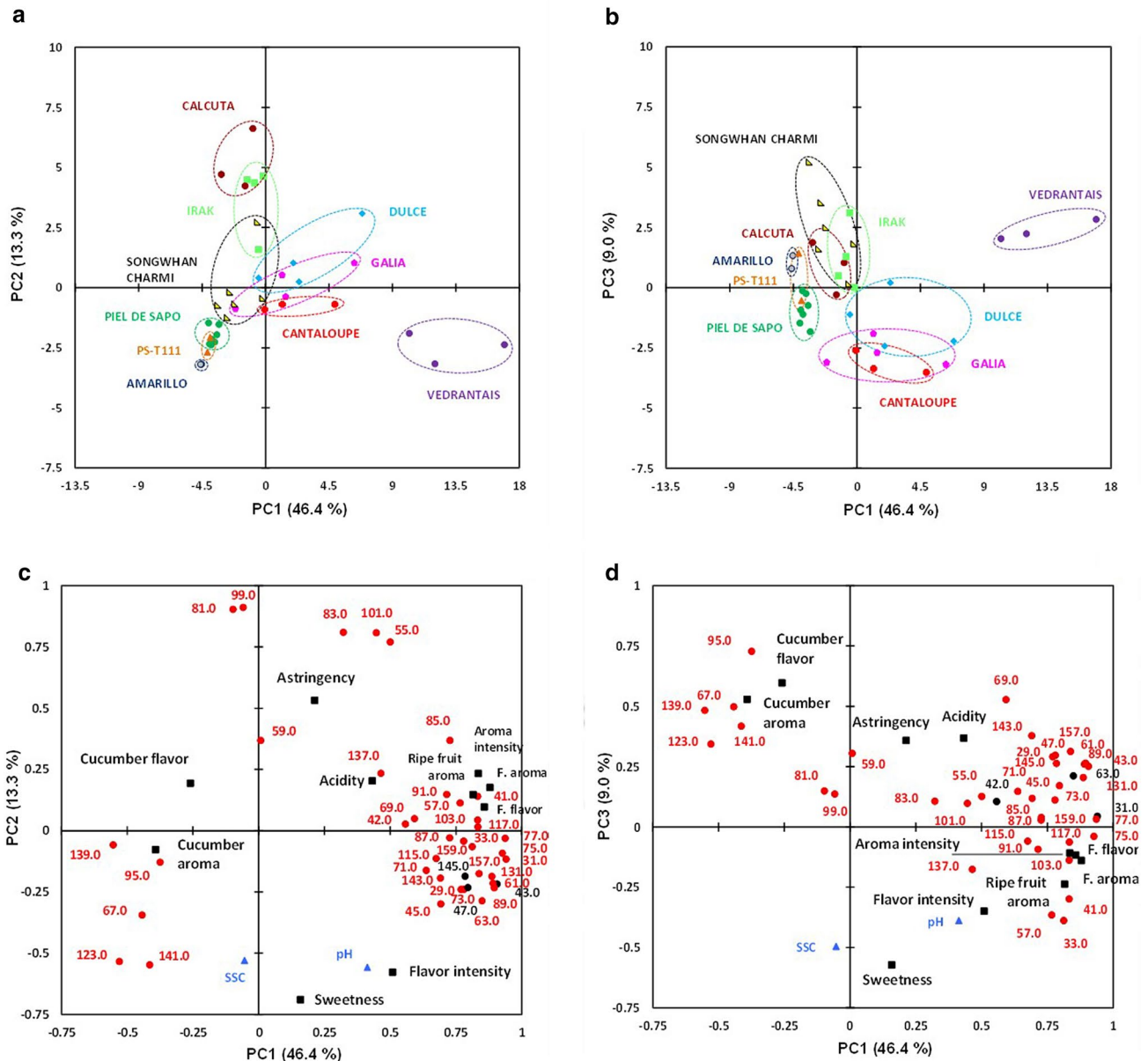


Fig. 1 Principal component analysis (PCA) performed on the sensory and PTR-MS data of the ten *Cucumis melo* L. fruit types: scores plot (upper) and loadings plot (lower) of the PC1 vs PC2 (a and c) and PC1 vs PC3 (b and d). SSC and pH are projected as supplementary variables

an impact over odor intensity, ripe fruit odor, and fermentative odor attributes. The same was observed for fermentative flavor but to a lower extent for flavor intensity. Fewer correlations were observed for the attributes of cucumber odor and flavor, sweetness, acidity, and astringency.

Alcohols A positive contribution of alcohols to the attributes of odor ($0.48^{**} \leq r \leq 0.76^{***}$) and flavor intensities ($0.36^{*} \leq r \leq 0.59^{***}$), ripe fruit odor ($0.42^{**} \leq r \leq 0.80^{***}$), and fermentative odor and flavor ($0.42^{**} \leq r \leq 0.82^{***}$) was observed. Total alcohols were reported to be positively correlated with the overall flavor [18], but that correlation was observed to change during storage for several flavor attrib-

utes [19]. Methanol and ethanol were reported to be associated with advanced ripening stage [18], whereas the diol alcohols with ester production in melon fruit [17]. Methanol was also negatively correlated with cucumber odor ($r = -0.51^{***}$) and flavor ($r = -0.40^{*}$).

Aldehydes Several aldehydes were positively correlated with odor ($0.54^{**} \leq r \leq 0.76^{***}$) and flavor intensity ($0.43^{**} \leq r \leq 0.56^{***}$), ripe fruit ($0.49^{***} \leq r \leq 0.76^{***}$), and fermentative odor and flavor attributes ($0.58^{***} \leq r \leq 0.85^{***}$). Most of these aldehydes (acetaldehyde, hexenal, heptanal, and decanal) were associated with a lack of maturity [34], although acetaldehyde was also observed to increase with maturity [18].

Table 5 Pearson correlation coefficients between VOCs, sensory attributes, SSC, and pH determinations^a

m/z	VOCs	Odor attributes ^b				Flavor attributes ^c				Taste attributes ^d			SSC	pH	Organoleptic description
		INT	RPF	FER	CMB	INT	FER	CMB	AST	SWT	ACD				
29.037	Fragment (alcohol)	0.50***	0.51***	0.56***	0.56***	0.36*	0.66***							0.46**	
31.017	Formaldehyde	0.76***	0.76***	0.80***	-0.44**	0.52***	0.85***					0.39*		0.62***	
33.034	Methanol	0.76***	0.80***	0.82***	-0.51***	0.59***	0.78***	-0.40*		0.37*				0.72***	
41.038	Fragment (alcohol, ester)	0.79***	0.81***	0.84***	-0.41**	0.52***	0.73***					0.36*		0.52***	
42.034	Acetonitrile, nitrile fragment	0.50**	0.49**	0.51***			0.48**								
43.018/43.053	Fragment (ester)/ Fragment (alcohol, ester, acetate)	0.61***	0.57***	0.66***		0.44**	0.69***				0.37*			0.54***	
45.033	Acetaldehyde	0.56***	0.49***	0.59***		0.56***	0.60***				0.42**			0.58***	Pungent, ethereal, fruity [39]
47.049	Ethanol	0.51**	0.51**	0.57***		0.36*	0.66***							0.47**	Ethanol [53], sweet [54]
55.054	Fragment	0.56***	0.48**	0.49***		0.43**			0.47**	-0.48**		0.39*		-0.66***	
57.069	Fragment (alcohol, ester)	0.75***	0.76***	0.81***	-0.35*	0.53***	0.69***					0.34*		0.54***	
59.049	Acetone				0.39*		0.46**								Pungent, somewhat sweet [39], green [45]
61.028	Acetic acid	0.59***	0.55***	0.64***		0.41**	0.67***				0.37*			0.50**	Acid [53] sour, pungent [39]
63.044	1,2-Ethanediol	0.60***	0.54***	0.65***		0.52***	0.67***				0.41**			0.61***	
67.054	Fragment (ester)	-0.52***	-0.50**	-0.58***			-0.49**								
69.070	Isoprene	0.50***	0.44**	0.56***			0.50***		0.38*		0.54***				
71.085	Fragment (alcohol)	0.48**	0.48**	0.52***		0.41**	0.52***							0.42**	
73.064	Butanal	0.63***	0.60***	0.69***		0.53***	0.66***				0.42**			0.49**	Pungent, green [54]
75.044	Methyl acetate	0.69***	0.67***	0.73***	-0.38*	0.50***	0.70***							0.65***	Fruity, slightly bitter [39]
77.059	1,2-Propanediol	0.70***	0.66***	0.74***	-0.35*	0.45**	0.71***							0.58***	
81.070	Fragment (terpene, sesquiterpene, aldehyde)					-0.70***			0.42**	-0.68***				-0.70***	
83.086	Fragment (alcohol, aldehyde, sesquiterpene)								0.38*	-0.51***				-0.74***	
85.099	Fragment (alcohol)	0.61***	0.59***	0.64***	-0.34*		0.54***		0.35*						

Table 5 (continued)

m/z	VOCs	Odor attributes ^b			Flavor attributes ^c			Taste attributes ^d			pH	Organoleptic description	
		INT	RPF	FER	CMB	INT	FER	CMB	AST	SWT			ACD
87.080	Methyl butanal	0.59***	0.60***	0.69***		0.43**	0.58***					0.48**	Almond, apple [54, 55]
89.059	Ethyl acetate/ methyl pro- panoate	0.58***	0.56***	0.64***		0.43**	0.67***			0.36*		0.54***	Ethereal, fruity, sweet/fruity, rum, sweet [39]
91.074	2,3-Butanediol	0.65***	0.63***	0.62***		0.59***							Fruit, onion [54]
95.085	Fragment (monoterpene)	-0.40*		-0.37*	0.75***		-0.44**	0.72***				-0.44**	
99.080	Hexenal					-0.66***		0.41**				-0.69***	Green [53]
101.095	3-Hexenol	0.48**	0.42**	0.48**	-0.34*		0.42**	0.50***				-0.37*	Herbal, green, grass, fresh [21, 53]
103.075	Ester (Ethyl propanoate, Isopropyl acetate, Methyl butanoate, Methyl isobu- tyrate, Propyl acetate)	0.68***	0.68***	0.70***	-0.34*	0.48**	0.60***					0.56***	Fruity, over-ripe, pungent, sweet [21]
115.111	Heptanal	0.59***	0.52***	0.62***		0.41**	0.60***			0.41*		0.45**	Citrus [44]
117.091	Ester (Butyl acetate, Ethyl butanoate, Isobutyl acetate, Methyl n-meth- ylbutanoate)	0.63***	0.61***	0.63***		0.46**	0.56***					0.60***	Sweet, fruity, candy [21, 44, 53]
123.117	Fragment (farnesene)	-0.60***	-0.55***	-0.63***			-0.55***						
131.107	Ester (Ethyl methylbu- tanoate, Ethyl pentanoate, Methyl hex- anoate, Pentyl acetate)	0.57***	0.56***	0.64***		0.42**	0.65***					0.50**	Fruity, melon, cantaloupe-like, sweet [21, 44, 53], ether-like, pineapple [39]
137.132	Limonene	0.47**	0.47**	0.41*		0.37*						0.37*	Citrus, mint [54], ethereal, fruity [5]
139.112	2,6-Nonadienal	-0.53**	-0.54***	-0.62***		-0.39**	-0.57***					-0.46**	Cucumber, melon, green [11, 39, 44]

Table 5 (continued)

m/z	VOCs	Odor attributes ^b			Flavor attributes ^c			Taste attributes ^d			SSC	pH	Organoleptic description		
		INT	RPF	FER	CMB	INT	FER	CMB	AST	SWT				ACD	
141.128	Nonenal	-0.50*	-0.47*	-0.52***									Cucumber, melon, green, fresh [11, 21, 44]		
143.143	Nonanal/nonenol	0.49**	0.49**	0.53***						0.42**		0.51**	Melon, citrus [39, 44]/ Green, floral [53], melon [39]		
145.123	Hexyl acetate/ethyl hexanoate	0.48**	0.46**	0.53***								0.51**	Fruity [44]		
157.159	Decanal	0.54***	0.53***	0.60***									Soap, orange peel, floral [54, 55]		
159.138	Ester (Heptyl acetate, Hexyl propanoate, 2-Methylbutyl butanoate)	0.66***	0.63***	0.62***					0.38**	0.63***			Clean, fresh, floral [53]		
Common quality indices															
	SSC								0.47**						
	pH								0.35*	-0.36*	-0.35*	-0.37*	0.67***	-0.45**	0.56***
									0.58***	0.42**	-0.42**	0.70***			0.56***

^aSignificance: *** for $p \leq 0.001$, ** for $p \leq 0.01$ and * for $p \leq 0.05$. Only significant correlation coefficients are shown

^bOdor attributes: INT Odor intensity, RPF Ripe fruit odor, FER Fermentative odor, CMB Cucumber odor

^cFlavor attributes: INT Flavor intensity, FER Fermentative flavor, CMB Cucumber flavor, AST Astringency

^dTaste attributes: SWT Sweetness, ACD Acidity

Acetaldehyde is particularly important as it increases fruit flavor and contributes to the perception of freshness [39]. Positive contributions of acetaldehyde to the flavor perception of citrus [40], kiwi [41], or tomato fruits [42] have also been observed. Verzera et al. [22], reported strong correlations between the typical odor and flavor descriptors of melon and several aldehydes, including methyl butanal, 2,6-nonadienal and nonenal. The latter two are associated with green or cucumber notes and considered key volatiles in the typical aroma of the non-climacteric fruits belonging to the *inodorus* cultivar [11]. In the present study, no significant correlations were observed between both C₉ aldehydes and cucumber odor or flavor, possibly due to the predominance of climacteric cultivars among the fruits analyzed. However, negative correlations were found between these compounds and odor intensity ($r = -0.53^{**}$; -0.50^{**}), ripe fruit odor ($r = -0.54^{***}$; -0.47^{*}), and fermentative odor ($r = -0.62^{***}$; -0.52^{***}) or flavor ($r = -0.57^{***}$; -0.45^{**}) attributes. The previous authors observed high negative correlations between 2,6-nonadienal or nonenal with ‘fruity’, ‘sweet-aromatic’, and ‘chemical’ flavor attributes, but also high positive correlations with ‘cucurbit’ attribute [19].

Esters The correlations found with intensity ($0.48^{**} \leq r \leq 0.69^{***}$), ripe fruit ($0.46^{**} \leq r \leq 0.69^{***}$) or fermentative odor ($0.53^{***} \leq r \leq 0.73^{***}$), and flavor ($0.56^{***} \leq r \leq 0.70^{***}$) are in agreement with the previous authors reporting good correlations ($r \geq 0.61$; $p < 0.05$) between ethyl, methyl, or acetate esters and melon sensory flavor [18]. High correlations ($r \geq 0.76$) between C₇ and C₉ esters and the fruity odor [20] or between C₅ and C₇ esters and fruity, pineapple-like, and sweet aromas were also observed [21]. Additionally, several works pointed out the importance of sulfur-containing esters to the odor and flavor of melon fruits [11, 20, 21], but these were not detected in the present work, possibly due to differences in the analytical methodology [34, 43]. Esters are particularly related to the fruity notes of climacteric cultivars, but their odor active values and, thus, their contribution to aroma was reported to be substantially lower than that of aldehydes and alcohols [44].

Terpenes Two terpene-related masses, monoterpene (95.085) and farnesene (123.117) fragments, were negatively correlated with odor intensity, ripe fruit, or fermentative odor and flavor. The former was positively correlated with cucumber odor ($r = 0.75^{***}$) and flavor ($r = 0.72^{***}$). On the other hand, isoprene and limonene showed positive correlations with odor intensity ($r = 0.50^{***}$; 0.47^{**}), ripe fruit ($r = 0.44^{**}$; 0.47^{**}), and fermentative odor ($r = 0.56^{***}$; 0.41^{*}) or flavor ($r = 0.50^{***}$; 0.37^{*}). Limonene was observed to contribute for the odor and flavor of melon [20].

Other compounds A nitrile compound at *m/z* 42.034 and acetic acid were correlated with intensity, ripe fruit, and

fermentative odor, as well as fermentative flavor attributes. Acetone was slightly correlated with cucumber odor ($r = 0.39^{*}$) and flavor ($r = 0.46^{**}$). Acetone is associated with solvent or ethereal descriptors, but its aromatic character was reported to change from ‘glue/alcohol’ in deionized water, to ‘sweet’ in ethanol–methanol–water solution, or ‘green’ in deodorized tomato homogenate [45].

Effect of SSC, pH, and volatiles over sweetness, acidity, and astringency attributes The determinations of SSC and pH were satisfactorily correlated with sweetness ($r = 0.67^{***}$; 0.70^{***}). Both parameters were also correlated with flavor intensity ($r = 0.47^{**}$; 0.58^{***}), although this could be due to an indirect effect of the high correlation between sweetness and flavor intensity ($r = 0.77$; $p \leq 0.001$). A slight negative correlation was found between SSC and astringency ($r = -0.37^{*}$). This was consistent with the negative correlation between sweetness and astringency attributes ($r = -0.57$; $p \leq 0.001$). SSC has a significant positive effect on the sweet and fruity descriptors, as well as a significant negative effect on the green, bitter, and astringent descriptors, among fruits, beverages, and flavors [12, 46]. A similar pattern was observed for 3-hexenol and hexenal, two C₆ green leaf volatiles, which were negatively correlated with sweetness ($r = -0.50^{***}$; -0.67^{***}) and positively with astringency ($r = 0.50^{**}$; 0.41^{**}). The correlation between hexenal and sweetness was reflected over flavor intensity ($r = -0.66^{***}$), but for 3-hexenol, positive correlations with intensity and ripe fruit odor or fermentative odor and flavor attributes ($0.42^{**} \leq r \leq 0.48^{**}$) were observed. The ortho- and retronasal perception of green leaf volatiles was observed to change from ‘green’ to ‘fruity’ descriptors due to the interaction of these compounds with sugars and acids [13], but the nature of these interactions can vary with the fruit species. Aprea et al. [14] observed a negative contribution of 3-hexenol to the sweet perception of apple, whereas Klee and Tieman [47] reported a positive contribution to the ‘overall flavor intensity’ and ‘liking’ of tomato. Other authors observed the negative contribution of hexenal to the ‘overall flavor intensity’ and ‘liking’ of strawberries and blueberries [47], as well as to the sweetness of table grapes [48]. Besides, the interactions between certain VOCs with sugars and acids affect the rate of release and persistence of these volatile compounds in the mouth and, thus, the perceived intensities of aroma and flavor attributes [15]. Moreover, a positive correlation between astringency and acidity was also observed ($r = 0.45$; $p \leq 0.01$). This opposed relationship of astringency with sweetness and acidity was observed in other fruits like strawberries [49], apples [50], or kiwifruits [51]. Regarding VOCs, the highest correlation of acidity was with isoprene ($r = 0.54^{***}$), a leaf volatile in the origin of several terpene compounds. Minor correlations were also observed with 1,2-ethanediol ($r = 0.41^{**}$), several aldehydes ($0.39^{*} \leq r \leq 0.42^{**}$) or acetic acid ($r = 0.37^{*}$). The interaction between acetaldehyde and sugars or acids is known

to enhance the ‘fruity’ and ‘tropical flavor’ attributes of tomato fruits [42], although in the present study, it was only correlated with acidity.

pH was positively correlated with SSC ($r=0.56^{***}$), whereas no significant correlation was observed between pH and acidity. The relationship between pH increase and sugar accumulation was previously observed [1, 2], and both processes are classified as ethylene-independent [5–7]. The melon genotypes with higher sugar levels have pH values closer to the neutral range, whereas the ones with low sugar levels show a broader range of pH values [1]. The characterization of the pH gene, with a major impact on fruit acidity, has contributed to explain the low level of acidity of sweet melon types [52]. Additionally, pH was strongly correlated with the majority of the VOCs, as it is a parameter involved in the regulation of several reactions of volatile production [16].

Conclusions

The sensory and PTR–MS analyses allowed the identification of specific odor and flavor traits associated with the melon cultivars evaluated, regardless of the group formation into *inodorus*, *cantalupensis*, and exotic fruits. These methodologies highlighted the enhanced sweetness of the *inodorus* and *cantalupensis* fruits, both commercial and elite cultivars, and the similar volatile profiles of ‘Iraq’ and *cantalupensis* melons. A reasonable correlation between melon sensory attributes and PTR–MS spectral data was observed. Our results provide new information for the improvement of melon fruit quality. As new cultivars are being developed with high sugar and high acid levels, the results presented herein can be used as a tool to achieve distinct taste combinations without compromising desirable odor and flavor traits. Additional research to explore these correlations on new cultivars with extended shelf-life would also be valuable (Table 6, Appendix).

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

Compliance with ethics requirements This article does not contain any studies with human or animal subjects.

Appendix

See Table 6.

Table 6 Quality indices determined among melon fruit types ($N=67$): mean values and standard deviation in brackets^a

Parameters	Cultivars (cv. group)			Commercial varieties (cv. group)						
	Climacteric			Non-climacteric						
	‘Dulce’ ^b (<i>cantalupensis</i>)	‘Védrantais’ (<i>cantalupensis</i>)	‘Iraq’ (<i>dudaim</i>)	‘Calcuta’ (<i>momordica</i>)	‘Songwhan charmi’ (<i>conomon</i>)	Piel de Sapo ‘T111’ (<i>inodorus</i>)	Galia (<i>cantalupensis</i>)	Cantaloupe (<i>cantalupensis</i>)	Amarillo (<i>inodorus</i>)	Piel de Sapo (<i>inodorus</i>)
pH	6.3 (0.2) ^{abc}	6.5 (0.1) ^a	5.2 (0.4) ^e	5.5 (0.2) ^{de}	5.6 (0.1) ^{de}	5.8 (0.1) ^{cde}	6.4 (0.1) ^{abc}	6.5 (0.1) ^{ab}	5.9 (0.3) ^{bcd}	5.7 (0.2) ^{cde}
SSC (°Brix)	8.2 (1.6) ^{cd}	9.6 (1.3) ^{bc}	4.7 (1.0) ^d	7.4 (4.7) ^{cd}	9.3 (1.1) ^{bc}	9.9 (0.4) ^{abc}	12.8 (2.6) ^{ab}	14.0 (2.9) ^a	10.6 (0.6) ^{abc}	12.6 (1.6) ^{abc}

^aValues with different letters in the same row indicate significant differences by Tukey’s HSD post hoc test ($p \leq 0.05$)

^bNumber of samples of each melon type: ‘Dulce’ ($n=6$), ‘Védrantais’ ($n=8$), ‘Iraq’ ($n=10$), ‘Calcuta’ ($n=10$), ‘Songwhan charmi’ ($n=8$), Piel de Sapo ‘T111’ ($n=6$), Galia ($n=6$), Cantaloupe ($n=3$), Amarillo ($n=3$), and Piel de Sapo ($n=7$)

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5.2 Publication 3: Correlation of sensory and instrumental aroma and flavor of peach fruits

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Quartile 1



Investigation of the aroma of commercial peach (*Prunus persica* L. Batsch) types by Proton Transfer Reaction–Mass Spectrometry (PTR-MS) and sensory analysis



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Benzeneacetaldehyde (PubChem CID: 998)
Decahydronaphthalene (PubChem CID: 7044)
 γ -Hexalactone (PubChem CID: 257369)
 γ -Octalactone (PubChem CID: 86852)
 γ -Valerolactone (PubChem CID: 98323)
Hotrienol (PubChem CID: 5366264)
Trimethylbenzene (PubChem CID: 7247).

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ABSTRACT

The aim of this study was to investigate the aroma and sensory profiles of various types of peaches (*Prunus persica* L. Batsch.). Forty-three commercial cultivars comprising peaches, flat peaches, nectarines, and canning peaches (pavías) were grown over two consecutive harvest years. Fruits were assessed for chemical aroma and sensory profiles. Chemical aroma profile was obtained by proton transfer reaction-mass spectrometry (PTR-MS) and spectral masses were tentatively identified with PTR-Time of Flight-MS (PTR-Tof-MS). Sensory analysis was performed at commercial maturity considering seven aroma/flavor attributes. The four types of peaches showed both distinct chemical aroma and sensory profiles. Flat peaches and canning peaches showed most distinct patterns according to discriminant analysis. The sensory data were related to the volatile compounds by partial least square regression. γ -Hexalactone, γ -octalactone, hotrienol, acetic acid and ethyl acetate correlated positively, and benzeneacetaldehyde, trimethylbenzene and acetaldehyde negatively to the intensities of aroma and ripe fruit sensory scores.

1. Introduction

Peach (*Prunus persica* L. Batsch) is a fruit species from the *Prunus* genus, which also includes almonds, apricots, cherries or plums. Several traits are used to characterize its cultivars: fruit shape (round or flat), skin type (peach or nectarine), flesh color (yellow or white), texture (melting or non-melting), stone type (freestone or clingstone) or flavor (low-acid or high-acid) (Byrne et al., 2012). According to these traits, peach fruit types can be classified in peaches, nectarines, flat peaches (or nectarines), and canning peaches (also named “Pavías”). The canning peaches are clingstone and non-melting peaches usually intended for the canning industry, but also grown for fresh consumption. There has been a growing interest in both flat peaches and pavías due to their distinct quality traits for consumers (Iglesias, 2015;

Montero-Prado, Bentayeb, & Nerín, 2013).

The increase of peach production is not being reflected in its consumption due to several factors. One of these factors is the focus on primary quality selection traits like fruit size and appearance. Another important factor is that fruits are often harvested before the appropriate ripening time to avoid damage during harvest and post-harvest manipulations, leading to the absence of the typical aroma and flavor or poor textural characteristics that compromise consumer acceptance (Reig, Iglesias, Gatius, & Alegre, 2013). Ultimately, the diversity of cultivars and their similarity in external traits (color, size, shape), together with the inexistence of a market classification based on internal quality (such as the color labels used to efficiently differentiate the sweet and non-sweet flavor of kiwifruit), are prone to affect acceptance and buying intention as consumers are often unable to

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differentiate most of the cultivars. This results in a continuous decrease of peach consumption in both the main producing and exporting European Union countries (Iglesias & Echeverría, 2009).

Peach quality is a complex concept and relies on diverse quality indices that have been proposed over the years. Fruit size, skin and flesh color, soluble solids content (SSC) for overall sweetness, and the ratio between SSC and titratable acidity (TA) are among the most common. The development of fruits that reach the maximum aroma and flavor on the tree in combination with sufficient firmness to avoid compromising management and marketing is a common objective of breeders (Iglesias & Echeverría, 2009). Peach flavor relies on chemical traits like sweetness, acidity, sugar to acid ratio or textural characteristics (Colaric, Veberic, Stampar, & Hudina, 2005; Delgado, Crisosto, Heymann, & Crisosto, 2013; Reig et al., 2013). Furthermore, other factors need to be considered to develop cultivars that match both internal and external peach quality, capable to achieve consumer acceptance, like antioxidant and nutritional compounds, volatile organic compounds (VOCs), and sensory attributes. The latter two will be addressed in the present paper.

In addition to sensory considerations, aroma and flavor are important internal fruit quality traits that reflect the diversity of biochemical processes occurring during ripening, along with appearance, texture or nutritional compounds. Aroma perception is characterized as the odor of a food product when volatile compounds enter the nasal passage and are perceived by the olfactory system (Meilgaard, Civille, & Carr, 2006). On the other hand, flavor perception is the multisensory interaction of the impressions of taste, smell, the trigeminal system, touch and visual and auditory cues, enabled by the act of eating (Auvray & Spence, 2008). The non-volatile constituents contribution to the sensory perceptions of peach fruit aroma and flavor has been widely studied (Colaric et al., 2005; Delgado et al., 2013; Iglesias & Echeverría, 2009; Reig et al., 2013). The same occurs with peach VOC emission, which is influenced by cultivar, tissue, processing, storage, ripening stage, harvest, and environmental conditions (Aubert & Milhet, 2007; Do, Salunkhe, & Olson, 1969; Eduardo, Chietera, Bassi, Rossini, & Vecchiotti, 2010; Engel et al., 1988; Horvat et al., 1990). However, only a few authors have related peach fruit' aroma and flavor attributes with VOCs profile (Spencer, Pangborn, & Jennings, 1978; Cano-Salazar, López, & Echeverría, 2013; Giné-Bordonaba, Cantín, Echeverría, Ubach, & Larrigaudière, 2014).

Chemical aroma of peach fruit is mainly evaluated by gas chromatography (GC) techniques, generally preceded by steam distillation or solid phase microextraction (SPME) (Wang et al., 2009; Eduardo et al., 2010; Sánchez, Besada, Badenes, Monforte, & Granell, 2012; Montero-Prado et al., 2013; Giné-Bordonaba et al., 2014). In this study, proton transfer reaction-mass spectrometry (PTR-MS) is used to quantify the peach VOCs. Headspace PTR-MS is a highly sensitive and fast technique (pptv, parts per trillion by volume detection and < 1 min. complete spectrum acquisition) without the need of sample pre-treatment. The method is based on the reaction of a protonated agent (H_3O^+) which performs a non-dissociative proton transfer to most of the common VOCs without reacting with any of the natural components of air (Lindinger, Hansel, & Jordan, 1998).

The aim of this study was the investigation of a collection of fruits comprising peaches, flat peaches, nectarines, and canning peaches for their typological aroma profiles by PTR-MS and sensory analysis. Fruits of forty-three commercial cultivars, grown over two consecutive harvest years under Mediterranean conditions, were chosen to provide a wide species variability.

2. Material and methods

2.1. Materials

The fruits (*Prunus persica* L. Batsch) of 43 cultivars with mainly yellow flesh comprising 13 peaches, 7 flat peaches, 18 nectarines, and 6

canning peaches (Table A.1, Appendix A.) were grown at the IRTA-Mas Badia Agricultural Experimental Station (42° 03'N 3° 03'E, Girona, Spain) over the harvest years of 2012 and 2013 (N = 86). Twenty fruits per cultivar and year were harvested at optimum commercial maturity from June to September, based on the range of flesh firmness (4.0–5.0 kg/0.5 cm² measured with an 8 mm diameter probe). Four fruits per cultivar and year were selected for sensory analysis, based on similar size and homogeneous color. Flesh from three fruits was assessed for common quality indexes (Table A.2, Appendix A.): titratable acidity (TA) and soluble solids content (SSC).

Flesh from five additional fruits was pool-sampled, vacuum-packed in double-layer aluminum bags and stored at –80 °C for further chemical determinations. The frozen samples of both harvest years were shipped under –20 °C to the RIKILT Wageningen Research (Wageningen, The Netherlands) and stored at the same temperature until the moment of analysis.

2.2. Methods

2.2.1. Quality analysis

The titratable acidity (TA) and soluble solids content (SSC) were assessed to explore the phenotypic variation among the four fruit types in common quality traits. TA was determined through manual titration with a 0.1 M NaOH solution and using a phenolphthalein indicator until an end point of constant pH (8.0 ± 0.1). SSC was assessed with a Quick-Brick TM 90 (Mettler-Toledo, GmbH, Germany) digital handheld refractometer as described by Bianchi et al. (2016).

2.2.2. PTR-MS profiling

Frozen samples were cut into pieces and subsequently ground, under liquid nitrogen, with a Grindomix GM 200 (Retsch, Düsseldorf, Germany) for 15 s at 10,000 rpm. Ground samples were stored at –20 °C and analyzed within 24 h. For each sample 2.0 g of ground powder were weighted in a 250 mL screw cap glass bottle and equilibrated in a water bath at 25 °C for 30 min. The temperature was selected to match the volatile emission in the headspace of the bottles and the conditions at which common consumers perceive the fruits. Bottles were attached to the inlet of the PTR-MS system (Ionicon GmbH, Innsbruck, Austria) where the headspace was drawn at a flow rate of 60 mL/min. The temperature of both the inlet and the drift chamber was 60 °C. MS data between 20 and 160 atomic mass units (amu) was collected with a dwell time of 200 ms. Blank measurements were carried out between samples to monitor background air. The analyses were performed in independent triplicates and an averaged mass spectrum per sample was calculated after background and transmission correction. The mass spectral data (m/z 20–160) of the 86 peach fruits was assessed after the removal of masses m/z 32 (O_2^+) and m/z 37 (water cluster ion) from the dataset.

2.2.3. PTR-ToF-MS tentative identification

From the ground powder as obtained in Section 2.2.1, a subset of samples was selected for volatile compounds tentative identification with a PTR-ToF-MS 8000 system (Ionicon GmbH, Innsbruck, Austria). Four samples per harvest year (n = 8), one from each peach type, were chosen to provide a representative set considering the variability observed in the PTR-MS results. The procedure was identical as in Section 2.2.2, with the exception that only 1.0 g ground powder was used. The chamber ionization conditions were kept as follows: drift temperature 60 °C, drift voltage 421 V and drift pressure 3.80 mbar. The instrument was operated at E/N value of 133 Townsend (1 Td = 10⁻¹⁷ cm² V⁻¹ s⁻¹). A further description of PTR-ToF-MS is given by Lindinger et al. (1998). Each sample measurement lasted 60 s with an acquisition rate of 1 spectrum/s. Baseline removal and spectra alignment by internal calibration of the ToF data were performed according to the procedure described by Capellin et al. (2010). VOCs were tentatively identified based on the PTR-ToF-MS results and the

Table 1
Peach sensory attributes and description used for sensory analysis.

Attributes	Description
Aroma	
Aroma intensity	Strength of peach overall aroma present in one sample.
Ripe fruit	Typical fruity aroma in a range from under to over ripe.
Plum aroma	Presence of plum fruit characteristic aroma.
Stone aroma	Presence of aroma associated with the stone/pit.
Flavor	
Flavor intensity	Strength of peach overall flavors detected during chewing.
Plum flavor	Presence of plum fruit characteristic taste.
Flavor persistence	Amount of flavor detected in mouth a couple of minutes after swallow.

existing literature after excluding the interfering ions (O_2^+ , NO^+ and water clusters) and their isotopologues.

2.2.4. Sensory analysis

The fresh fruits were assessed at harvest by an 8 member trained panel, following the procedure described by Bianchi et al. (2016). Briefly, seven aroma and flavor descriptors (Table 1) were chosen during training sessions in which the panelists evaluated different commercial peach and nectarine samples. Fruits were cut in halves and the same fruit was assessed by two panelists. The pair of panelists assessing the same fruit sample changed at every tasting session according to a balanced design. In each tasting session, 4 fruits per cultivar were hand peeled and their flesh assessed in different presentation orders to block first-order and carry-over effects (MacFie, Bratchell, Greenhoff, & Vallis, 1989). Sensory evaluation was performed using a non-structured 10 cm lineal scale, in which 0 meant low intensity of the descriptor and 10 meant high intensity of the descriptor.

2.2.5. Statistical analysis

The sensory and VOCs datasets were evaluated using a two-way ANOVA, considering the type of peach (peach, nectarine, flat peach or pavia) and the harvest year as fixed factors. Due to the lack of normality detected for the majority of VOCs, a non-parametric Kruskal-Wallis test was also carried out. Since similar results were obtained in both cases (ANOVA and Kruskal-Wallis) the parametric option (ANOVA) was kept. In addition, the two-way ANOVA allows correcting the effect of the harvest year and is a robust method regarding the lack of normality (Schmider, Ziegler, Danay, Beyer, & Bühner, 2010). The interaction 'type of fruit x harvest year' was considered but then discarded because it was not significant ($p > 0.05$) for any parameter evaluated.

A Tukey's HSD post hoc test ($p \leq 0.05$) was performed to test the existence of statistical differences between the fruit typologies. The 36 significantly different VOCs ($p < 0.05$) obtained from the ANOVA results were submitted to a principal component analysis (PCA) and all the orthogonal factors obtained were used to perform a discriminant analysis (DA) to avoid possible multicollinearity issues. The impact of the VOCs over the fruits' sensory perception was assessed through a partial least square (PLS) regression model. The analyses were carried out with XLSTAT 2017 software (Addinsoft, Paris, France).

3. Results and discussion

3.1. VOC profiling

As mentioned before (Section 1), the peach fruit VOC emission is influenced by factors like cultivar, storage, ripening stage or harvest conditions. It is also known that the VOC profile is affected by the different experimental conditions and methodologies used: liquid-liquid microextraction (Aubert & Milhet, 2007) steam distillation (Eduardo

et al., 2010) or SPME (Abidi, 2012; Sánchez et al., 2012; Wang et al., 2009) coupled to gas chromatographic techniques. The comparison of the results described herein with previous works must be carefully addressed. In the present work the determinations were performed at harvest. PTR-MS high sensitivity allowed the headspace VOCs to be drawn at room temperature (25 °C), simulating the conditions at which consumers perceive the fruits.

PTR-ToF-MS analysis allowed the tentative identification of most of the compounds (Table 2) with the exception of 11 masses (m/z 35, 38, 39, 44, 46, 52, 58, 62, 65, 82, 84 and 98). The ANOVA results showing the significantly different masses among peach fruit types are reported in Table 2. A burst in ethylene production regulates the onset of the ripening process in climacteric fruit. Ethylene production was observed to be different between other peach fruit traits such as acid and non-acid flavor (Iglesias & Echeverría, 2009). However, in this study ethylene was not significant between peach typologies. The masses with the highest headspace amounts were methanol, acetaldehyde and ethanol, but only the former two showed significant differences. Methanol was significantly higher in flat peaches and lower in nectarines and canning peaches. Acetaldehyde higher amounts were also observed in flat peaches together with nectarines. Spadoni et al. (2015) observed higher amounts of methanol, followed by acetaldehyde and ethanol in peaches. Other authors reported higher concentrations of ethanol than acetaldehyde for intact tree-ripened nectarines (Takeoaka et al., 1988).

3.1.1. Fatty acid derived compounds

Fatty acid-derived straight-chain alcohols, aldehydes, ketones, acids, esters and lactones are mainly formed by α -oxidation, β -oxidation and the lipoxygenase pathway (Schwab & Schreier, 2002).

The most abundant fatty acid related masses were m/z 61 and 89. Acetic acid and ethyl acetate were significantly higher in canning peaches. Acetic acid is involved in the formation of esters that contribute to the peach aroma (Salunkhe, Do, & Maga, 1976) and was previously observed among the VOCs of peaches and other *Prunus* fruits (Krammer et al., 1991). Ethyl acetate was reported as one of the major esters in peaches and nectarines (Rizzolo et al., 2013; Wang et al., 2009). Mass m/z 75, attributed by PTR-ToF-MS to methyl acetate (75.043) and 2-methylpropanol (75.079) was significantly higher in peaches and lower in nectarines. The former is a methyl ester of short chain fatty acids resulting from the β -oxidation pathway (Bartley, Stoker, Martin, Hatfield, & Knee, 1985) while 2-methylpropanol derives from the amino acid metabolism. Other esters observed were propyl acetate/ethyl propanoate (103.076), butyl acetate/methyl isovalerate (117.092), pentyl acetate/methylbutyl acetate (131.107), hexyl acetate (145.123), and methyl octanoate (159.140) but at lower amounts (< 1 ppbv) and not significantly different among peach types. The same was observed for the two diol alcohols, 2,3-butanediol (91.074) and 1,8-octanediol (147.137). Several fragments detected were also associated with esters (m/z 41.038, 43.017, 43.054, 53.038, and 57.069). Mass m/z 99, formed by 2,5-furandione (99.010), 2-furylmethanol (99.046) and 2-hexenal (99.081), was significantly higher in nectarines and lower in peaches. The concentration of 2-hexenal was reported to differ significantly within the part of the fruit (Aubert & Milhet, 2007) or cultivar (Eduardo et al., 2010). 2,5-furandione and 2-furylmethanol are furan related compounds involved in VOCs formation, although their origin is not well established. Other furans observed at lower amounts (< 1 ppbv) were 2-ethylfuran, significantly higher in nectarines and lower in peaches and canning peaches, or 2-pentylfuran, significantly higher in flat peaches. 2,4-heptadienal and 2-nonenal were significantly higher in flat peaches and nectarines and lower in peaches and canning peaches. Formaldehyde, 2-butenal, 2-pentenal, and 1-penten-3-ol, 2-heptenal, and decanal were not significantly different for any type of fruit, although 1-penten-3-ol was found to be significantly different within the part of the fruit (Aubert & Milhet, 2007).

Masses m/z 101 and 115 were both comprised by a lactone, γ -

Table 2Tentative identification by PTR-ToF-MS (left side) of the VOCs determined by PTR-MS on the *Prunus persica* cultivars (right side): ANOVA results (Mean ± Standard Deviation) for fruit type expressed in ppbv.

m/z	Tentative identification ¹	Sum formula	Fruit type			
			Peach (n = 26)	Flat peach (n = 14)	Nectarine (n = 34)	Canning peach (n = 12)
28.017	Hydrogen cyanide	CH ₂ N ⁺	1.3 ± 1.3	1.5 ± 1.2	1.1 ± 0.8	1.0 ± 0.6
28	N.I.					
29.037	Ethylene	C ₂ H ₅ ⁺	12.5 ± 6.5	17.9 ± 13.8	13.4 ± 6.8	16.2 ± 15.4
31.018	Formaldehyde	CH ₃ O ⁺	8.8 ± 4.6	11.3 ± 8.4	7.7 ± 2.8	8.4 ± 4.9
33.033	Methanol [20]	CH ₅ O ⁺	1219.7 ± 1332.8 ^{ab}	1486.8 ± 1928.4 ^a	531.8 ± 338.8 ^b	428.0 ± 154.8 ^b
35	N.I.		2.5 ± 2.8 ^{ab}	3.0 ± 4.1 ^a	1.1 ± 0.7 ^b	0.9 ± 0.3 ^b
38	N.I.		3.3 ± 0.5	3.2 ± 0.4	3.3 ± 0.5	3.6 ± 0.5
39	N.I.		14.7 ± 3.4 ^b	15.8 ± 3.7 ^{ab}	19.3 ± 8.2 ^a	14.6 ± 2.4 ^b
41.038	Fragment (alcohol, ester) [21, 23]	C ₃ H ₅ ⁺	19.5 ± 8.9	20.3 ± 10.9	24.6 ± 13.5	18.9 ± 10.6
42.033	Acetonitrile	C ₂ H ₄ N ⁺	3.2 ± 3.2	17.5 ± 42.4	23.6 ± 56.5	7.2 ± 6.2
43.017	Fragment (ester) [21, 23]	C ₂ H ₃ O ⁺	82.5 ± 64.8 ^b	54.5 ± 30.6 ^b	56.2 ± 25.9 ^b	183.1 ± 215.5 ^a
43.054	Fragment (alcohol, ester, acetate) [21, 23]	C ₃ H ₇ ⁺				
44	N.I.		2.3 ± 1.6 ^b	2.0 ± 0.8 ^b	2.2 ± 1.3 ^b	4.5 ± 4.8 ^a
45.034	Acetaldehyde [3, 15, 18, 20]	C ₂ H ₅ O ⁺	1208.9 ± 720.5 ^b	1802.5 ± 890.1 ^a	1328.7 ± 424.9 ^{ab}	909.4 ± 518.9 ^b
46	N.I.		27.6 ± 16.8 ^b	41.2 ± 20.7 ^a	30.3 ± 9.9 ^{ab}	20.9 ± 12.1 ^b
47.049	Ethanol [3, 5, 15, 18, 20, 14]	C ₂ H ₇ O ⁺	265.9 ± 113.5	346.9 ± 239.4	265.0 ± 107.0	328.4 ± 257.0
51.023	Fragment	C ₄ H ₃ ⁺	7.2 ± 7.8 ^{ab}	8.6 ± 11.0 ^a	3.2 ± 2.0 ^b	2.6 ± 0.8 ^b
51	N.I.					
52	N.I.		0.1 ± 0.1 ^a	0.1 ± 0.2 ^a	< 0.1 ^b	< 0.1 ^{ab}
53.038	Fragment (ester) [23]	C ₄ H ₅ ⁺	1.0 ± 1.0 ^b	1.6 ± 1.3 ^{ab}	2.6 ± 3.2 ^a	0.9 ± 0.7 ^b
55.054	Fragment (aldehyde) [23]	C ₄ H ₇ ⁺	48.1 ± 43.9 ^b	74.3 ± 58.1 ^{ab}	124.0 ± 154.2 ^a	46.0 ± 31.3 ^b
57	N.I.		39.4 ± [13].9 ^b	66.2 ± 44.7 ^{ab}	143.6 ± 206.4 ^a	51.1 ± 45.7 ^{ab}
57.069	Fragment (alcohol, ester) [21, 23]	C ₄ H ₉ ⁺				
58	N.I.		1.5 ± 1.4 ^b	2.4 ± 1.5 ^{ab}	5.0 ± 7.0 ^a	1.8 ± 1.5 ^{ab}
59.049	Acetone [3]	C ₃ H ₇ O ⁺	15.8 ± 7.0	15.3 ± 5.9	17.2 ± 7.1	18.7 ± 17.1
61.028	Acetic acid [6, 14]	C ₂ H ₅ O ₂ ⁺	56.6 ± 59.1 ^b	16.7 ± 19.7 ^b	19.4 ± 15.5 ^b	180.2 ± 241.7 ^a
62	N.I.		1.4 ± 1.3 ^b	0.5 ± 0.5 ^b	0.6 ± 0.4 ^b	4.3 ± 5.7 ^a
63.044	Ethylene glycol [21]	C ₂ H ₇ O ₂ ⁺	2.0 ± 1.0	2.5 ± 1.3	2.1 ± 0.7	2.3 ± 1.8
65	N.I.		2.2 ± 1.1	2.9 ± 2.2	2.1 ± 0.9	2.8 ± 2.3
69.047	1H-Pyrazole [12]	C ₃ H ₅ N ₂ ⁺	3.9 ± 1.3	4.3 ± 1.9	4.9 ± 1.9	3.9 ± 0.9
69.069	Isoprene [23]	C ₅ H ₆ ⁺				
71.049	2-Butenal [5]	C ₄ H ₇ O ⁺	1.1 ± 1.3	1.1 ± 0.8	1.1 ± 0.5	1.3 ± 0.9
73.064	2-Butanone [3]	C ₄ H ₈ O ⁺	3.7 ± 4.9	3.9 ± 2.3	2.4 ± 1.1	2.5 ± 1.2
75.043	Methyl acetate [3, 18]	C ₃ H ₇ O ₂ ⁺	14.2 ± 24.6 ^a	2.5 ± 3.6 ^{ab}	1.8 ± 2.0 ^b	5.8 ± 6.0 ^{ab}
75.079	2-Methylpropanol [3]	C ₄ H ₁₁ O ⁺				
81.044	Pyrazine	C ₄ H ₅ N ₂ ⁺	7.5 ± 5.3 ^b	12.8 ± 8.9 ^{ab}	25.7 ± 30.8 ^a	8.1 ± 6.3 ^{ab}
82	N.I.		0.6 ± 0.5 ^b	1.0 ± 0.7 ^{ab}	1.9 ± 2.2 ^a	0.6 ± 0.5 ^b
83.086	Hydrocarbon [3]/Fragment [21]/ Dimethylbutadiene [20]	C ₆ H ₁₁ ⁺	25.0 ± 23.7 ^b	42.1 ± 35.5 ^{ab}	73.4 ± 92.1 ^a	24.0 ± 18.2 ^b
84	N.I.		1.6 ± 1.6 ^b	2.7 ± 2.3 ^{ab}	4.7 ± 6.1 ^a	1.6 ± 1.2 ^b
85.064	2-Pentenal [5, 10]	C ₅ H ₉ O ⁺	1.5 ± 1.2	1.1 ± 0.7	3.0 ± 5.5	0.9 ± 0.5
85.100	Hydrocarbon [3]/Fragment (alcohol) [21]	C ₆ H ₁₃ ⁺				
87.044	2,3-Butanedione [3, 5, 19]	C ₄ H ₇ O ₂ ⁺	1.0 ± 0.6	1.3 ± 0.3	1.2 ± 1.0	0.9 ± 0.3
87.080	1-Penten-3-ol [3, 5, 9]	C ₅ H ₁₁ O ⁺				
89.059	Ethyl acetate [5, 10, 18, 19, 22]	C ₄ H ₉ O ₂ ⁺	5.6 ± 7.6 ^b	1.8 ± 3.2 ^b	1.3 ± 1.1 ^b	21.6 ± 31.7 ^a
91.074	2,3-Butanedione [22]	C ₄ H ₇ O ₂ ⁺	0.1 ± 0.2	< 0.1	< 0.1	0.1 ± 0.2
95.049	Phenol [5, 6]	C ₆ H ₇ O ⁺	0.3 ± 0.2 ^b	0.4 ± 0.3 ^{ab}	0.5 ± 0.3 ^a	0.2 ± 0.2 ^b
97.065	2-Ethylfuran [5, 15]	C ₆ H ₉ O ⁺	0.2 ± 0.1 ^b	0.3 ± 0.1 ^{ab}	0.4 ± 0.2 ^a	0.2 ± 0.1 ^b
97.101	1-Methylcyclohexene [13]	C ₇ H ₁₃ ⁺				
98	N.I.		0.2 ± 0.2 ^b	0.3 ± 0.2 ^{ab}	0.7 ± 1.0 ^a	0.2 ± 0.2 ^{ab}
99.010	2,5-Furandione [12]	C ₄ H ₃ O ₃ ⁺	5.7 ± 5.6 ^b	10.2 ± 7.6 ^{ab}	23.0 ± 33.9 ^a	7.7 ± 7.4 ^{ab}
99.046	2-Furylmethanol [2]	C ₅ H ₇ O ₂ ⁺				
99.081	2-Hexenal [2, 5, 9, 10, 11, 15, 19]	C ₆ H ₁₁ O ⁺				
101.060	γ-Valerolactone [1, 5, 8]	C ₅ H ₉ O ₂ ⁺	1.1 ± 1.1 ^b	2.3 ± 2.0 ^{ab}	3.7 ± 5.1 ^a	1.1 ± 1.1 ^{ab}
101.095	Hexanal/3-Hexenol [2, 3, 5, 9, 10, 11, 19]	C ₆ H ₁₃ O ⁺				
103.076	Propyl acetate [3, 5, 19]/Ethyl propanoate [3, 5]	C ₅ H ₁₁ O ₂ ⁺	0.1 ± 0.1	0.1 ± 0.0	0.1 ± 0.1	0.1 ± 0.1
107.049	Benzaldehyde [1, 2, 3, 5, 7, 10, 11, 12]	C ₇ H ₇ O ⁺	4.3 ± 6.9	4.4 ± 4.8	3.4 ± 3.7	2.3 ± 1.5
109.070	Benzyl alcohol [1, 3, 5, 6, 7, 11, 19]	C ₇ H ₉ O ⁺	0.3 ± 0.1	0.3 ± 0.1	0.3 ± 0.1	0.3 ± 0.1
111.080	2,4-Heptadienal [15, 17, 14]	C ₇ H ₁₁ O ⁺	0.1 ± 0.1 ^b	0.2 ± 0.1 ^a	0.2 ± 0.1 ^a	0.1 ± 0.0 ^b
113.095	2-Heptenal [10, 15, 19]	C ₇ H ₁₃ O ⁺	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	< 0.1
115.075	γ-Hexalactone [2, 3, 5, 9, 10, 11, 12]	C ₆ H ₁₁ O ₂ ⁺	0.5 ± 0.3 ^b	0.4 ± 0.1 ^{bc}	0.3 ± 0.2 ^c	0.8 ± 0.3 ^a
115.108	Heptanal [10, 20, 22]	C ₇ H ₁₅ O ⁺				
117.092	Butyl acetate [3, 5, 10, 19]/Methyl isovalerate [1, 3]	C ₆ H ₁₃ O ₂ ⁺	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.0	< 0.1
119.107	Hexylene glicol	C ₆ H ₁₅ O ₂ ⁺	< 0.1 ^b	< 0.1 ^{ab}	< 0.1 ^a	< 0.1 ^{ab}
121.066	Benzeneacetaldehyde [5, 11,12, 15, 14]	C ₈ H ₉ O ⁺	0.2 ± 0.1 ^b	0.3 ± 0.1 ^a	0.2 ± 0.1 ^{ab}	0.2 ± 0.1 ^{ab}
121.100	Trimethylbenzene [3, 5]	C ₉ H ₁₃ ⁺				
123.117	Fragment (farnesene) [23]	C ₉ H ₁₅ ⁺	0.2 ± 0.1 ^{bc}	0.2 ± 0.1 ^a	0.2 ± 0.1 ^{ab}	0.1 ± 0.1 ^c
127.112	6-Methyl-5-hepten-2-one [3, 5, 9, 10, 16, 20] [22]	C ₈ H ₁₅ O ⁺	0.1 ± 0.0	0.1 ± 0.0	0.2 ± 0.1	0.1 ± 0.0
129.091	γ-Heptalactone [2, 3, 5, 9, 11, 15]	C ₇ H ₁₃ O ₂ ⁺	< 0.1	< 0.1	< 0.1	< 0.1
		C ₇ H ₁₃ O ₂ H ⁺				

(continued on next page)

Table 2 (continued)

m/z	Tentative identification ¹	Sum formula	Fruit type			
			Peach (n = 26)	Flat peach (n = 14)	Nectarine (n = 34)	Canning peach (n = 12)
129.127	Octanal [9, 10, 15, 20, 22, 14]	C ₈ H ₁₇ O ⁺				
131.107	Pentyl acetate/Methylbutyl acetate [1, 3, 5, 9, 19] [20]	C ₇ H ₁₅ O ₂ ⁺	< 0.1	< 0.1	< 0.1	< 0.1
135.111	<i>p</i> -Cymene [3, 5, 15, 17, 22, 14]	C ₁₀ H ₁₅ ⁺	< 0.1	< 0.1	< 0.1	< 0.1
137.133	Myrcene [3, 15, 22]	C ₁₀ H ₁₇ ⁺	1.4 ± 1.4 ^{ab}	2.1 ± 2.4 ^{ab}	2.5 ± 2.7 ^a	0.6 ± 1.0 ^b
138.064	Aminobenzoic acid	C ₇ H ₈ NO ₂ ⁺	0.1 ± 0.2 ^{ab}	0.2 ± 0.2 ^{ab}	0.3 ± 0.3 ^a	0.1 ± 0.1 ^b
139.113	2-Pentylfuran [3, 4, 10, 15, 20]	C ₉ H ₁₅ O ⁺	0.1 ± 0.1 ^b	0.2 ± 0.1 ^{ab}	0.1 ± 0.1 ^b	0.1 ± 0.0 ^b
139.145	Decahydronaphthalene	C ₁₀ H ₁₉ ⁺				
141.129	2-Nonenal [5, 10, 15, 14]	C ₉ H ₁₇ O ⁺	0.1 ± 0.1 ^b	0.2 ± 0.1 ^a	0.1 ± 0.1 ^{ab}	0.1 ± 0.0 ^b
143.108	γ-Octalactone [2, 3, 9, 10, 11, 16, 19]	C ₈ H ₁₅ O ₂ ⁺	0.3 ± 0.1	0.2 ± 0.0	0.3 ± 0.1	0.3 ± 0.1
143.143	Nonanal [4, 10, 11, 16, 19, 20]	C ₉ H ₁₉ O ⁺				
145.123	Hexyl acetate [3, 5, 9, 10, 11, 17, 20]	C ₈ H ₁₇ O ₂ ⁺	0.2 ± 0.2	0.1 ± 0.0	0.1 ± 0.1	0.1 ± 0.0
147.137	1,8-Octanediol	C ₈ H ₁₉ O ₂ ⁺	< 0.1	< 0.1	< 0.1	< 0.1
151.113	Carvone [12, 22]/Thymol [14]	C ₁₀ H ₁₅ O ⁺	< 0.1	< 0.1	< 0.1	< 0.1
153.128	Hotrienol [2, 3, 9, 20]	C ₁₀ H ₁₇ O ⁺	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.1	0.1 ± 0.0
155.108	2-Nonen-4-olide	C ₉ H ₁₅ O ₂ ⁺	0.2 ± 0.2 ^{ab}	0.2 ± 0.2 ^{ab}	0.3 ± 0.3 ^a	0.2 ± 0.1 ^b
155.143	Linalool [11, 16, 19, 20]/α-Terpineol [3, 7, 9, 10]	C ₁₀ H ₁₉ O ⁺				
157.159	Decanal [10, 19, 20, 22]	C ₁₀ H ₂₁ O ⁺	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0	0.1 ± 0.0
159.140	Methyl octanoate [3, 19]	C ₉ H ₁₉ O ₂ ⁺	< 0.1	< 0.1	< 0.1	< 0.1

Values with different letter within row indicate significant differences by Tukey's HSD post hoc test ($p \leq 0.05$).

N.I. (not identified): compounds not identified by PTR-ToF-MS. Bold compounds not previously reported among peach fruit VOCs.

¹ References: [1] Do et al., 1969; [2] Engel et al., 1988; [3] Takeoaka, Flath, Guntert, & Jennings, 1988; [4] Horvat et al., 1990; [5] Narain, Hsieh, & Johnson, 1990; [6] Kramer, Winterhalter, Schwab, & Schreier, 1991; [7] Aubert, Ambid, et al., 2003; [8] Aubert, Günata, et al., 2003; [9] Aubert & Milhet, 2007; [10] Wang et al., 2009; [11] Eduardo et al., 2010; [12] Brandi et al., 2011; [13] Pereira, Pereira, & Câmara, 2011; [14] Abidi, 2012; [15] Sánchez et al., 2012; [16] Eduardo et al., 2013; [17] Montero-Prado et al., 2013; [18] Rizzolo et al., 2013; [19] Giné-Bordonaba et al., 2014; [20] Spadoni et al., 2015; [21] Farneti et al., 2015; [22] Dabbou et al., 2016; [23] Ting et al., 2016.

valerolactone (101.060) or γ-hexalactone (115.075), together with hexanal/3-hexenol (101.095) and heptanal (115.108), respectively. Nectarines showed significantly higher amounts of *m/z* 101 and lower of *m/z* 115, while canning peaches had the higher amounts of the latest. Other lactones found were γ-heptalactone (129.091) and γ-octalactone (143.108) but no significant differences were observed among peach fruit types. Previous studies reported γ-decalactone, and in lesser extent δ-decalactone, as the most abundant lactones in the pulp of peach and nectarine (Wang et al., 2009) while γ-hexalactone was observed to be dominant for some cultivars (Eduardo et al., 2010). Variable results can be found in the literature regarding γ-valerolactone. The amounts of this lactone were reported to increase with maturity stage and to be higher in tree ripe than artificially ripe peaches (Do et al., 1969). However, Aubert, Günata et al. (2003) observed that γ-valerolactone was significantly higher for tree ripe than unripe nectarines but also significantly higher for unripe fruits stored in ripening chambers at 26 °C than tree ripe ones. The *m/z* 155, associated to 2-nonen-4-olide (155.108) and linalool/α-terpineol (discussed in Section 3.1.3), was also significantly higher in nectarines and lower in canning peaches. Analogs of this lactone were previously observed in peaches and nectarines (Aubert & Milhet, 2007; Engel et al., 1988; Takeoaka et al., 1988). Horvat et al. (1990) reported the lactone distribution to differ between peaches and nectarines but Wang et al. (2009) did not observe significant differences between both types of fruits. More than 10 lactones have been observed among peach fruit volatiles (Abidi, 2012; Aubert & Milhet, 2007; Eduardo et al., 2010; Engel et al., 1988). However, in our study only C₅–C₈ γ-lactones were observed. This was in agreement with the results from Narain et al. (1990) of headspace measurements in peach. The differences with other works are prone to be due to the different methodologies of volatile assessment. These differences were observed by Takeoaka et al. (1988) who compared the volatile profiles of nectarines with both headspace and steam distillation sampling techniques and reported lower number of lactones with the former. Derail, Hofmann, and Schieberle (1999) compared the aroma profile of fresh peach juice and cooked pulp by simultaneous steam-distillation/extraction and observed that the increase of the amounts of lactones was thermally induced. The authors observed an

increase of the flavor dilution factors of 128 times for δ-decalactone, 32 times for γ-decalactone, or 16 times for γ-jasmolactone in the cooked extracts. More recently, Rizzolo et al. (2013) detected a low proportion of lactones using a static headspace technique and reported that equilibration at 70 °C during 30 min was enough to increase γ-decalactone and γ-dodecalactone amounts. Despite being key compounds for the peach fruit aroma definition, these lactones were not detected in the present study. The differences from previous works may be due to differences in the techniques, mainly between GC-MS and PTR-MS, and measurement conditions, such as higher temperatures used with steam distillation, solvent, SPME, and headspace extraction procedures, compared to the headspace analysis at 25 °C. Other factors to take into account are the use of low pressures, long equilibration or extraction times, and large quantities of sample material.

3.1.2. Amino acid derived and nitrogen-related compounds

Pyrazine (*m/z* 81.044) had higher amounts in nectarines and lower in peaches. Pyrazine was previously observed in apricots (Solís-Solís, Calderón-Santoyo, Schorr-Galindo, Luna-Solano, & Ragazzo-Sánchez, 2007) and is produced by further interactions occurred after Maillard reaction, with a wide diversity of aromas depending on the side group of each pyrazine compound (Buchbauer, Klein, Wailzer, & Wolschann, 2000; Maga & Sizer, 1973). Phenol and aminobenzoic acid were also significantly higher in nectarines while benzeneacetaldehyde in flat peaches. Previously reported in *Prunus* fruits (Krammer et al., 1991), phenol is formed by addition of a hydroxyl group to a benzene ring and is the basis of phenolic compound formation (Saltveit, 2009). The valine-derived volatile 2-methylpropanol (Gonda et al., 2010) was identified at *m/z* 75 together with methyl acetate (Section 3.1.1). Acetonitrile, *m/z* 69 comprised by 1H-pyrazole (69.047) and isoprene (69.069), and benzyl alcohol (109.170) showed no significant differences among fruit type. 1H-pyrazole was recently reported in peaches by Brandi et al. (2011).

The compounds involved in cyanogenesis were not significantly different for any peach fruit type. Hydrogen cyanide in peach fruit is originated from the enzymatic degradation of cyanogenic glycosides, amygdalin and prunasin, together with benzaldehyde (Poulton, 1993).

The latest can also occur as an amino acid decomposition product and its concentration was reported to increase during maturity (Do et al., 1969) being the most abundant aldehyde observed in peaches and nectarines (Narain et al., 1990; Wang et al., 2009). Acetone is an end product of cyanogenesis and was previously observed among the VOCs of several fruits including peaches (Takeoaka et al., 1988).

3.1.3. Terpene compounds and hydrocarbons

The isoprene-related compounds identified in the VOCs profile were observed at lower amounts. Myrcene and the m/z 155, associated to linalool/ α -terpineol (m/z 155.143), were significantly higher in nectarines while m/z 123.117, assigned to a farnesene fragment, was significantly higher in flat peaches. Canning peaches showed the lowest amounts of these compounds. Terpene compounds are formed by several isoprene units and its metabolism is in the origin of several *Prunus*' fruit VOCs (Krammer et al., 1991). Myrcene is an acyclic monoterpene precursor of linalool (Brodkorb, Gottschall, Marmulla, Luddeke, & Harder, 2010) and was reported to be the most abundant terpene in peaches and nectarines (Aubert & Milhet, 2007; Eduardo et al., 2010; Wang et al., 2009). No significant differences were observed for p-cymene (135.111), carvone (151.113) and hotrienol (153.128) but these were only detected at trace amounts. Sunthonvit, Srzednicki, and Craske (2007) found linalool and hotrienol to be the main terpenes in tree-ripened nectarines.

Masses m/z 83.086 and 85.100 were previously described as hydrocarbons (Takeoaka et al., 1988) but recently identified as fragments of diverse origins (alcohols, aldehydes, terpenes) by PTR-ToF-MS in apple fruit (Farneti et al., 2015). The former was also recently reported as dimethylbutadiene (Takeoaka et al., 1988). This compound was significantly higher in nectarines, followed by flat peaches and lower in peaches and canning peaches. Other minor hydrocarbons observed were trimethylbenzene, 1-methylcyclohexene and decahydronaphthalene, analog of naphthalene compounds previously observed among peach fruits.

3.1.4. Discriminant analysis

The subset of the 36 significantly different PTR-MS masses obtained with the ANOVA results were submitted to a principal component analysis (PCA) and the matrix of orthogonal PCs used to perform a DA (Fig. 1). The PCA loadings for each VOC allowed the identification of the compounds with the higher contribution to each principal component, helping to explain the specific differences between fruit typologies observed in the DA plot. The higher positive loadings of fragments of several origins (m/z 43), acetic acid, ethyl acetate, and m/z 115 comprised by γ -hexalactone and heptanal on PC 2 were responsible for the distinction of canning peaches from the other fruits. Nectarines were differentiated from the former ones due to high positive loadings of pyrazine, γ -valerolactone together with hexanal/3-hexenol (m/z 101), m/z 83 and 55, m/z 99 comprised by 2,5-furandione, 2-furylmethanol and 2-hexenal, m/z 57, and m/z 58 on PCs 1 and 4. Peaches had intermediate characteristics between the former two, although the negative loadings of the compounds above mentioned for nectarines contributed for their negative scores, and thus, the opposed the projection of both peaches and nectarines. Flat peaches were distinguished from the rest of fruits due to the high positive loadings of m/z 51, methanol, m/z 35, and acetaldehyde on PCs 3 and 5.

The first three factors explained 100% of the variance in the PTR-MS data (45%, 37% and 18%, respectively) with 100% of correctly classified samples. The clearest separation was observed between flat peaches and canning peaches with the former ones being the most differentiated peach type. Canning peaches were also overlapped with peaches but these were only slightly overlapped with nectarines. The group formation was consistent with the sensory analysis' results detailed below, but the separation was more distinct for the volatile profiles.

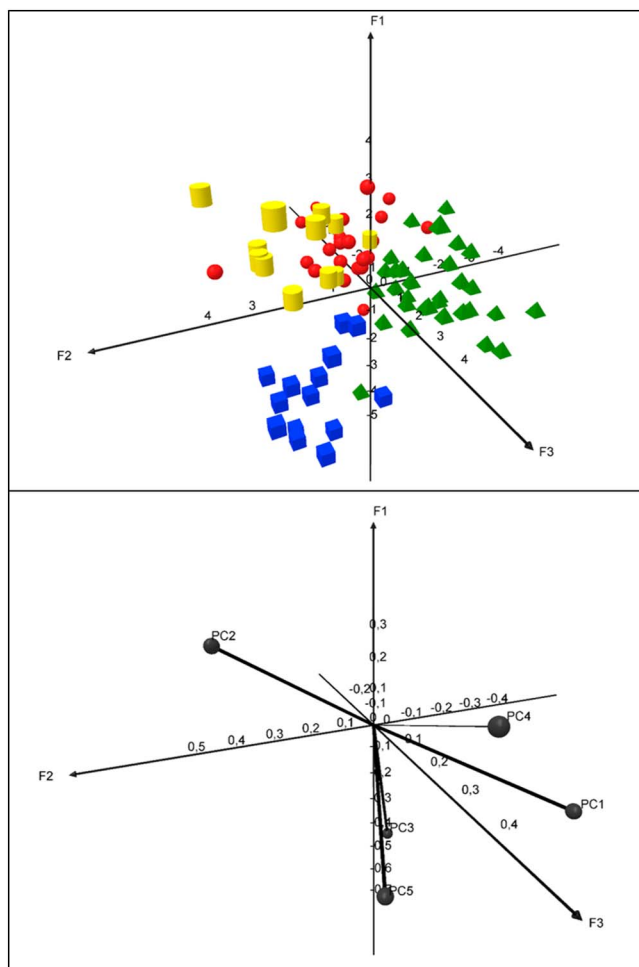


Fig. 1. Scores (upper) and loadings (lower) plot of the discriminant analysis (DA) performed on the PTR-MS data of the *Prunus persica* cultivars according to their typology: peaches (red spheres), nectarines (green pyramids), flat peaches (blue cubes), and canning peaches (yellow cylinders). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

3.2. Sensory analysis

ANOVA results showed that panelists detected significant differences for five out of the seven sensory attributes analyzed among types of fruits (Table 3). Aroma intensity and ripe fruit highest scores were observed for canning peaches, followed by peaches, flat peaches, and with nectarines having the lowest scores. A slightly different trend was observed for flavor intensity. Canning peaches were still equally higher scored for this attribute but were followed by flat peaches, peaches, and nectarines. Reig et al. (2013) also observed significantly higher overall flavor scores for flat peaches compared to peaches and nectarines. The relationship between the highest aroma intensity and ripe fruit attributes was reflected by the flavor intensity for canning peaches. However, with regard to flat peaches it is more likely to be due to their lower titratable acidity (TA) when compared to the other peach fruit types (Table A.2, Appendix A.). Aroma intensity and ripe fruit aroma attributes were most strongly correlated ($r = 0.91$; $p \leq 0.001$) among the sensory traits and both were similarly correlated with flavor intensity ($r = 0.68$; $p \leq 0.001$ and $r = 0.70$; $p \leq 0.001$ respectively). Flavor persistence was significantly higher scored for canning peaches and peaches, with flat peaches having the least persistent flavor and nectarines showing an intermediate behavior. This attribute was similarly related to fruit aroma ($r = 0.46$; $p \leq 0.001$) and aroma and flavor intensities ($r = 0.51$; $p \leq 0.001$ and $r = 0.54$; $p \leq 0.001$).

Aroma and flavor attributes associated with plum fruit were not

Table 3
ANOVA results (Mean \pm Standard Deviation) of the aroma and flavor attribute scores among the *Prunus persica* cultivars.

Attributes	Type of fruit			
	Peach (n = 26)	Flat peach (n = 14)	Nectarine (n = 34)	Canning peach (n = 12)
Aroma				
Aroma intensity	5.06 \pm 1.01 ^b	4.65 \pm 0.79 ^{bc}	4.38 \pm 0.93 ^c	5.93 \pm 1.00 ^a
Ripe fruit	4.32 \pm 1.12 ^{ab}	3.87 \pm 0.95 ^{bc}	3.25 \pm 0.78 ^c	5.08 \pm 1.22 ^a
Plum aroma	1.39 \pm 0.56	1.18 \pm 0.38	1.50 \pm 0.50	1.07 \pm 0.46
Stone aroma	1.48 \pm 0.62 ^a	1.30 \pm 0.51 ^{ab}	1.69 \pm 0.74 ^a	0.86 \pm 0.43 ^b
Flavor				
Flavor intensity	4.77 \pm 0.80 ^b	5.15 \pm 0.51 ^{ab}	4.58 \pm 0.77 ^b	5.48 \pm 0.79 ^a
Plum flavor	1.68 \pm 0.62	1.58 \pm 0.45	1.44 \pm 0.51	1.41 \pm 0.52
Flavor persistence	4.53 \pm 0.77 ^a	3.91 \pm 0.52 ^b	4.36 \pm 0.78 ^{ab}	4.66 \pm 0.35 ^a

Values with different letter within row indicate significant differences by Tukey's HSD post hoc test ($p \leq 0.05$).

significantly different for any type of peach. The stone aroma attribute showed three significantly different groups with nectarines and peaches having the highest scores and canning peaches the lowest ones. A negative relationship was observed between stone aroma and ripe fruit aroma ($r = -0.26$; $p \leq 0.05$) or aroma and flavor intensities ($r = -0.30$; $p \leq 0.01$ and $r = -0.27$; $p \leq 0.05$), suggesting that stone aroma was the dominant attribute in those fruits with lower scores of ripe or typical aroma. This relationship was also found by Spencer et al. (1978) who stated that the woody and other background aromas might be masked by fruity aromas in peach. Nevertheless, Delgado et al. (2013) related the woody notes of the stone/pit with an aroma combination able to drive consumers' liking of peach.

Discriminant analysis (Fig. 2) was performed in order to understand the differences and similarities among the fruit types perception. The first three factors accounted to explain 100% of the variance (61.4%, 30.6% and 8.0% respectively), resulting in 87% of correctly classified samples according to the confusion matrix. Ripe fruit and aroma intensity were the most discriminate attributes, followed by stone aroma and flavor intensity. Flavor persistence was the least discriminate attribute while plum aroma and flavor did not show any significant ability to discriminate between samples, in agreement with the ANOVA results for these attributes. The overlapping observed reflected the similarities between the four types of peach fruits. However, it was possible to visualize a group formation according to each peach type with the clearest separation between flat peaches and canning peaches or an opposed location of peaches and nectarines. Likewise, canning peaches were mainly grouped along with peaches while flat peaches appeared to have an intermediate behavior between peaches and nectarines.

To the best of the authors' knowledge, no studies have evaluated the sensory profile of peaches considering the relationship between the different peach fruit types. Despite the high variability observed, possibly as a result of the internal quality traits (texture, organic acids, soluble sugars), these results highlight an enhanced organoleptic perception of canning peaches and flat peaches regarding aroma and flavor intensities. This variability is prone to result from the varietal innovation of the past years, mainly concerned with peaches and nectarines and, more recently, with a higher focus over flat peaches or the significant focus over canning peaches in some Spanish breeding programs (Iglesias, 2015).

3.3. Relationships between sensory analysis and VOCs

PLS regression was performed using the volatile compound masses and the significantly different sensory attributes among peach fruit types. The determination coefficients showed satisfactory correlations between the VOCs and the aroma intensity ($R^2 = 0.58$) and ripe fruit aroma ($R^2 = 0.57$), but lower values were observed for flavor attributes and stone aroma. The standardized regression coefficients (" β coeffi-

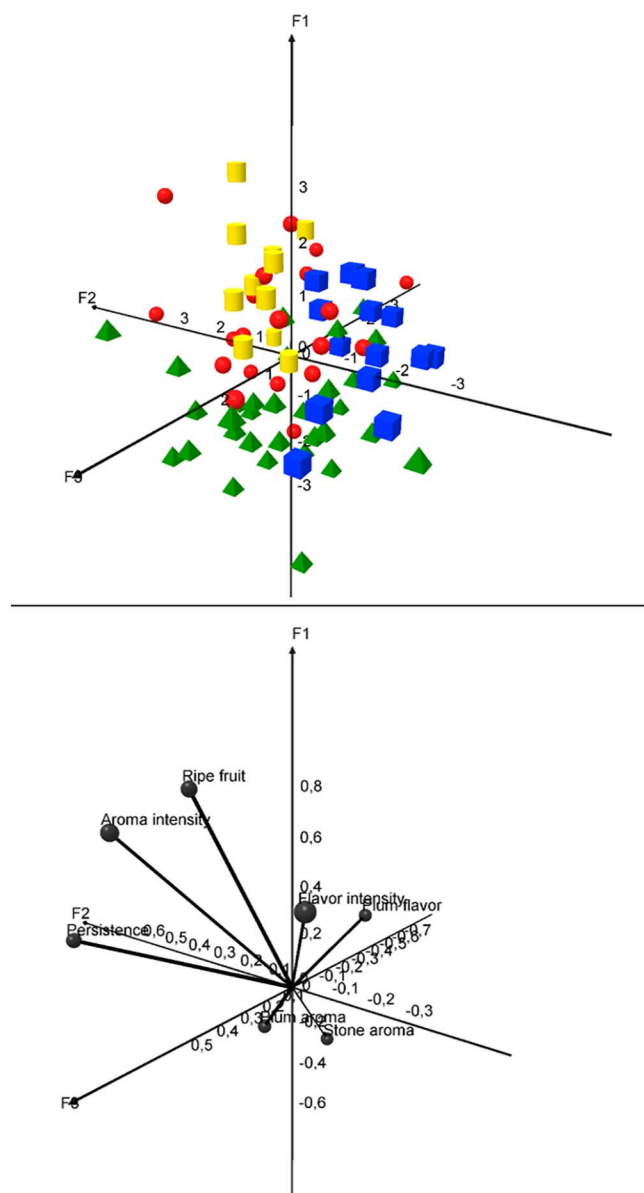


Fig. 2. Scores (upper) and loadings (lower) plot of the discriminant analysis (DA) performed on the sensory data of the *Prunus persica* cultivars according to their typology: peaches (red spheres), nectarines (green pyramids), flat peaches (blue cubes), and canning peaches (yellow cylinders). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 4

Partial least square (PLS) regression results: standardized regression coefficients indicating the relative contribution of the volatile organic compounds (VOCs) to the sensory attributes of peach fruits^a.

<i>m/z</i>	VOCs	Aroma intensity	Ripe fruit	Stone aroma	Flavor intensity	Persistence	Organoleptic description ^b
43.017	Fragment (ester)	0.07**	0.06*		0.05**	0.05**	
43.054	Fragment (alcohol, ester, acetate)						
44	N.I.	0.05*	0.05*		0.04*	0.05*	
45.034	Acetaldehyde	-0.08*	-0.06*		-0.06*	-0.08*	Pungent, ethereal, fruity [3]
46	N.I.	-0.08*	-0.06*		-0.06*	-0.08*	
57	N.I.	-0.04*	-0.04**	0.02*	-0.03*	-0.02*	
57.069	Fragment (alcohol, ester)						
58	N.I.	-0.04*	-0.04**	0.02*	-0.03*	-0.02*	
61.028	Acetic acid	0.08**	0.07**		0.06**	0.06**	Sour pungent, cider vinegar, acidic tangy [3]
62	N.I.	0.07**	0.07**		0.06**	0.06**	
63.044	Ethylene glycol					-0.04*	
73.064	2-Butanone	-0.06*				-0.07*	Chemical, slightly fruity, green [3]
75.043	Methyl acetate	0.07*	0.07*		0.05*	0.07*	Fruity, slightly bitter [3]
75.079	2-Methylpropanol						Wine [3], Pungent [6], Licorice, alcoholic, chemical [8]
81.044	Pyrazine	-0.03*	-0.04*		-0.02*		Green, earthy, nutty, woody [2]
82	N.I.	-0.03*	-0.03*		-0.02*		
85.064	2-Pentenal	0.02*				0.02*	Fruity, strawberry [4] Green [6]
85.100	Hydrocarbon/Fragment (alcohol)						
89.059	Ethyl acetate	0.06**	0.06**		0.05**	0.05**	Ethereal, fruity, sweet [3]
97.065	2-Ethylfuran	-0.04*	-0.04*		-0.03*		Rubber, pungent, acid [4], Sweet-ethereal, burnt [6]
97.101	1-Methylcyclohexene						
98	N.I.	-0.04*	-0.04**	0.02*	-0.03*	-0.02*	
99.010	2,5-Furandione	-0.04*	-0.04**	0.02*	-0.03*	-0.02*	Faint acrid [3]
99.046	2-Furylmethanol						Warm, oily, burnt, sweet, caramel [3]
99.081	2-Hexenal						Almond, herbal, apple, plum [3] Green, banana-like [1]
107.049	Benzaldehyde	-0.05*	-0.04*		-0.04*	-0.06*	Bitter almond [3, 8]
115.075	γ -Hexalactone	0.12***	0.11**		0.09**	0.11***	Coconut, fruity [1], vanilla-like, warm, herbaceous, sweet [3]
115.108	Heptanal						Fatty, harsh, pungent, green, citrus [3, 8]
121.066	Benzeneacetaldehyde	-0.08*	-0.07*		-0.06*	-0.08*	Harsh, hawthorn, floral, pungent, bitter, sweet [3]
121.100	Trimethylbenzene						Musty [5]
123.117	Fragment (farnesene)		-0.05*				
137.133	Myrcene					0.04*	Woody, resinous, musty, balsamic, ethereal [8]
138.064	Aminobenzoic acid					0.04*	
139.113	2-Pentylfuran	-0.06*	-0.06*		-0.05*	-0.06*	Fatty, butter, warm, sweet [8]
139.145	Decahydronaphthalene						
143.108	γ -Octalactone	0.08*	0.07*		0.06*	0.08*	Coconut [1], creamy, apricot, peach, sweet [3]
143.143	Nonanal						Fatty, wax, citrus, green, melon skin, floral [3, 8]
153.128	Hotrienol	0.09*	0.08*		0.07*	0.09*	Sweet, tropical, fennel, ginger [6]
155.108	2-Nonen-4-olide					0.04*	Overripe orange, oak [7]
155.143	Linalool/ α -Terpineol						Sweet, fruity, floral, tea-like [1, 6]/Floral, sweet [6]
	R ²	0.58	0.57	0.07	0.34	0.44	

^a Significance: standardized regression coefficients (“ β coefficients”) were significant at $p \leq 0.05$ (*), $p \leq 0.01$ (**) and $p \leq 0.001$ (***). Only significant coefficients are shown. N.I. (not identified): compounds not identified by PTR-ToF-MS. Bold compounds not previously reported among peach fruit VOCs.

^b References: [1] Derail et al., 1999; [2] Buchbauer et al., 2000; [3] Burdock, 2001; [4] Jordán, Margaría, Shaw, & Goodner, 2002; [5] Longchamp, Barry-Ryan, & Devereux, 2009; [6] Narain, Nigam, & Galvão, 2010; [7] Stamatopoulos, Frérot, Tempère, Pons, & Darriet, 2014; [8] Bonneau, Boulanger, Lebrun, Maraval, & Gunata, 2016.

clients”) highlighted the compounds with the higher contribution to the perception of peach fruit by reporting the relative weight of each *m/z* in the PLS model (Table 4). The greater the absolute value of a coefficient, the greater its impact over a sensory attribute.

Globally, aroma intensity and ripe fruit aroma attributes were related with the same volatile compounds and to a similar extent. These relations were also observed for flavor intensity and persistence, although to a lower extent. The highest positive contributions to the intensity and ripe fruit aromas were from *m/z* 115, comprised by γ -hexalactone and heptanal, acetic acid, hotrienol, *m/z* 143, comprised by γ -octalactone and nonanal, an unidentified compound (*m/z* 62), *m/z* 43 comprised by fragments of diverse origins, ethyl acetate, and *m/z* 75 comprised by methyl acetate and 2-methylpropanol. When an *m/z* was comprised by more than one compound, as for *m/z* 115 or 143, the impact over the sensory descriptors could not be easily attributed. However, the positive standardized regression coefficients of *m/z* 115 and 143 (both comprised by a γ -lactone and an aldehyde) allowed to relate their contribution to the intensity and ripe fruit aromas with the

fruity notes of γ -lactones and not the green notes of the aldehydes, which were expected to show a negative contribution for these attributes. These results are in agreement with Spencer et al. (1978) who reported γ -lactones to be responsible for the peachy background aroma. Ethyl and methyl acetates are responsible for the fruity aroma and flavor of several fruits like apricots (Defilippi, Manríquez, Luengwilai, & González-Agüero, 2009), apples (Karlsen, Aaby, Sivertsen, Baardseth, & Ellekjaer, 1999) or melons (Obando-Ulloa et al., 2008), among others. Acetic acid seems to be related with unpleasant attributes but its role in fruit perception is not fully understood. Our results suggest that in peach fruit it might act as an enhancer of other volatile compounds. Acids significantly affect the sensory perception of the peachy aroma attribute in mango (Malundo, Shewfelt, Ware, & Baldwin, 2001) while ethyl acetate was reported to increase in parallel with acidity in kiwifruit (Marsh, Friel, Gunson, Lund, & MacRae, 2006).

The highest negative relation with aroma intensity and ripe fruit aroma was observed for *m/z* 121, comprised by benzeneacetaldehyde

and trimethylbenzene, followed by acetaldehyde, an unidentified compound (m/z 46), and m/z 139, comprised by 2-pentylfuran and decahydronaphthalene. Benzeneacetaldehyde and 2-pentylfuran are associated with immature fruit notes. Both compounds were found to be negatively correlated with ground color in peach, while the former was also negatively correlated with fruit weight, SSC, and positively correlated with firmness (Sánchez et al., 2012). Trimethylbenzene has been associated with both pleasant and unpleasant attributes in different food products but its odor description is not entirely clear. Contrarily to previous studies (Baldwin, Goodner, & Plotto, 2008), acetaldehyde had a negative impact over peach fruit perception. The high amounts of this compound might have elicited unpleasant pungent aromas (Voon, Hamid, Rusul, Osman, & Quek, 2007) while the interaction with acids enhanced the sour perception of this fruit (Baldwin et al., 2008). A naphthalene compound was reported to be negatively correlated with overall, fruity and floral peach aromas, as well as positively correlated with overcooked and woody aromas (Spencer et al., 1978). Other negative contributions were observed from 2-butanone and benzaldehyde. The latter was also previously observed to correlate negatively to SSC and positively to firmness (Sánchez et al., 2012).

The differences between sensory and volatile profiles might be due to the influence of the non-volatile constituents, such as organic acids or soluble sugars, over peach fruit sensory perception (Colaric et al., 2005). The effect of added sugars or acids is known to enhance the sensory perception of several fruit pulps or juices (Malundo et al., 2001; Marsh et al., 2006). Likewise, the interaction of certain volatiles with organic acids or sugars is reported to significantly change the perception of the aroma and flavor attributes when compared to the volatile

alone (Baldwin et al., 2008). Other factors to take into account are the different sensory and instrumental release rate of certain VOCs or the possible influence of textural parameters. Ingham, Linforth, and Taylor (1995) reported significantly lower amounts of C6 aldehydes in the nose space, during in vivo aroma release while eating strawberries, than in headspace measurements. The influence of textural parameters on VOCs release during fruit perception was recently studied by Ting et al. (2016) using apple cultivars.

4. Conclusions

These results highlight the distinct volatile and sensory profiles associated with peach typologies. The development of new cultivars should compromise between the improvement of the sensory quality and the preservation of the typological aroma profiles. Furthermore, the lack of a greater agreement between sensory and volatile profiles, particularly for flavor attributes, indicates the need of further research concerning not only the relationship between sensory attributes and volatile compounds but also their link with the non-volatile constituents (organic acids and soluble sugars) of peach fruits.

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Appendix A

Table A.1

Fruit cultivars analyzed in this study: breeding program, peach fruit type and flesh color.

Cultivar	Breeding program (origin)	Fruit type	Flesh color
African Bonnigold	ARC (South Africa)	Canning peach	Yellow
Amiga	A. Minguzzi (Italy)	Nectarine	Yellow
ASF 04.05 Nj	Agro Selection Fruits (France)	Nectarine	Yellow
Early Maycrest	Toeus (USA)	Peach	Yellow
Fercluse	INRA-Bordeaux (France)	Canning peach	Yellow
Fergaron	INRA-Bordeaux (France)	Canning peach	Yellow
Honey Glo	Zaiger Genetic Inc. (USA)	Nectarine	Yellow
IFF 1230	CREA-Forlí (Italy)	Peach	Yellow
IFF 1233	CREA-Forlí (Italy)	Peach	Yellow
IFF 331	CREA-Forlí (Italy)	Peach	White
IFF 628	CREA-Forlí (Italy)	Peach	Yellow
IFF 691	CREA-Forlí (Italy)	Peach	Yellow
IFF 800	CREA-Forlí (Italy)	Nectarine	Yellow
Lami Nectar	A. Minguzzi (Italy)	Nectarine	Yellow
Maycrest	Minami (USA)	Peach	Yellow
Mésebrine	INRA-Bordeaux (France)	Flat nectarine ^a	Yellow
Nectabang	Agro Selection Fruits (France)	Nectarine	Yellow
Nectabelle	Agro Selection Fruits (France)	Nectarine	Yellow
Maillarqueen	Agro Selection Fruits (France)	Nectarine	White
Nectaprima	Agro Selection Fruits (France)	Nectarine	Yellow
Nectariane	Agro Selection Fruits (France)	Nectarine	Yellow
Nectareine	Agro Selection Fruits (France)	Nectarine	Yellow
Nectagala	Agro Selection Fruits (France)	Nectarine	Yellow
Nectarperle	Agro Selection Fruits (France)	Nectarine	White
Nectarcrisp	Agro Selection Fruits (France)	Nectarine	Yellow
Nectavista	Agro Selection Fruits (France)	Nectarine	Yellow
Orion	CREA-Rome (Italy)	Nectarine	Yellow
Red Valley	CIV Ferrara (Italy)	Peach	Yellow
Rubirich	Zaiger Genetics Inc. (USA)	Peach	Yellow

Spring Belle	Batistini (Italy)	Peach	Yellow
Star Nat	La Vipesa (Spain)	Flat peach	White
Summer Rich	Zaiger Genetics Inc. (USA)	Peach	Yellow
Summer Sun	ARC (South Africa)	Canning peach	Yellow
Sweet Prim	Agro Selection Fruits (France)	Peach	White
Sweet Ring	CREA-Forlì (Italy)	Flat peach	Yellow
Crispdelice	Agro Selection Fruits (France)	Peach	Yellow
Transvalia	ARC (South Africa)	Canning peach	Yellow
UFO-3	CREA-Rome (Italy)	Flat peach	White
UFO-4	CREA-Rome (Italy)	Flat peach	White
UFO-6	CREA-Rome (Italy)	Flat peach	White
UFO-7	CREA-Rome (Italy)	Flat peach	White
Venus®	CREA-Rome (Italy)	Nectarine	Yellow
Villa Giulia	CREA-Rome (Italy)	Canning peach	Yellow

^a Mésembrine was considered a flat peach in agreement with a previous work of Reig et al. (2013).

Table A.2

Values (Range and Mean \pm Standard Deviation) of the quality indexes determined among the *Prunus persica* cultivars analyzed (averaged triplicates).

Parameters	Type of fruit			
	Peach (n = 26)	Flat peach (n = 14)	Nectarine (n = 36)	Pavía (n = 12)
TA (g malic acid/L)				
Range	2.61–10.25	1.10–5.20	2.38–12.40	4.21–9.38
Mean \pm SD	6.19 \pm 2.31	2.76 \pm 1.03	5.36 \pm 2.65	6.99 \pm 1.54
SSC (°Brix)				
Range	7.34–11.85	9.89–13.97	8.31–14.53	7.24–13.87
Mean \pm SD	9.49 \pm 1.21	11.47 \pm 1.18	11.64 \pm 1.42	10.59 \pm 1.88

Appendix B

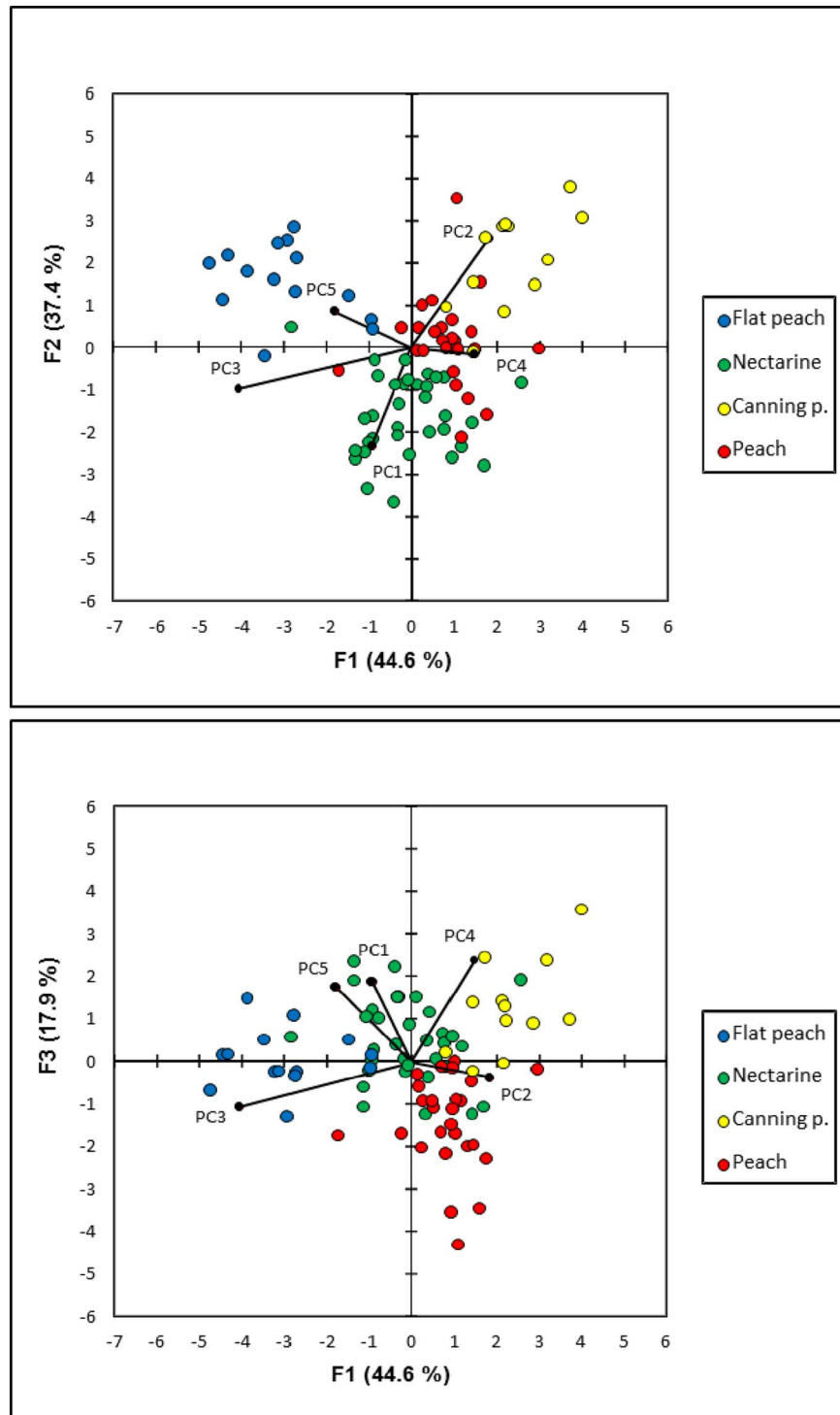


Fig. B.1. Biplots of the discriminant analysis (DA) performed on the PTR-MS data of the *Prunus persica* cultivars according to their typology: Factor 1 vs Factor 2 (upper) and Factor 1 vs Factor 3 (lower)

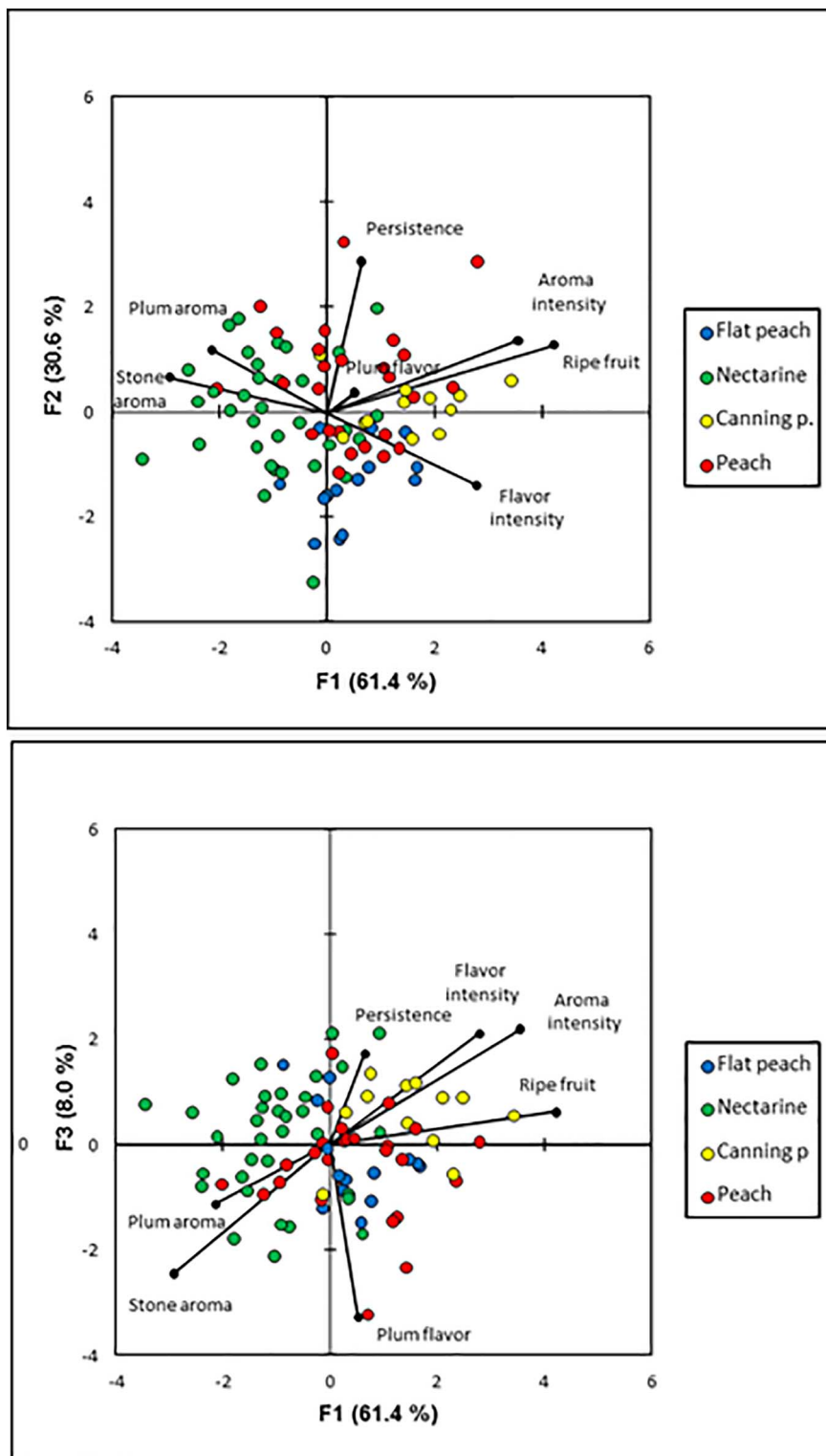


Fig. B.2. Biplots of the discriminant analysis (DA) performed on the sensory data of the *Prunus persica* cultivars according to their typology: Factor 1 vs Factor 2 (upper) and Factor 1 vs Factor 3 (lower).

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6. Main results and discussion

The correlation of sensory and instrumental methods combines the parameters perceived through the human senses and the ones measured through physicochemical determinations for a complementary assessment of key quality traits. A varying degree of correlation was observed between the methods performed herein. This allowed understanding the relationship between the different physicochemical parameters and the sensory perception of the melon and peach fruit cultivars evaluated. Despite the moderate to high agreement found between the sensory and instrumental analyses for several parameters, some differences were also observed concerning the results provided by both types of methodologies.

There are several factors known to affect the differences between perceived and instrumentally determined food quality traits. The complex oral processes occurring during mastication are known to affect the perception of texture. This is prone to limit the extent of correlation between sensory and instrumental methods since the latter cannot always consider aspects of the oral processes such as temperature in the mouth, the interaction of saliva with food, dynamic aspects of the movement of the food through the mouth and mastication time, and differences between individuals (Szczesniak, 2002; Bourne, 2004; Wilkinson *et al.*, 2010; de Lavergne *et al.*, 2017). The aspects of physiological oral behavior and the physicochemical characteristics of food also influence the release of the aroma and flavor from the food matrix and, thus, its perception. This results in differences between the release of compounds in the nose/mouth and during headspace measurements (Ingham, Linfort & Taylor, 1995; van Ruth, O'Connor & Delahunty, 2000; Arvisenet, Billy, Poinot, Vigneau, Bertrand & Prost, 2008; Ployon, Morzel & Canon, 2017). In addition, aroma perception of complex matrices relies on compounds that preserve their individuality and are still perceived within the matrix, as well as on compounds that lose their individual features but

contribute to the overall perception of the matrix. The existence of cross-modal interactions between aroma, taste, and texture, or the multisensory integration taking place in the perception of flavor also have to be taken into account. But regardless of how the different stimuli are projected, the information of all the senses is combined and interpreted by the brain to form the overall sensory perception of food (Keast & Breslin, 2002; Adams & Taylor, 2012; Thomas-Danguin *et al.*, 2016; Spence, 2016; Romagny, Coureaud & Thomas-Danguin, 2018). Furthermore, the majority of these aspects have been widely investigated using model foods or solutions with known concentrations of compounds, whereas the study of the phenomena underlying the sensory perception in the context of real food matrices is still far more complex (Marsh, Friel, Gunson, Lund & MacRae, 2006; Poinot *et al.*, 2013).

6.1 Correlation of sensory and instrumental texture of melon fruits

The relationship between the sensory and instrumental texture of the melon fruit types was evaluated by PCA and Pearson's correlation analysis. The instrumental texture measurements showed higher correlations with the sensory attributes more dependent on the mechanical properties of food: hardness, chewiness, and crunchiness. These attributes are particularly important for the consumer acceptance of fruit and vegetables due to their role in the perception of freshness and wholesomeness (Fillion & Kilcast, 2002). Sensory and instrumental hardness were correlated to a good extent but the same was not observed between sensory and instrumental chewiness. This could be due to an unequal contribution of each parameter involved in the definition of instrumental chewiness (the multiplication of hardness \times springiness \times cohesiveness) (Meullenet *et al.*, 1998). Consistently, instrumental chewiness was higher correlated with hardness and springiness than with cohesiveness. Regarding crunchiness, this was satisfactorily correlated with hardness, fracturability, springiness, and also chewiness.

The perception of crunchiness is complex, and it is an attribute that enhances or extends textural satisfaction and food enjoyment, either on its own or involved in any texture combination (Szczesniak & Khan, 1984). Crunchiness is highly influenced by the chewing sounds and it is thought to be the most auditory-dominant textural attribute. It is also the one that most integrates the audition sense into the perception of texture and, thus, into the multisensory perception of flavor (Zampini & Spence, 2010). Since both chewiness and crunchiness are hardness derived attributes, the role of hardness over these attributes must be well understood when improving the textural quality traits of melon fruits. While a few studies have pointed out that consumers might reject excessively hard melons and prefer medium to less hard fruits (Pardo *et al.*, 2000; Escribano *et al.*, 2010; Lázaro & de Lorenzo, 2015), it is important to consider that a higher hardness may require a bigger chewy effort and beyond a certain level, it can prevent the perception of crunchiness. Besides, most consumers are not willing to invest more than 20 chews unless the product provides pleasant flavor and/or texture experiences (Muñoz & Civille, 1987). In this context, excessively hard fruits could also reduce the intensity of the perceived flavor, either by preventing structural breakdown and release of volatile and taste compounds from the matrix, as observed for kiwi and apple fruits using *in vitro* and *in vivo* methods (Friel, Wang, Taylor & MacRae, 2007; Arvisenet *et al.*, 2008; Ting *et al.*, 2012), or even by focus the attention on the texture attributes in the expense of that paid to the flavor ones, as observed for different model foods (Weel, Boelrijk, Alting, van Mil, Burger, Gruppen, Voragen & Smit, 2002; Gierczynski, Laboure & Guichard, 2008).

Fibrousness, mealiness, and initial juiciness showed to be less related to the instrumental measurements as these attributes depend on the geometrical properties of food and its moisture content. In the present study, fibrousness was observed to be the most homogeneous attribute within the different melon fruits. Initial juiciness was

satisfactorily predicted by the weight losses, reflecting the usefulness of this method to predict juiciness during the first chews of different foods of plant origin. A careful interpretation is required as juiciness perception is formed by the combination of several aspects, other than the amount of juice released during chew. It involves the force with which the juice squirts out of the matrix, the release rate and the flow properties of the juice, the contrast in consistency between liquid and solid particles, as well as the effect of the juice over the secretion of saliva (Szczesniak & Ilker, 1988). Juiciness is one of the most desirable and appealing attributes in fruit, especially for fruits of refreshing flesh and highly consumed during the summer period like melons. Further than the effect on the transfer and delivery of aroma and flavor from the food matrix, juiciness has a direct effect on the oral processes occurring during the mastication of complex matrices such as fresh fruits. Juicier fruits increase the easiness and number of swallows and, thus, the release of VOCs in the mouth and the flavor perception, although this depends on the cultivar, their VOC concentration, and the combination with other textural parameters (Ting *et al.*, 2016). The latter authors also observed a relationship between the perception of juiciness and crunchiness due to a combined effect of the cell rupture and juice release for the sound produced during chewing. On the contrary, mealiness is one of the most undesirable attributes in fruit and its perception is generally associated with excessive softness and lack of free juice. It could be expected this lack of free juice to have the opposite effect on the perception of flavor. However, provided a fruit is flavorful and within a certain level of mealiness, sufficient juice release can be enough to assure flavor perception (Harker, Amos, Echeverría & Gunson, 2006). In the present study, the higher correlations between mealiness and instrumental parameters were found with cohesiveness and adhesiveness, rather than with hardness and weight losses. The weakening of cohesive and adhesive forces is consistent with both mealiness and softness. Although mealiness occurs in parallel with softness, it can also be

developed in addition to softness, and it was suggested to be more correlated with the rate of softening than with softness itself (Segonne, Bruneau, Celton, Le Gall, Francin-Allami, Juchaux, Laurens, Orsel & Renou, 2014).

Moreover, the DA showed a higher ability of sensory attributes, SSC, and pH than instrumental texture parameters to discriminate between the different melon fruit types. Regarding the exotic cultivars, the climacteric fruits from the *dudaim* ('Irak') and *momordica* ('Calcuta') cv. groups were discriminated from the rest of the fruits due to their higher mealiness, whereas the *conomon* ones ('Songwhan charmi') were discriminated for its crunchiness. The latter, together with 'Piel de Sapo-T111' accession, was as hard and chewy as the commercial fruits. Regarding the non-climacteric fruits of the *inodorus* cv. group, no discrimination was observed between the commercial variety and the 'T111' accession of the Piel de Sapo fruits, while Amarillo showed intermediate mealiness and initial juiciness. Similarly, when comparing the climacteric fruits of the *cantalupensis* cv. group, no discrimination was observed between the 'Dulce' and 'Védrantais' elite cultivars, while commercial varieties (Galia and Cantaloupe) reflected the focus of melon breeders over hardness and SSC.

6.2 Correlation of sensory and instrumental aroma and flavor of melon fruits

The ANOVA of the sensory attributes and VOCs headspace concentration allowed to identify specific aroma and flavor traits associated with the different melon cultivars. The opposed profiles of climacteric fruits of the *cantalupensis* cv. group and non-climacteric fruits of the *inodorus* cv. group was in agreement with previous works (Kourkoutas, Elmore & Mottram, 2006; Obando-Ulloa, Moreno, García-Mas, Nicolai, Lammertyn, Monforte & Fernández-Trujillo, 2008; Escribano *et al.*, 2010; Fredes, Sales, Barreda, Valcárcel, Roselló & Beltrán, 2016). Climacteric fruits belonging to the *cantalupensis* cv. group ('Dulce', 'Védrantais', Galia, and Cantaloupe) showed higher

concentrations of alcohols, aldehydes, and esters, together with higher scores for the attributes of odor intensity, ripe fruit odor, and fermentative odor and flavor. The opposite was observed for the non-climacteric fruits of the *inodorus* cv. group (Amarillo, Piel de Sapo, and 'T111'). However, these differences were not perceived at the level of the flavor intensity, as the fruits of both cv. groups were highly scored for this attribute. This could be due to an effect of sweetness perception over the flavor intensity of *inodorus* fruits. Regarding the fruits of the exotic cv. groups, *dudaim* ('Irak'), *momordica* ('Calcuta'), and *conomon* ('Songwhan charmi'), distinctive volatile profiles were observed whereas these fruits were perceived as the least sweet. The fruits of the *dudaim* cultivar ('Irak') showed several similarities with the VOC profile of the *cantalupensis* fruits but were perceived as the most astringent of all. Similar results concerning the volatile profile of *dudaim* and *cantalupensis* fruits were previously observed (Güler, Karaka & Yetisir, 2013). In contrast, the fruits of *momordica* ('Calcuta') and *conomon* ('Songwhan charmi') cultivars showed an intermediate VOC profile between *cantalupensis* and *inodorus*. The former also showed the lowest scores for flavor intensity, and the latter the highest scores for cucumber odor and flavor attributes. A lower volatile concentration along with a lower sweetness perception is consistent with the limited flavor intensity perceived for 'Calcuta' fruits. The similarities observed between the VOC profile of *dudaim*, *conomon*, and *momordica* fruits and the VOC profile of either *cantalupensis* or *inodorus* fruits is consistent with the intermediate ripening expression observed for the exotic melon cultivars, regardless of their classification as climacteric or non-climacteric (Saladié, Cañizares, Phillips, Rodriguez-Concepcion, Larrigaudière, Gibon, Stitt, Lunn & Garcia-Mas, 2015; Esteras Rambla, Sánchez, López-Gresa, González-Mas, Fernández-Trujillo, Bellés, Granell, & Picó, 2018).

The relationship between the sensory attributes and VOCs was evaluated through PCA and Pearson's correlation analysis. The volatile profile of the melon fruits comprised 83 masses, of which 40 were found to be significantly correlated with the sensory attributes. The majority of alcohols (methanol, ethanol, diol alcohols) and aldehydes (acetaldehyde, butanal, methyl butanal, hexenal, and decanal) were positively correlated with the attributes of odor intensity, ripe fruit odor, fermentative odor and flavor, and also flavor intensity, although to a lower extent. The positive contribution of alcohols and aldehydes to the odor and flavor attributes of melon fruit was observed by other authors (Senesi, Di Cesare, Prinzevalli & Lo Scalzo, 2005; Verzera, Dima, Tripodi, Conduro, Crinò, Romano, Mazzaglia, Lanza, Restuccia, Paratore, 2014) but these figures may change with the maturity stage or under storage (Beaulieu & Lancaster, 2007). In previous works using deodorized tomato matrices, the enhancement of flavor perception was observed to be due to interactions between ethanol and methanol with characteristic VOCs, or between ethanol and acetaldehyde with sugars and acids (Tandon, Baldwin & Shewfelt, 2000; Baldwin, Goodner & Plotto, 2008). The positive contribution of acetaldehyde to the flavor perception of citrus and kiwi fruits was also reported (Baldwin, Nisperos-Carriedo, Shaw & Burns, 1995; Friel *et al.*, 2007). Acetaldehyde increases fruity flavor and contributes to the perception of freshness, but it can impart pungent and unpleasant flavors at high concentrations (Pesis, 2005; Plotto, Margaría, Goodner & Baldwin, 2008). Two C₉ aldehydes, 2,6-nonadienal and nonenal, were negatively correlated with the intensity, ripe fruit, and fermentative odor and flavor attributes of melon. These compounds are typically associated with green or cucumber notes and considered key volatiles in the typical aroma of the non-climacteric fruits of the *inodorus* cultivar (Kourkoutas *et al.*, 2006). However, in the present study, these were not correlated with cucumber odor and flavor, possibly due to the predominance of climacteric cultivars among the fruits analyzed.

The correlations between most of the esters (C₃ - C₉) and the intensity, ripe fruit, and fermentative odor and flavor attributes were within the ranges previously reported for melon attributes such as fruity, pineapple-like, floral, sweet, and candy (Vallone, Sivertsen, Anthon, Barrett, Mitcham & Zakharov, 2013; Lignou, Parker, Baxter & Mottram, 2014). Esters have a high impact over the aroma of the climacteric melon cultivars, but at high concentrations can lead to off-flavors associated with overripe and fermented notes and, thus, to consumer rejection. The changes in the odor quality of esters with increasing concentration were observed for an orange juice matrix and suggested to be due to physiological interactions (Plotto *et al.*, 2008). On the contrary, a lower contribution of esters than alcohols and aldehydes was reported for the aroma of the climacteric 'Jiashi' cultivar, but the interactions between VOCs and fruit matrix were not taken into account (Pang, Guo, Qin, Yao, Hu & Wu, 2012). Other volatile compounds or precursors such as isoprene, limonene, and acetic acid were positively correlated with the intensity, ripe fruit, and fermentative odor and flavor attributes, and acetone with the attributes of cucumber odor and flavor. This is consistent with the changes of the acetone aromatic character with the media, from "glue" and "alcohol" descriptors in water, to "sweet" in a solution of ethanol-methanol-water, and "green" in a deodorized tomato matrix, observed by Tandon *et al.* (2000).

Additionally, two C₆ green leaf volatiles, 3-hexenol and hexenal, were negatively correlated with both sweetness and SSC. The opposite was observed between the two compounds and astringency. The orthonasal and retronasal perception of green leaf volatiles was observed to change due to their interactions with sugars and acids (King *et al.*, 2006), but the nature of these interactions might depend on the fruit species. Similar results were observed for apples (Aprea *et al.*, 2017), table grapes (Maoz, Kaplunov, Raban, Dynkin, Degani, Lewinsohn & Lichter, 2020), strawberries, and blueberries, but the opposite was observed for tomato fruits (Baldwin *et al.*, 2008;

Klee and Tieman, 2018). Despite the low level of acidity of the melon fruits evaluated, some positive correlations were also observed between acidity and isoprene, 1,2-ethanediol, several aldehydes, or acetic acid. The interactions between certain VOCs with sugars and acids affect the release and persistence of these volatile compounds in the mouth and, thus, aroma and flavor perception, but several mechanisms can be involved and some remain unclear (Marsh *et al.*, 2006; Baldwin *et al.*, 2008; Aprea *et al.*, 2017; Arvisenet *et al.*, 2019).

6.3 Correlation of sensory and instrumental aroma and flavor of peach fruits

The analysis of the sensory scores and the VOCs headspace concentrations through ANOVA and DA allowed to obtain the distinctive profiles associated with each fruit typology: peach, nectarine, flat peach, and canning peach ("pavía"). Canning peaches showed an enhanced sensory profile due to their higher aroma intensity, ripe fruit aroma, flavor intensity, and flavor persistence. The higher positive loadings of a fragment (m/z 43), acetic acid, ethyl acetate, and m/z 115 comprised by γ -hexalactone and heptanal allowed the distinction of canning peaches from the rest of the fruits. Peaches and flat peaches showed an intermediate perception for aroma attributes, while flat peaches had higher flavor intensity than peaches. The flat cultivars were differentiated due to the higher positive loadings of fragments and unidentified compounds at m/z 35 and 51, methanol, and acetaldehyde. Nectarine fruits were perceived as the least aromatic but as flavorful as peaches. The distinction of nectarines was based on the high positive loadings of pyrazine, m/z 101 comprised by γ -valerolactone and hexanal/3-hexenol, m/z 99 comprised by 2,5-furandione, 2-furylmethanol and 2-hexenal, as well as fragments and unidentified compounds at m/z 55, 57, 58, and 83. Peaches had intermediate characteristics between canning peaches and nectarines and were further differentiated from the latter due to the negative

loadings of the same compounds mentioned for nectarines. A higher overall flavor perception for flat peaches than peaches and nectarines was previously observed by Reig *et al.* (2013). The distribution of certain key volatile compounds of peach fruit, such as lactones, was also observed to differ between peaches and nectarines (Horvat, Chapman Jr, Robertson, Meredith, Scorza, Callahan & Morgens, 1990), although other authors reported no significant differences between both fruit typologies (Wang, Yang, Li, Yang, Wang, Zhao & Jiang, 2009). Despite the higher flavor intensity of flat peaches, the flavor of peaches and nectarines was perceived as more persistent. Similarly, peaches and nectarines had the highest scores for the stone aroma attribute, and canning peaches the lowest. The woody notes associated with stone or pit aroma might be masked by fruity aromas (Spencer, Pangborn & Jennings, 1978) but were reported to be related with an aroma combination able to drive consumers' liking of peach (Delgado *et al.*, 2013).

The correlation between the sensory attributes and the VOCs headspace concentrations was performed through a PLS regression model to highlight the compounds with a higher contribution to the fruit perception. The volatile profile of the peach fruits comprised 68 masses, and 28 were found to have a significant contribution to the aroma and flavor of peach fruit. Aroma intensity, ripe fruit aroma, flavor intensity, and flavor persistence attributes were related to the same compounds, although the latter two to a lower extent. The higher positive contribution for these attributes was observed from m/z 115, comprised by γ -hexalactone and heptanal, acetic acid, hotrienol, m/z 143, comprised by γ -octalactone and nonanal, an unidentified compound (m/z 62), fragments (m/z 43), ethyl acetate, and m/z 75 comprised by methyl acetate and 2-methylpropanol. Several lactones, in particular γ -lactones, were observed to be responsible for the 'peachy' background aroma (Spencer *et al.*, 1978) and acetate esters for the fruity aroma and flavor of different fruit species. Acetic acid seems to be

related to unpleasant attributes but its role in fruit perception is not fully understood. Our results suggest that in peach fruit it might act as an enhancer of other volatile compounds. As observed in the previous section for melon fruits, interactions between certain VOCs with sugars and acids can affect aroma and flavor perception. Changes in the levels of sugars and acids were observed to affect the perception of 'peachy' aroma of mango fruits and suggested to be due to physicochemical interactions at the fruit matrix level, or to psychological interactions at a cognitive level (Malundo, Shewfelt, Ware & Baldwin, 2001). However, the enhancement of retronasal aroma by taste can also be due to the co-existence of these interactions with other perceptual effects (Arvisenet *et al.*, 2019).

The higher negative contribution for the aroma and flavor attributes of peach fruit was observed from m/z 121, comprised by benzeneacetaldehyde and trimethylbenzene, followed by acetaldehyde, an unidentified compound (m/z 46), and m/z 139, comprised by 2-pentylfuran and decahydronaphthalene. Negative correlations were observed between a naphthalene compound and overall, fruity and floral peach aromas (Spencer *et al.*, 1978). Benzeneacetaldehyde and 2-pentylfuran are associated with immature fruit notes. Negative correlations were observed between the former and peach quality traits like fruit weight and SSC, or between both compounds and ground color (Sánchez, Besada, Badenes, Monforte & Granell, 2012). Trimethylbenzene has been associated with both pleasant and unpleasant attributes in different food products but its odor description is not entirely clear. Contrarily to what was observed for melon fruit in the previous section, as well as for other fruit species, acetaldehyde showed a negative contribution to peach fruit perception. The interaction between acetaldehyde and acids can affect sour perception (Baldwin *et al.*, 2008), but other VOCs, as well as proteins, aminoacids, and polyphenols, could also have been involved. The interactions between acetaldehyde and ethanol, or both ethanol and acetic acid, were observed to

affect the perception of acetaldehyde in complex mixtures and at specific concentration ratios (Lopetcharat, 2002). Additionally, no significant contribution to the aroma and flavor perception of peach fruit was observed for several compounds including methanol, ethanol, m/z 101 comprised by γ -valerolactone and hexanal/3-hexenol, m/z 129 comprised by γ -heptalactone and octanal, and $C_5 - C_9$ esters, among others. However, their role to the peach fruit perception should be further investigated as these compounds have been reported as main contributors to the aroma of mature peach fruit (Pesis, 2005; Sánchez *et al.*, 2012; Eduardo, Chietera, Pirona, Pacheco, Troggio, Banchi, Bassi, Rossini, Vecchiotti & Pozzi, 2013).

6.4 Main limitations

The present work contributes to the existing knowledge about key quality attributes of melon and peach fruits by providing complementary information for their quality improvement. A limit has to be accepted for what can be measured by sensory and instrumental analyses, whereas a certain level of variation will remain unexplained when using statistical methods to correlate both types of data (Martens *et al.*, 1994). However, some limitations concerning the sample set, the experimental design, or the methodologies applied have to be addressed.

Different aspects of the experimental design of the present research work were considered to lower, as much as possible, the intrinsic variations of a biological matrix of such complexity as fresh produce. However, the effect of intra-fruit variation over the results obtained is still an aspect that needs to be considered when analyzing fruit quality traits. Additionally, the sensory and physicochemical analysis cannot always be performed simultaneously when working with fresh produce. In this work, the sensory analysis was performed on the same day as the instrumental texture, pH, and SSC, but this was not the case for TA and VOCs. As the fruit flesh used for these analyses was

vacuum-packed and frozen at -80 °C, it is not unusual to expect that minor degradations could affect the results. It has been observed that frozen storage of fruit affects vitamins or phenolic compounds, whereas contradictory results are reported for the volatile fraction (de Ancos, Ibañez, Reglero & Cano, 2000; Celli, Ghanem & Brooks, 2016).

There are some limitations to consider about the sensory analysis, even when working with trained panelists. Despite their intensive training, panelists may still be sensitive to perceptual effects that prevent the single assessment of the different components of flavor (Arvisenet *et al.*, 2016; 2019). On the other hand, additional research is needed if the mechanisms behind the correlations observed are to be understood. Some of the limitations associated with the instrumental methods applied herein were already mentioned in previous sections. Briefly, the instrumental methods do not consider the aspects related to the oral processes that can affect sensory perception and limit the extent of the correlations. These methods could be combined with model mouth devices or in-vivo flavor release approaches. However, their application to a large number of fruit cultivars could be substantially challenging and it might be appropriate to develop more specific research objectives first. The tentative identification of the VOCs is another limitation. Although it was possible to obtain sum-formulas for most compounds, additional confirmation of their identity using internal standards is still needed. Moreover, other multivariate statistical methods different from the ones applied herein could have also been used to provide complementary information on the relationships between sensory and physicochemical parameters. However, a straightforward interpretation of the results could be compromised (Qannari & Schlich, 2006).

6.5 Future perspectives

Additional research to validate the results obtained with the consumer preferences for melon and peach fruits would be valuable. Although the direction of these correlations is not expected to change, it is important to understand the extent to which these quality attributes or combinations of attributes influence consumer acceptance for both fruit species. This may contribute to a better differentiation of the existing cultivars in the market and establish priorities for the breeding of new cultivars. The existence of consumer segments with clear preferences for specific fruit cultivars should also be considered. This will help bring consumer choices one step closer to fulfilling their quality expectations and, thus, melon and peach fruits one step closer to achieving commercial success.

Similarly, research considering the evaluation of the sensory and instrumental texture of peach fruits should be performed. The distinctive textural traits of peach fruits of melting and non-melting flesh are known to be involved in attribute combinations able to influence consumer acceptance. One example is the preference for fruits with completely yellow skin and non-melting flesh (such as canning peaches) within some European markets (Byrne *et al.*, 2012). The existence of two consumer segments, one with a preference for sweeter and melting-texture varieties, and another for crisp and non-melting fruits with high flavor intensity has also been observed (Olmstead *et al.*, 2015). In addition, strong relationships between key textural attributes, such as hardness and juiciness, and different TPA textural parameters were reported for peaches and nectarines (Contador, Díaz, Hernández, Shinya & Infante, 2016).

It is also worth mention that numerous efforts are being made on the development of genetic and genomic tools to regulate major quality traits of melon and peach fruit (Fernández-Trujillo *et al.*, 2011; Byrne, 2012). However, more research is still needed to fully understand the mechanisms that control the physiological and

metabolic changes involved in the development of texture, aroma and flavor occurring during fruit ripening (Eduardo *et al.*, 2013; Vegas, Garcia-Mas & Monforte, 2013; Ríos, Argyris, Vegas, Leida, Kenigswald, Tzuri, Troadec, Bendahmane, Katzir, Picó, Monforte & Garcia-Mas, 2017).

7. Conclusions

The main objective of this thesis was to investigate distinctive quality attributes of melon and peach fruit cultivars through sensory and instrumental analyses. In this context, and according to the individual objectives proposed, the following conclusions were drawn:

1. The evaluation of sensory and instrumental texture shows that melon fruit species has a wide variation for multiple textural traits. The use of both methodologies reflects the ripening behavior of the different fruit cultivars and the improvement of commercial varieties for key textural traits. Despite the significance of each individual trait, the textural quality of melon fruit is defined by the relationship between multiple traits and its impact over texture perception.
2. The analysis of sensory attributes and volatile compounds of the different melon fruits shows specific odor and flavor traits associated with each cultivar group. In agreement with their intermediate ripening expression, the fruits of the exotic cultivars have intermediate quality traits between the climacteric and non-climacteric reference cultivars. The improvement of melon quality and the development of new cultivars with higher acidity need to consider the impact of volatile compounds over the perception of taste attributes.
3. The assessment of sensory attributes and volatile compounds of the four types of peach fruits underlines the distinctive aroma and flavor profiles of peaches, nectarines, flat peaches, and canning peaches. The enhanced sensory quality of flat peaches and canning peaches reflects the focus of the varietal innovation over both typologies. These profiles can be further developed and support a

communication strategy aiming to provide objective information to the consumers about the distinctive quality of each type of peach fruit.

4. The correlation of sensory and instrumental methods allows understanding the effect of different physicochemical parameters over the sensory attributes of melon and peach fruits. The identification of textural parameters or volatile compounds with a positive or negative contribution for the sensory perception, either directly or by their interaction with other quality traits, provides valuable information for a comprehensive assessment of quality. The application of these methodologies can be used for the improvement of melon and peach fruit quality without compromising other valuable quality traits.

5. Moreover, these results can be used by fruit breeding programs in the development of more targeted research approaches or the creation of models to predict the sensory quality of melon and peach fruit cultivars. This can also be of interest to the food and beverage industry aiming to develop appropriate formulations of melon and peach products and flavors.

8. References

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