UNIVERSIDAD MIGUEL HERNÁNDEZ DE ELCHE

ESCUELA POLITÉCNICA SUPERIOR DE ORIHUELA

PROGRAMA DE DOCTORADO EN RECURSOS Y TECNOLOGÍAS AGRARIAS, AGROAMBIENTALES Y ALIMENTARIAS

Study of the Nutritional, Functional and Sensory Properties of Quince (*Cydonia oblonga* Miller) and quince-based products

TESIS DOCTORAL

Przemyslaw Jerzy Szychowski

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Prof. Dr. D. Ángel Antonio Carbonell Barrachina, Catedrático de Universidad y Coordinador del Programa de Doctorado en Recursos y Tecnologías Agrarias, Agroambientales y Alimentarias (ReTos-AAA) de la Universidad Miguel Hernández de Elche (UMH),

CERTIFICA:

Que la Tesis Doctoral titulada "**Study of the nutritional, functional and sensory properties of quince (*Cydonia oblonga* Miller) and quince-based products**" del que es autor el Licenciado **D. Przemyslaw Jerzy Szychowski** ha sido realizada bajo la dirección del **Dr. Ángel A. Carbonell Barrachina** y la codirección de la **Dra. Francisca Hernández García**, profesores de la UMH, actuando como tutor el Dr. Francisco Miguel Burló Carbonell (UMH). Considero que la tesis es conforme en cuanto a forma y contenido a los requerimientos del Programa de Doctorado ReTos-AAA, por tanto, es apta para su exposición y defensa pública.

Y para que conste a los efectos oportunos firmo el presente certificado en Orihuela a diez de febrero de dos mil veinte.

Dr. D. Ángel A. Carbonell Barrachina

Coordinador Programa Doctorado ReTos-AAA

Esta memoria ha sido presentada por **D. Przemysław Jerzy Szychowski,** Máster en Ciencia y Tecnología de los Alimentos, para obtener el grado de doctor.

D. Przemysław Jerzy Szychowski

Esta Tesis Doctoral ha sido dirigida por el **Dr. Ángel Antonio Carbonell Barrachina,** Catedrático de Universidad de la Universidad Miguel Hernández, del Departamento Tecnología Agroalimentaria y codirigida por la **Dra. Francisca Hernandez García,** catedrática de Universidad de la Universidad Miguel Hernández, del Departamento de Producción Vegetal y Microbiología.

Dr. Ángel Antonio Carbonell Barrachina

Dra. Francisca Hernández García

Orihuela, a 10 de febrero de 2020

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To my fiancée who was always believing in me and supporting me all the time.

To my parents; Grzegorz and Irena

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Structure of the Doctoral Thesis

For the elaboration of this Doctoral Thesis, the methodology based on the publication of research articles has been followed. The aim of this doctoral thesis is to obtain the title of Doctor. For this purpose, the current regulations of the University Miguel Hernández of Elche have been followed in the writing of the thesis.

The Doctoral Thesis is structured in the following parts:

1. Introduction.
2. Objectives.
3. Materials and Methods.
4. Publications.
5. Result and discussion.
6. Conclusions.
7. References.

The **Introduction** contains a brief bibliographic review of quinces as a fruit, their morphology, history, physico-chemical and sensory properties, development of new products, production of liqueurs and drying as a preservation method. The second part describes the objectives estimated in this doctoral thesis.

The following part **Materials and Methods -** a brief description of the methodology used to achieve the objectives.

The published scientific publications that make up this doctoral thesis are listed below.

- The first article is entitled "Technological aspects as the main impact on quality of quince liquors", published in the Journal of Food Chemistry. The polyphenolic compounds and antioxidant activity together with influence of variety and manufacturing factors were monitored in quince liquors obtained using one quince cultivar and two clones.
- The second article is entitled "Kinetics, biocompounds, antioxidant activity, and sensory attributes of quinces as affected by drying method", published in Journal of Food Chemistry. Drying kinetics, bioactive compounds, antioxidant activity, and the main sensory parameters were determined in dried quinces, cultivar *Leskovač*, as affected by the drying method.

Results and discussion: gives a brief summary of the results obtained in each of the chapters.

Conclusions: general conclusions of the Doctoral Thesis

Future research: brief descriptions on future research lines that are opened after the current dissertation.

References: indicating the references used in the supplementary sections to the publications.

Abstract - Resumen

Abstract

Quinces are attracting interest due to their health promoting properties. Quinces are high in phytic, malic and quinic acids, as well as in fructose, sorbitol and glucose, giving them an intriguing balance between sourness, astringency and sweetness. Total polyphenol content (TPC) and total antioxidant activity (TAA) are significantly higher in quince peel than in pulp. The predominant fatty acids are linoleic (54.7%) and oleic (35.5%) acids, which is reflected in a ratio of ~9–10 unsaturated to saturated fatty acids. Quince cultivars can be classified for different uses: (i) PUM fruits are better suited for preparation of functional quince-based products because of their high TPC and TAA, while (ii) other clones, such as OHM14, ZM6 and OHM13, are appropriate for fresh consumption because of their equilibrated levels of sourness and sweetness and their high quince flavor. The core of this PhD dissertation was to develop and analyze quince-based processed product, including quince liquors and dried quinces.

Initially, phytochemical profiles of 24 quince liquors have been analyzed as technological variant combinations. Liquors were obtained after macerating quinces from three varieties (Vranja, ALM3 and ZM2), with or without skin, at two ratios of quince:ethanol (50:50 and 25:75), and at two alcohol content (60% and 30%). Polyphenols were identified by LC-PDA-QTOF/MS and quantified by UPLC-PDA and UPLC-FL. A total of 18 polyphenolic compounds were identified and classified as 5 flavan-3-ols, 5 phenolic acids, and 8 flavonols. Flavan-3-ols were the most abundant group followed by hydroxycinnamates and flavonols. The highest contents of total polyphenols (1000 mg/100 mL) and antioxidant activity (37.1 mmol Trolox/100 mL) were found in the liquors prepared using fruits with skin and 50:50 quince:ethanol ratio. Quinces skin was the main source of phenolic acids, and especially flavonols. Quince liquor's high antioxidant activity and polyphenolic content may be considered as a promising new alcoholic beverage.

The final step of this research was to find best drying preservation method. Drying kinetics, bioactive compounds, antioxidant activity, and the main sensory parameters were determined in dried quinces, cultivar *Leskovač*, as affected by the drying method. The highest total polyphenols content was observed in dried samples obtained after freeze drying and convective drying at 50 °C. The best treatment for drying was vacuum-microwave drying at 480 W, considering only sensory attributes, because it led to intermediate dark color and high intensities of basic tastes and key flavor attributes. Ultimately, the parameters analyzed were used to suggest convective drying at 60 ° C as the most appropriate drying method for quinces, because it had a high content of total phenolic compounds (2^{nd} best treatment out of 10), a good sensory profile, was inexpensive, and had no negative effects on nutritional or sensory parameters; the only downside was its long drying time.

Resumen

Los membrillos están atrayendo interés debido a sus propiedades promotoras de la salud. Los membrillos son ricos en ácidos fítico, málico y quínico, así como en fructosa, sorbitol y glucosa, lo que les proporciona un equilibrio interesante entre acidez, astringencia y dulzura. El contenido total de polifenoles (TPC) y la actividad antioxidante total (TAA) son significativamente mayores en la piel de membrillo que en la pulpa. Los ácidos grasos predominantes son el linoleico (54,7%) y el oleico (35,5%), lo que se refleja en una proporción de ~9-10 ácidos grasos insaturados a saturados. Los cultivares de membrillo se pueden clasificar para diferentes usos: (i) los frutos del clon PUM son adecuados para la preparación de productos funcionales a base de membrillo debido a su alto TPC y TAA, mientras que (ii) otros clones, como OHM14, ZM6 y OHM13, son apropiados para consumo fresco debido a sus niveles equilibrados de acidez y dulzura y a su alto sabor a membrillo. El núcleo de esta tesis doctoral fue desarrollar y analizar productos procesados a base de membrillo, incluyendo licores de membrillo y membrillos secos.

Inicialmente, se analizaron los perfiles fitoquímicos de 24 licores de membrillo como combinaciones de variantes tecnológicas. Se obtuvieron licores después de macerar membrillos de tres variedades (Vranja, ALM3 y ZM2), con o sin piel, en dos proporciones de membrillo:etanol (50:50 y 25:75), y con dos contenidos de alcohol (60% y 30%) Los polifenoles fueron identificados por LC-PDA-QTOF/MS y cuantificados por UPLC-PDA y UPLC-FL. Se identificaron un total de 18 compuestos polifenólicos y se clasificaron como 5 flavan-3-ols, 5 ácidos fenólicos y 8 flavonoles. Los flavan-3-ols fueron el grupo más abundante seguido de hidroxicinamatos y flavonoles. Los contenidos más altos de polifenoles totales (1000 mg /100 mL) y actividad antioxidante (37,1 mmol Trolox /100 mL) se encontraron en los licores preparados usando frutos con piel y una relación membrillo:etanol de 50:50. La piel de los membrillos fue la principal fuente de ácidos fenólicos, y especialmente de flavonoles. La alta actividad antioxidante del licor de membrillo y su contenido polifenólico nos hacen considerarla como una nueva bebida alcohólica prometedora.

El paso final de esta investigación fue encontrar el mejor método de conservación mediante secado. Se determinó el efecto del tipo de secado sobre la cinética de secado, los compuestos bioactivos, la actividad antioxidante y los principales parámetros sensoriales en membrillos secos del cultivar Leskovač. El mayor contenido total de polifenoles se observó en muestras secas obtenidas después de liofilización y secado por convección a 50 °C. El mejor tratamiento para el secado fue el secado al vacío con microondas a 480 W, considerando solo los atributos sensoriales, porque condujo a un color oscuro intermedio y altas intensidades de sabores básicos y atributos clave de sabor. Finalmente, los parámetros analizados se usaron para sugerir el secado por convección a 60 °C como el método de secado más apropiado para los membrillos, porque lleva a un producto seco con un alto contenido de compuestos fenólicos totales (el segundo mejor tratamiento de los 10 analizados), un buen perfil sensorial, era económico, y no tuvo efectos negativos en los parámetros nutricionales o sensoriales; el único inconveniente fue su prolongado tiempo de secado.

Chapter 1.- Introduction

1. INTRODUCTION

1.1 Fresh quinces

1.1.1. Morphology

Quince (*Cydonia oblonga* Mill.) is an old fruit species that has been grown for over 4000 years. It belongs to the family *Rosaceae* (rose), subfamily *Maloideae* (*Pomoidae*), (pome fruit). The subfamily *Maloideae* has about 1000 species and 30 genera, including the genus *Cydonia*, which has only the species of *Cydonia oblonga* Mill., with a large number of varieties (Radović *et al.,* 2016 and Rodríguez-Guisado *et al.,* 2009).

Within the oblong species there are 5 subspecies (Roversi, 1987):

- *Cydonia oblonga* sub. *maliformis* Mill.
- *Cydonia oblonga* sub. *pyriformis* Kirchn.
- *Cydonia oblonga* sub. *lusitanica* Mill.
- *Cydonia oblonga* sub. *pyramidalis* Dipp.
- *Cydonia oblonga* sub. *marmorata* Dipp.

Quince cultivars are divided into three groups on the basis of their fruit shape. They have pear-shaped (*Cydonia oblonga* var. *pyriformis*), apple-shaped (*Cydonia oblonga* var. *maliformis*) and bellshaped (*Cydonia oblonga* var. *campanuloformis*) fruits. According to some authors, within this species two further varieties can be distinguished: *Cydonia oblonga* var. *piramidalis* and *Cydonia oblonga* var. *lusitanica* (Radović *et al.,* 2016).

Quince is a northern Iran, Caucasia and Kopet Dagh domestic plant. It is likely that the quince first entered the Mediterranean region in classical times — the Romans was using it. The tree is small (5–7 m in height), sometimes thickly branched and bent as if deformed by wind and the weight of its foliage, but often upright with strong branches. It has oval-shaped leaves with woolly texture underneath, and bloom with solitary pink and white flowers at the ends of short young shoots in May. Its fruit is similar to that of pear and apple, but in each carpel or segment it has many ovules — up to 20 instead of two. (Vaughan *et al.,* 2009). Quince fruit is a pome with numerous seeds. The fruits are relatively large in size (10-12 cm in diameter), with variable dimensions and asymmetric shapes, as well as exhibit a characteristic fragrance. Its skin is covered with an abundant hair that disappears as the fruit matures. The white-yellow pulp, which is easily oxidized to air exposure, is firm, generally acidic and astringent; it is not suitable for consumption when raw (Silva *et al.,* 2004).

Studies of 22 cultivars showed that the Brna cultivar was found to produce fruit with an average weight of 472.1 g. The cv. Bereckého also produced fruits with the average weight of nearly 400 g. On the other hand, the lowest average weight of fruits (89.7 g) was recorded in the case of the apple-shaped form of the cv. Juranská (Rop *et al.,* 2011).

1.1.2. Physico-chemical parameters

The raw fruit is hard and unpalatable, but when cooked the flesh turns brownish pink with a fine flavor. It contains approximately 6% sugar, 15 mg of vitamin C (per 100g) and is a great potassium source. The malic acid percentage is high (0.8%). It is rich in pectin and used as a flavoring used in cooking apples and pears to produce jellies, jams and paste. Quince jelly is turned into a candy — cotignac in France and Spain. Similar products are marmelo (Spain) and marmelada (Portugal)—these could be the origin of the English "marmalade", a term that was used for all fruit pastes, but now mainly for citrus products. The fruit composition of the temperate quince per 100 g of edible portion is: water 84.2 g, energy 3 kcal, protein 0.3 g, fat 0.1 g, total carbohydrate 6.3 g, total fiber 5.8 g, potassium 200 mg and vitamin C 15 mg (Vaughan *et al.,* 2009).

Studies of Leonel *et al.,* (2016) shown that weight of different quince fruits from 68.6 g to 175.1 g. Equatorial diameter vary from 60.5 mm to 73.3 mm and longitudinal diameter from 50.8 mm to 60.9 mm. Fruit firmness results was 52 N minimum and 72.2 N maximum. Analyzed color of skin with Lab parameters:

- *L**= 68.6 to 77.8
- *a**= -15.8 to -3.2
- *b**= 49.6 to 67.3

Analyzed color of pulp with *L***a***b** parameters:

- *L**= 76.1 to 80.1
- *a**= -1.8 to -0.9
- *b**= 28.8 to 35.1

Different studies have shown that the content of **d**ry **m**atter (DM) in pear-shaped quince forms was very high (e.g. in the cv. Blanár as much as 21.84% w/w). However, some apple-shaped forms of quinces also found high DM content: e.g. in the cv. Leskovačka it was as much as 19.59 %. Statistically significant differences in the content of vitamin C have also been found. The measured values ranged from 41.12 mg/100 g **f**resh **w**eight, fw (cv. Hruškovitá) to as much as 79.31 mg/100 g fw (cv. Muškátová). High contents of pectins were found out in the cvs Morava (3.07 g/100 g fw), Ironda (3.06 g/100 g fw), and Jurák (2.94 g/100 g fw), while the lowest one was determined in the cv.

Kocůrova (1.87 g/100 g fw). With regard to the mineral elements, the highest potassium content was found in Otličnica and Hruškovitá cvs. (251.99 mg per 100 g fw and 222.14 mg/100 g fw, respectively) (Rop *et al.,* 2011).

When measuring soluble solid contents, the differences between the individual cultivars were statistically significant and ranged from 12.0% (cv. Muškatová) to 17.7% (cv. Pinter). The Brna cultivar showed a low total acids content (only 0.36 g/100 g fw). On the other hand, in the cv. Pinter, the total content of acids was 1.53 g/100 g fw (Rop *et al.,* 2011).

Study of 11 quince fruit cultivars for industrial use in juices showed average values of the following parameters: juice yield 64.1%, dry matter 11.8%, **t**otal **s**oluble **s**olids (TSS) 12.2 ºBrix, pH level 3.2, **t**otal **t**itratable **a**cidity (TTA) 1.02 g of malic acid per 100 mL, TSS/TTA ratio of 12.0. For analysis, juice yield is typically not taken into account, but it is an important parameter for the juice industry, as many processing decisions will be taken on this value (Wojdyło *et al.,* 2014).

Chemical composition of volatile fractions from the fruit and leaf of quince (*Cydonia oblonga* Mill.) has shown that the dominant components were ethyl 2-methylbutanoate, (*E*,*E*)-α-farnesene, ethyl-(2*E*,4*Z*)-decadienoate, pentadecanol, β-acoradienol, ethyl decanoate, ethyl octanoate, (*E*)-nerolidol, ethyl dodecanoate, 14-hydroxy-9-epi-(*E*)-caryophyllene, (2*Z*,6*E*)-farnesol, β-cedrene. Volatile fraction of the fruit was also characterized by ethyl-(4*Z*)-decenoate, ethyl 9-dodecenoate, ethyl hexanoate, ethyl nonanoate and β-cyclocitral, where in the leaf *n*-octanal, *n*-hexanol, *n*-nonanal and benzaldehyde were present. Quince fruit are rich in fatty acid esters. Among the volatiles, ethyl 2-methylbutanoate and ethyl-(2*E*,4*Z*)-decadienoate were the most abundant which can be responsible for flavor (Veličković *et al.,* 2016).

1.1.3. Quince history

The first mention of quince fruits is found in Greek mythology in a story about "Golden Apple of Discord". Eris, the Goddess of discord, tossed the apple with dedication "for the most beautiful" between three ancient Greek Goddesses—Athena, Hera and Aphrodite. Paris was the one who resolved the dispute, by giving the "Golden Apple" to the Goddess of Love, Aphrodite. In exchange, she promised Paris the most beautiful woman on Earth—Eleni, who was married to the King of Sparta. The assurances of Aphrodite set off a chain of events, which ultimately led to the ten year long Trojan War. Although, the "Apple of Discord" did not refer to apple fruit at all, but a quince.

Quince fruits became famous in ancient history mainly thanks to the story of Eleni. Solon, famous Athenian legislator, strengthen this association by introducing quince fruits

at wedding ceremonies. Nowadays, people of the former Thrace region use quince as a way of honoring old habits. The newlyweds consume a pair of quince before sleep in order to start their marriage with a fresh and sweet breath the following morning.

In Greek, quince is kythoni or in some regions kydoni. Hippocrates (circa 460-370 before Christ) prescribed quince juice as a refreshing remedy for a variety of ailments. Roman physician, Claudius Galen, used in his practice the purée of the Portuguese variety of "marmelerio" quinces - from the name which now derives the term marmalade (Vad, 1996).

The ancient Greeks were able to grow and graft quince of remarkable quality. Nevertheless, with the advancements of agricultural science and fruit hybridization, it is now possible to create juicier flesh and softer texture of the fruit. Thanks to their efforts new varieties of quince have been created, many of which transcend the original, wild growing quince trees.

Quince most probably comes from the ancient city of Smyrna, Turkey. It was a very valuable fruit in antiquity. The quince was a very common theme used in art especially in drawings, wall paintings and mosaics at the lost city of Pompeii, Italy.

The quince motif also appears in Christianity. The Book of Genesis claim that Adam and Eve tasted the forbidden fruit in the Garden of Eden. Despite all those ancient manuscripts referring to the forbidden fruit as an apple, it is more likely that the fruit was actually a quince. This is supported by the fact that quince trees historically precede apple trees.

According to Sanchez-Monge (1974) quinces originate from the area somewhere between the Caspian Sea and Azerbaijan.

1.1.4. Consumption and cultivation of quinces fruits

Cultivation of quince is fairly simple, due to its easy-to-grow, drought-tolerant shrub. Cultivated with plenty of light the trees can produce better flowers, but in shady spots quince also does well. It can grow in heavy clay as long as the pH levels are not too high and it can adapt to different types of soil. It can grow for years without pruning, protection from insects and disease problems, which makes it an extremely resilient plant.

Quince is hardy and requires a cold period below 44.6°F (approximately 7°C) to flower properly. It is cultivated all over the world in warm-temperature to temperate climates. The person who decides to grow quince should do it in a sunny places and water regularly, though the mature shrub is drought tolerant. For creating deciduous bonsai specimens, quince is one of the most popular species.

Quince can be propagated in various ways. While seeds offer the most natural way of cultivation, layering and cutting is used more commonly, due to decreased time required for the plant to reach maturity. Some +types+ of quince are cultivated solely by cutting or grafting layers onto the rootstock of its plant. Pruning is a common way to form quince into standard fruit-bearing tree. It should grow as a single stem until it reaches height of five to six feet (approx. 150-180cm).

Certain types of pears benefit from their genetic similarities with quince, which can be helpful in the process of dwarfing. For those purposes, young plants are shortened to approximately 18-20 inches in height (~45-50cm), which can help quince increase its yield and withstand low temperatures. Higher yields can also be achieved by cross-fertilization, although the plant itself is self-fertile. Fruits can remain on the tree until they fully ripen. With moderately high temperatures throughout the year quince are often consumed raw. In cooler climates the harvest happens shortly before the first wave of frost.

Majority of quince are only edible after they had been softened by frost, followed by natural decay. They are commonly used in producing various types of marmalade, jam, jelly, as well as pudding. Word "marmalade" derives from late 15th century Portuguese "*marmelada*" (quince jam). The fruits are prepared by peeling and roasting, baking or stewing. When cooked long enough, the flesh changes color to red. They can be used to improve the flavor of jam and apple pies when used in adequate amount. They can also be chosen as an ingredient in vinification. Wine produced with quince fruit falls into a group of "dessert wines", typically served after a meal, with dessert. The taste is sweet, balanced with high acidity.

Early defoliation may occur due to vulnerability to fungal diseases, especially in hot weather (during wet summers) (Cumo, 2013).

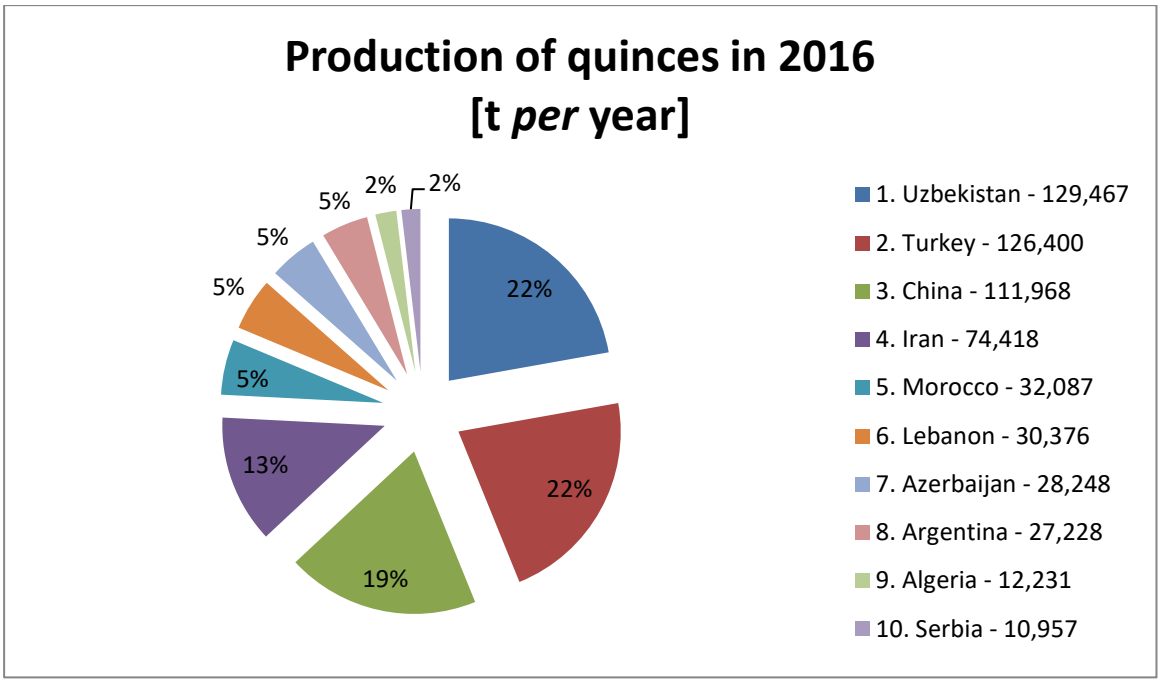


Figure 1. Top 10 countries with the biggest production of quinces in 2016 (factfish GmbH Munich, Germany).

According to the same source total worldwide quince production in 2016 was as much as 677,949 t.

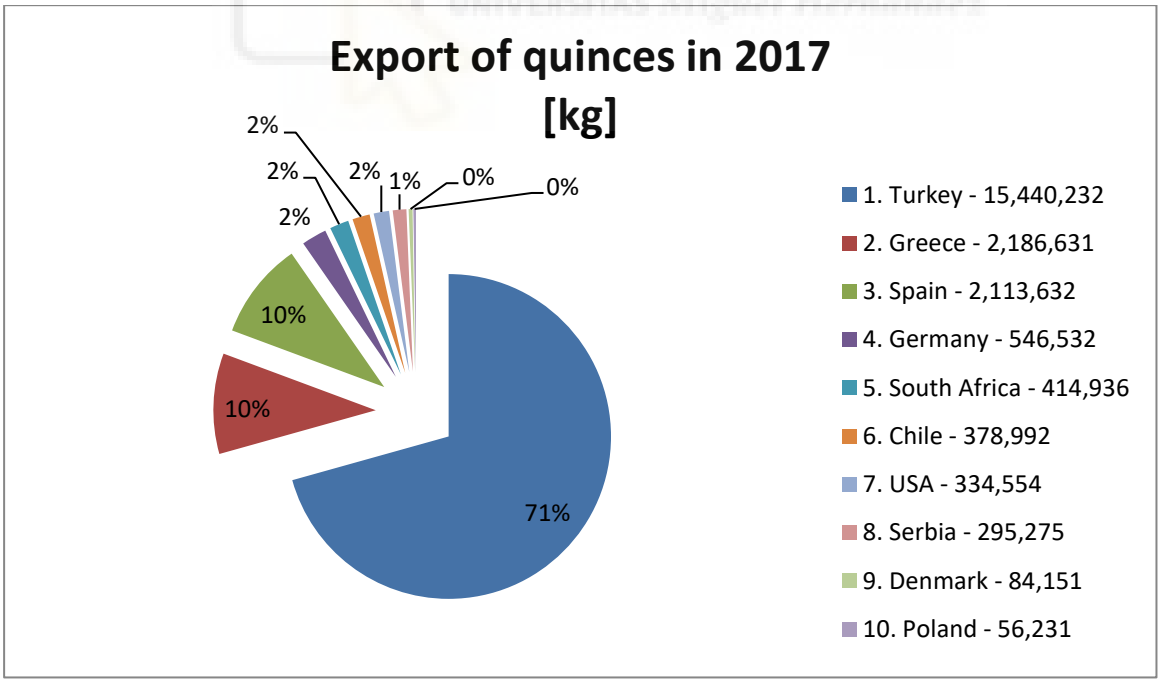


Figure 2. Top 10 countries with the biggest export of quinces in 2017 (UN Comtrade Database).

1.1.5. Sensory parameters of raw fruit

Food quality can be seen through sensory quality, which plays a very important role in the evaluation and quality control of food products. Sensory evaluation of food quality is carried out using sensory perception (taste, smell, touch, sight, hearing). In the case of food products, the sense of taste is the most important and is assigned the highest importance factor in scoring. There are five types of taste: sweet, salty, sour, bitter, salty and umami. In recent years, the fatty taste has been separated, which is not yet included in Polish legal regulations.

An organoleptic assessment may be carried out by any consumer. It involves examining the organoleptic characteristics of the so-called sensations arising in human consciousness as a result of the perception, by the organs of the senses, of external stimuli. The assessment may produce different results depending on the sensitivity of the assessor's senses, his or her state of health, environmental conditions and many other factors. These are subjective assessments.

Sensory analysis evaluates and measures the quality characteristics of food products using previously tested senses (taste, hearing, touch, sight, smell), which are a kind of measuring instrument. It is carried out by a specialized team of trained people with proven sensory sensitivity under well-defined external conditions to ensure that the quality characteristics are perceived correctly. Therefore, in contrast to organoleptic evaluation, sensory analysis is a more objective method (Szpakowska *et al.,* 2012).

Descriptive sensory analysis aims to define a product profile based on all perceived sensory characteristics. That’s why it differs from other sensory testing methods.

Descriptive sensory testing is one of the most sophisticated tools at the disposal of sensory researchers. Detection (discrimination) and description of both qualitative and quantitative sensory elements of a product are tested by trained teams of judges. The quality characteristics of the product include: aroma, appearance, taste, texture, aftertaste and sound properties of the product etc. that distinguish it from others. The sensory judges then quantify these aspects of the product in order to make it easier to describe the perceived characteristics of the product (Murray *et al.,* 2001).

As an example of quince sensory analysis Legua *et al.,* (2013) analyzed 5 fruits from different clone. Nine quince clones (AM4, CTM7, CTM8, CTM10, MOM1, OHM4, OM6, ZM4 and ZM6) were used for their research. Ten expert tasters evaluated both pulp astringency and chewiness expressing astringency as high or low and chewiness as hard, semi-soft or soft. All evaluated clones, according to the sensory panel, were considered as semi-soft with the exception of the clones AM4 and MOM1, which were classified as hard by all the

panelists. Most of the clones had high pulp astringency, except AM4, OM6 and ZM4, which scored low pulp astringency and could be considered good for fresh consumption.

Another three quince clones (MB 1, MB 2, MB 5) were analyzed by Rodríguez-Guisado *et al.,* (2009). The results have shown that these clones have low levels of pulp astringency. Only MB 5 was soft in regards to the chewiness, while other two clones were semi-soft.

1.2 New quince products development

Processing usefulness of common quince fruit for the production of purées and homogeneous juices was analyzed by Wojdyło (2011). The obtained quince preparations were compared to preparations made from apples. The processing usefulness was determined on the basis of:

- changes in the color of the flesh caused by the oxidation of polyphenolic compounds
- assessment of the usefulness of macerating enzymes for pulp processing in the production of juices
- the possibility of the production of turbid juices
- the possibility of using quince fruit for the production of mixed juices and purées with the addition of other species of fruit

The biological activity of quince fruits and the products obtained from them was determined by testing polyphenolic compounds and vitamin C.

The quince fruit in comparison to apples was characterized by greater susceptibility to the enzymatic browning reaction. Therefore, quince fruit required intensive protection against enzymatic oxidation processes during processing. The addition of an inhibitor of oxidative transformation in the form of rhubarb juice during the production of quince fruit products caused slowing down of the enzymatic browning reactions to a much greater extent than after using ascorbic acid. The use of enzyme preparations for maceration of pulp in the production of quince fruit juices significantly increased the process efficiency, the extensiveness of polyphenolic compounds to the juice, including procyanidins polymers and increase of antioxidant activity in relation to the control sample. Quince fruit can be used to produce juices, including turbid juices. There were no significant differences in the efficiency of the pressing process when receiving turbid juices between quince fruit and apples. Quince fruit extends the raw material base for processing and is characterized by a high content of polyphenolic compounds and high antioxidant activity. It is a recommended component in processed products, the consumption of which is of great importance in the prevention of cancer.

Increased demand for food enriched with physiologically active components led to developing a new quince snack product with improved taste due to the infusion of the alternative sweetener (stevia), while retaining its functional properties. During this experiment, researchers evaluated selected attributes of the snack enriched with prebiotic (inulin) and alternative sweetener (stevia). Ascorbic acid was chosen as anti-browning agent with use of vacuum impregnation. The tissue of the quinces is highly suitable for vacuum infusion. For development of functional food and obtaining high quality products, it was concluded that the combination of vacuum impregnation and ultrasound is the most reliable method. This combination resulted in the highest weight gain and maintained the highest springiness. The quinces dried with pre-treatment have significantly lower color changes and browning index (Jovanovic-Malinovska *et al.,* 2012).

In another studies, quince jam and jelly were prepared and assessed for their nutritive quality and acceptability. The pulp from the fruit was extracted by hot break method and was used for preparation of jam and jellies. Chemical (TSS, Titratable acidity, Ascorbic acid, total sugars, reduced sugars, pectin, ash) and organoleptic (color, flavor, body, taste, overall acceptability) parameters of quince jam and jelly were studied. It was concluded that quince is highly nutritious fruit crop that is underutilized. Quince fruit can have many health benefits for our bodies. After analyzing quince ham and jelly it was concluded that those products are a great source of malic acid and ascorbic acid, besides other phytochemicals. Organoleptic parameters of prepared products showed that they can be widely commercialized and popularized for human consumption. Sensory evaluation of jam and jelly showed great acceptability. Considering both of its nutritious and organoleptic qualities, quince jelly turned out to be the best on this basis (Sharma *et al.,* 2011).

1.3 Fruit liquors

The production of fruit liquors, as well as spirits (distillates) from fermented fruits has been widely practiced around the world for several centuries (Santos *et al.,* 2014). The most popular spirit-based beverages are fruit spirits and liquors, usually made from plums, melons, pear, cherries, citrus and apples. "Fruit spirit is an alcohol-based beverage produced exclusively via ethanol fermentation and distillation of fleshy fruit or must of such fruit, with or without stones" according to European Community Regulation EC 110/2008. The minimum ethanol content is 37.5% volume in fruit spirits. Another group of alcoholic drinks are liqueurs. Those beverages are made mainly from fruits, amongst other components. The word "liquor" originates from Latin *liquefacere*, which means "to melt" or "to dissolve". Legal regulations show that liqueurs are colorless, sweetened spirit-based beverages produced by flavoring ethanol or the distillate of agricultural origin. 15% volume is the minimum content of ethanol in liqueurs. Fruit juices, herbs (flowers, seeds and

roots), fruits (stones, peel and whole fruits), wines and dairy products can be used in liqueurs production (Śliwińska *et al.,* 2014). Fruits treated with alcohol trigger the release and extraction of active components from the raw material. Biologically active compounds, such as polyphenols, are reduced by manufacturing process and storage. Transformations in anthocyanins and flavanols cause changes in color to brown. According to the research of Sokół-Łętowska *et al.,* 2014, the best solution to improve the preservation of phenolic compounds, anthocyanins, phenolic acids and flavonols in the liqueurs is to store them in a temperature of 15°C in a presence of sucrose.

1.3.1 Popular fruit liquors history

Low alcohol beverages have probably been known since the dawn of time. Archaeological research indicates that several centuries before Christ, the raw materials like honey, grape juice and grain were used in fermentation process of the beverages. The secrets of making meads, wine and beer were known by Egyptians, Babylonians, Phoenicians, Greeks and Romans as early as the 9th century BC. The first written information about the production of alcoholic beverages comes from Hippocrates (460-377 BC) and Aristotle (334-322 BC). The breakthrough in the production of alcohol was due to the Arabic alchemists who developed simple techniques for evaporating and strengthening alcohol solutions (distillation). As a result, distillation methods evolved and spread all over the world. Description of stripping process (simple distillation) did not appear until the III-XI AD period, in the manuscripts of Greek, Egyptian, Syrian and Arab alchemists.

Evaporation from the wine of flammable fumes (spirits of wine) with intoxicating power was then considered to be the action of supernatural forces. During Middle Ages and the Renaissance people used archaic Latin names for a concentrated aqueous solution of ethanol *aqua ardens* ("scalding water") or *aqua vitae* ("water of life"). Those generic names referred to majority of distillates, but eventually became exclusive to distillates of liquors.

At the end of thirteenth century professor Arnold de Villeneuve in Montpellier described the process of distillation apparatus. Thanks to his efforts, liquid-based medical elixirs became widely popular among alchemists, medics and monks during middle-ages.

The secret of "burning" wine was strictly protected for hundreds of years, just like the ability of distilled spirits to extract medical and aromatic components from herbs, flowers, fruits and roots. Monasteries became the biggest producers of medicinal elixirs, however monks and their rigorous rules meant that the recipes and ingredients were kept a secret for centuries to come.

Many modern varieties of liquors were invented by pharmacists. They used them in many medical treatments, primarily as a cure for various diseases.

In the past, alcohol was distilled with addition of herbs, fruits, flowers, spices, nuts and almonds due to their properties of decreasing the unpleasant aroma of the spirit. That way, through many experiments, a product that can be described as the "ancestor" of liquors was created (Latin *liquefacere* – melt, dissolve).

One of the most famous liquors is called amaretto. Although it is an almond liqueur, it owes its aroma not only to almonds, but also to apricot stones. Its strong and sweet taste is reminiscent of marzipan. It is noticeable in even the most sophisticated and complex cocktails. According to the legend, amaretto recipe was first created in the 16th century. The Italian painter Bernardino Luini received it from the owner of a local inn, which was his model of the Mother of God in "La Madonna e l'Adorazione". This painting remains in the town of Saronno (north of Milan, near the border with Switzerland) where the most famous almond liquors are produced (Kolanowski, 2006).

1.3.2. Liquors analyses

Determination of antioxidant activity and phenolic compounds evaluation in liquors and spirits was analyzed by Santos *et al.,* (2014). $ABTS^{\bullet+}$ and DPPH methods were used for antioxidant activity and Folin-Ciocalteau method for phenolic compound evaluation, and they showed high correlation with total phenolic content. Antioxidant activity and total phenolic content developed only from the fruits. If the liquors or spirits age in wooden barrel, this is also the source of phenolic compounds. The results of this work showed that DPPH method is not so good for analyzing antioxidant activity in products like spirits because of their low total antioxidant capacity. $ABTS^{\bullet+}$ method was suitable to determine this parameter in liquors.

Pomegranate fruit extracts and liquors were analyzed by Galego *et al.,* (2013). They observed that decrease in the total polyphenol content for macerates and liquors should reflect the dilution induced by the preparation process, which is about two times for macerates and four times for the final product in their studies. The degradation/precipitation of the polyphenols can also lead to a decrease in their contents.

Cosmulescu *et al.,* (2014) analyze different alcoholic extracts prepared from green fruits of 'Sibisel 44' walnut cultivar for their, among others, total phenolics and antioxidant activity. The antioxidant activity of these extracts was investigated by the 2,2'-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging method while total phenolic content was determined by using the Folin-Ciocalteu assay. Highest total phenolic was found in samples with 70% ethanol used for extraction. The variation was similar in terms of antioxidant capacity, the highest level of this parameter was found in extracts made from 70% ethanol.

1.4 Drying of fruits

Drying is one of the most popular methods for preserving food. The main goal of drying agricultural products is to reduce moisture to a level that allows for long-term safe storage. On the other hand, consumer resistance to the use of chemical additives in food preservation has increased the size of the market for additive-free dehydrated alternatives, due to the rapid growth of the fast food industry. Drying can be defined as a simultaneous operation of heat and mass transfer in which a material's water activity is reduced by evaporating water into an unsaturated gas stream (Askari *et al.,* 2009).

So far, no "panacea" has been discovered that protects the human body from cardiovascular diseases, cancer or aging. Scientific research shows that many degenerative processes are caused by free radicals. Although some changes cannot be stopped, a proper diet can have a positive effect on human health. Increased consumption of fruits and vegetables significantly reduces the risk of cancer and cardiovascular diseases. This beneficial effect on our body is attributed to the antioxidant compounds contained in them. Unfortunately, many products, especially vegetables, should be thermally processed before consumption. Also, the technological processes that vegetable raw materials are subject to can significantly affect the content of antioxidants in the product and change their antioxidant potential (Kidoń *et al.,* 2007)

Drying is very important method of preservation especially for handling and distribution of agricultural products such as fruits and vegetables. High moisture content is main cause of microbial spoilage and deteriorative chemical reactions so reducing it leads to extend the shelf life. However, it can be noticed that quality is decreasing during drying process and degradation of nutrients can be observed (Bruijn *et al.,* 2015).

1.4.1 Drying as a preservation method

Drying is the oldest method of preserving food, which is also an important process in the food industry today. Many industries use this process in specific, most often final stages of food production. During the drying process, the weight and volume of the dried materials is reduced, which reduces packaging costs, facilitates transport and storage (Nowacka *et al.,* 2010).

As the shelf life of dried food increases, the amount of nutrients decreases. Studies of dried plums, parsley and peppers show that vitamin C losses occur during storage. Due to the loss of vitamin C and changes of polyphenolic compounds during storage, the antioxidant capacity of food may also decrease significantly (Nowacka *et al.,* 2010).

Drying, as a method of product preservation, limits the growth of microorganisms and the course of biochemical reactions, and can affect sensory characteristics and chemical composition (Król *et al.,* 2015).

1.4.2 Mathematical models of food drying

Equation for calculating moisture ratio:

$$MR = \frac{(M_t - M_e)}{(M_i - M_e)}$$

where, *MR* is the moisture ratio, M_t, M_e and M_i are moisture content at particular time during drying, final moisture content and initial moisture content in g water/g dry matter, respectively (Horuz *et al.,* 2017).

Since the M_e value is very low compared to the M_i and M_t values, the M_e value can be ignored and the ratio of moisture can be expressed as:

$$MR = \frac{M_t}{M_i}$$

There are different mathematical models for food drying, for instance:

a) Newton model $MR = \exp(-kt)$
b) Page model $MR = \exp(-kt^n)$
c) Modified Page model $MR = \exp(-(kt)^n$
d) Henderson and Pabis model $MR = \mathrm{aexp}(-\mathrm{kt})$
e) Logarithmic model $MR = \mathrm{aexp}(-\mathrm{kt}) + \mathrm{c}$
f) Wang and Singh model $MR = 1 + \mathrm{at} + \mathrm{b}t^2$

To choose appropriate method for analysis it is crucial to compare moisture ratio to drying equations. The cases where coefficient of determination R^2 of the mathematical models is the highest, indicate a good fit (Goyal *et al.,* 2007).

1.4.3 Energy aspects in food drying

Total global energy consumption has increased from 4661 Mtoe (**m**illion **t**ons of **o**il **e**quivalent) in 1973 to 9555 Mtoe in 2016. This means that the increase was 104%. Although the industry's share of total energy consumption has decreased during this period, it is still over 28%. The food industry is a significant part of the global and Polish economy. In Poland, the energy consumption of the food industry is estimated at about 10% of direct energy consumption. Such a high energy intensity is also related to the very high emission of carbon dioxide, one of the most important greenhouse gases, which in 2016 amounted to 32316 Mt of CO_2 (International Energy Agency 2018). For many years, numerous measures have been taken to reduce energy consumption and greenhouse gas emissions, implementing the concept of sustainable development. The actions taken can be divided into indirect actions, such as those related to the creation of new legal regulations and direct actions related to the creation and use of new technologies supporting individual processes and operations. One of the most frequently used unit operations in the food industry is drying, which is also a very energy-intensive operation. Among the methods aimed at accelerating this process and reducing its energy consumption one can mention the use of ultrasound, pulsed electric field or high pressures (Wiktor *et al.,* 2012).

Another approach is the use of unconventional or combined (hybrid) drying techniques, e.g. microwave convection drying or radiant convection drying. Such activities, by shaping the kinetics of the process and physical and chemical properties of the product, most often have a positive impact on the economic calculation of drying. Hybrid two-stage drying is an interesting solution with a high potential for reducing drying time. This technology consists in removing water from the material to a certain moisture content using one method (e.g. convection) and then drying using another technique (e.g. microwave drying). This type of operation may not only lead to the elimination of defects of some drying methods, but also enables the creation of food of a certain quality, the so-called designed food (Witrowa-Rajchert, 2011).

1.4.4 Changes in the main quality attributes during food dehydration

In general, the cycle of dehydration affects all quality parameters of fruits and vegetables. To yield high-quality products, drying operations must be optimized. In terms of quality, color is a key parameter that governs the acceptance of any food by the

consumer in the first contact with the product, and mechanical properties are of great interest in characterizing the response of the consumer to the first bite. Drying generally results in changes in the color of foods. Normally, more intense treatments result in more noticeable changes in color. Process conditions also affect dried products ' external and internal appearance.

The quality of food refers to three main parameters: nutritional value, acceptability and safety Nearly any form of raw food processing will adversely affect some of its nutritional value. Acceptability requires other qualities such as visual appeal, taste, and texture. A product's overall quality is determined by a variety of criteria, including freshness, predicted appearance, flavor, and texture. Changes in quality that may occur in drying products include changes in: optical, sensory, structural, textural, rehydration, and nutritional properties (Askari *et al.,* 2009).

The browning reaction which takes place during the drying process is one of the causes of color changes. This reaction is influenced by the temperature as well as its distribution. In addition, during drying, the temperature distribution determines the transfer of moisture from the food materials. Distribution of temperature was shown to affect both the appearance and structure of dried food materials. Predicting the distribution of temperature during drying can therefore provide a controlled optical appearance (Joardder *et al.,* 2013).

Temperature increases in foods can cause several biochemical reactions: Maillard reactions, vitamin degradation, fat oxidation, denaturation of thermally unstable proteins, enzyme reactions (which can be either activated or inhibited), and so on. Maillard reactions taking place during the drying process can lead to significant changes such as changes in antioxidant activity and the presence of Amadori compounds. Vitamin C (ascorbic acid) is an essential nutrient and is often taken as an indicator of the process's nutrient value. Ascorbic acid, preceded by hydrolysis and further oxidation, can be oxidized to dehydroascorbic acid under aerobic conditions. Water activity and temperature affect this degradation (Bonazzi *et al.,* 2014).

The drying procedure has a significant impact on three of the essential tastes, sweetness, softness, and bitterness intensities. Also other sensory parameters like: burnt notes, fruit ID (flavor of freshly harvest fruits), hardness, crunchiness, juiciness, fruit and vegetable notes are affected by drying process. Different fruits need different sensory parameters to be analyzed.

In the research of Wojdyło *et al.,* (2016) it was found that the jujube fruit content of polyphenols and antioxidant capacity showed similar behaviors as affected by the drying

methods. Because of that it can be assumed that the amount of polyphenols is largely responsible for dried jujube fruits antioxidant activity. Freeze dried samples showed the highest antioxidant activity. Other types of drying like convective drying, vacuum microwave drying and combination of this two methods showed lower values. That means that antioxidant activity is decreasing during drying processes.

Convective drying of fruit and vegetables is often used in industry, due to the simplicity of construction and easy operation of equipment. However, long drying times and high temperatures lead to many unfavorable changes in the raw material, including texture, color, shrinkage, loss of nutritional value, including a decrease in polyphenol content and loss of antioxidant properties (Rząca *et al.,* 2007).

According to Calín-Sánchez *et al.,* (2013) the drying time can be reduced considerably (about 75%), and the quality of the finished food product can be improved by applying microwave energy to the material instead of drying by hot air. Therefore, the thermal degradation of essential nutrients is significantly reduced and the retention of factors of food quality, such as color, is achieved.

1.5 Quality parameters, biocompounds, antioxidant activity and sensory attributes of Spanish qunices

This study focused on analyses of raw quinces to determine the main quality parameters of this minor crop in both pulp and peel. The main quality parameters of Spanish quince fruits as affected by clone were analyzed (Szychowski et al., 2014).

There were no statistically significant differences among the clones regarding pH, which variation was very small (3.96 – 4.09). The crude fiber content in all clones was more or less the same, with values ranging from 1.25 in OHM2 to 1.90 g 100-1 dw in OHM14. Significant differences were found regarding total soluble solids (TSS) which value range from 15.10 to 17.20 °Brix. The highest values were observed in ZM6, PUM and OHM13. Titratable acidity (TA) showed the highest value 5.46 in clone OHM13 and the lowest in OHM14 4.03 g/L. The clones PUM, OHM14 and ZM9 have statistically similar moisture contents which ranged from 72.9% OHM13 to 81.4% in OHM2 (Szychowski et al., 2014).

In general, it can be said that the high content of TSS, the low value of TA and high values of MI in some quince clones clearly indicated that they are suitable for fresh consumption. The differences in main quality parameters might be caused by genetic factors (Szychowski et al., 2014).

Quinces are a good source of phenolic compounds, which are linked to their high intensity of bitterness and astringency. The total phenolic content (TPC) concentrations in the peel of quince fruits ranged from 327 mg GAE per 100 g in ZM9 to 581 mg GAE 100 g−1 in PUM, and it had a mean value of 404 mg GAE 100 g−1; while this parameter took values in the pulp of quince fruits ranging from 44.8 mg GAE 100 g−1 in OHM14 to 101 mg GAE 100 g−1 in PUM, and it had a mean value of 50.8 mg GAE 100 g−1. In all analyzed clones, quince peel had higher concentration of TPC than pulp. TPCpeel/TPCpulp vary from 6.3 to 10.5 (Szychowski et al., 2014).

Total antioxidant activity (TAA) was measured in both the peel and the pulp of the quince fruits. The TAA was measured, for the first time, separately in hydrophilic (H-TAA) and lipophilic (L-TAA) fractions, and results showed highly significant differences among quince clones and between pulp and peel. It is important to highlight that the TAA in peel was higher than TAA in pulp in all quince clones studied. The values of H-TAA in the pulp samples ranged from 11.7 mg100 g−1 in OHM14 to 84.2 mg 100 g−1 in PUM and in the peel samples from 129 mg 100 g−1 in ZM6 to 269 mg 100 g−1 in PUM. The values of L-TAA in the pulp samples ranged from 6.87 mg 100 g−1 in OHM14 to 14.9 mg 100 g−1 in PUM, and in the peel samples from 120 mg 100 g−1 in OHM14 to 288 mg100 g−1 in OHM2. The ratio TAApeel/TAApulp ranged from 6.5 to 15.4. If quince-based products (juices, liquors, etc.) should require high antioxidant activity, they should include the peel in their formulations or a prolonged maceration process is required (Szychowski et al., 2014).

The profile of organic acids consisted of 5 compounds: phytic, malic, quinic, citric, and tartaric acids. The predominant acids in ripe quinces were phytic and malic acids, with much lower concentrations of quinic, citric and tartaric acids; this is: phytic acid >> malic acid > quinic acid > citric acid > tartaric acid. Phytic acid content ranged from 227 mg 100 g−1 fw (fresh weight) in PUM to 545.53 mg 100 g−1 fw in ZM9; while malic and quinic acid contents ranged from 65.0 (PUM) to 99.8 (OHM13) mg 100 g−1 fw and from 7.97 (ZM6) to 15.2 (PUM) mg 100 g−1 fw, respectively. On the other hand, fructose and glucose were the main sugars of ripe quince fruits. Fructose contents (range: 416–584 mg 100 g−1 fw) were higher than those of glucose (range:82.5–112 mg 100 g−1 fw) (Szychowski et al., 2014).

The fatty acids, FA, profile clearly showed the predominance of linoleic and oleic acids, which represented ~90% of the total FAs. The most abundant FA was linoleic acid and ranged from 53.6% in PUM seeds to 56.2% in OHM14. The FAs abundance followed the order: C18:2 > C18:1 >> C16:0 > C18:0 > C20:0 > C16:1. It is very important to highlight the high content of polyunsaturated fatty acids (PUFA) and monounsaturated fatty acids (MUFA) compared to saturated fatty acids (SFA); with ranges being

approximately 53–56%, 34–37%, and 9–10%, respectively. These contents led to values of the ratio UFA/SFA of 9–10. The content of oil in the seeds was affected by the quince clone, with OHM2 and ZM6 having the highest contents, above 22% (Szychowski et al., 2014).

Comparing all the results among with sensory analyses led to create hierarchical CA, using the linkage method among groups. Presence of five clusters was indicated (Szychowski et al., 2014):

- *Cluster 1*: Included the clone PUM, and it was mainly character-ized by high total antioxidant activities (e.g. H-TAApeel, H-TAApulp, TAApulp, TAApeel) values.
- *Cluster 2*: Included the clones OHM2 and ZM9, and it was characterized by high contents of moisture, stearic acid and phytic acid. Fruits from these two clones were scored high in bitterness and astringency, but at the same timehad high scores also for fruity flavor
- *Cluster 3*: Included the clone ZM6, and it was characterized byhigh contents of malic acid, linoleic acid, polyunsaturated fatty acids (PUFA), and oil. Fruits from thisclone had intense quince flavor and simultaneously high intensities of both sourness and sweetness.
- *Cluster 4*: Included the clone OHM14, and it was characterized by high contents of crude fibre, linoleic acid, PUFA, phytic acid, total organic acids and linoleic acid.
- *Cluster 5*: Included the clone OHM13, and it was characterized by high contents of total soluble solids, maturity index, glucose, fructose, total sugars, malic acid and palmitic acid. Fruits from this clone obtained high scores of quince flavor, sourness and sweetness.

Chapter 2.- Objectives

2.1 General aim

The main 3 aims of this PhD thesis are:

- Determine the quality parameters, bio-compounds, antioxidant activity and sensory parameters of raw Spanish quinces.
- Make liquor from quinces that consumers will like and will preserve or increase healthy properties.
- Find the best drying method of preservation the quinces.

In order to meet this aims, several specific objectives have been considered and will be described in the section 2.2.

2.2 Specific objectives

- Elimination of seasonality by averaging the values obtained for raw quinces from harvests in 2 consecutive years.
- Providing following analyses of raw fruit: total soluble solids, titratable acidity, maturity index, moisture content, crude fiber, total polyphenols content in peel and pulp, antioxidant activity in hydrophilic and lipophilic phase of peel and pulp, total antioxidant activity in peel and pulp, organic acids and sugars.
- Analyzing the results to check which quinces are good for preparation of functional products and which for the fresh consumption.
- For liquor manufacturing using 3 types of quinces, fruits with and without skin, different ration fruit:alcohol (50:50 and 25:75) to check which combination is the best to obtain high content of polyphenol compounds and antioxidant activity.
- For quinces preservation with drying using different methods of drying to check which one is the best to obtain products similar to fresh one according to its sensory profile, phenolic content and antioxidant activity. Freeze drying will be used as a control method. The following methods were checked for this purpose: convective drying in 50, 60 and 70°C, Vacuum-microwave drying with 120 and 480 W, combined drying, consisting of an initial stage of convective pre drying at 50, 60 or 70°C followed by a final stage of vacuum-microwave finish drying at 480-120 W.

Chapter 3.-

Materials and Methods

3.1. Plant material

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

For second article about fruit liquors one quince cultivar (*Vranja*) and two clones (ALM3 and ZM2) were used; all of them were appropriate for food manufacturing and widely grown in Spain. The selected plant materials belong to the same quince gene bank as above. Fruits were harvested at commercial ripening stage (total soluble solids > 15 °Brix and maturity index > 30) at the end of September and first October 2012, and 20 homogeneous fruits (based on color, size and absence of defects) were selected from each variety (5 fruits from each tree) and used for manufacturing of liquors; about 6 kg of fresh quinces per each variety was used in this study.

For third article about quince drying fresh quince fruits (*Cydonia oblonga* Miller, cultivar *Leskovač*) were harvested from the Medical Garden of Wrocław Medical Academy (Wrocław, Poland). 2 kg of quinces were randomly harvested at commercial ripening as determined by fruit color, and change of peel from hairy to waxy appearance (avoiding injured and sunburned fruits) and were processed in October 2013.

3.2. Main quality parameters

For the following analyses, samples of 30 quinces per clone were randomly selected from the 40 picked from the field (rejecting any slightly damaged fruits), and then divided into 3 subsamples of 10 fruits. They were hand-peeled and peel and pulp were cut in small pieces to obtain homogeneous samples. Samples were immediately frozen in liquid N2, ground and stored in freezer at −40°C until analysis. All analyses were run in triplicate for each year; this is, a total of 6 replicates (3 replicates per year × 2 years) were conducted for each analysis.

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

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

3.3. Total polyphenols content (TPC)

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

3.4. Antioxidant activity

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

The DPPH and ferric reducing ability of plasma (FRAP) assay were prepared as described previously by Wojdyło, Oszmiański, Teleszko, *et al.,* (2013). For all analyses, a standard curve was prepared using different concentrations of Trolox. All determinations were performed in triplicate using a Shimadzu UV-2401 PC spectrophotometer (Kyoto, Japan). The results were corrected for dilution and expressed in mmol Trolox/100 mL.

For dries quinces manuscript the antioxidant activity [ABTS+ and FRAP (ferric reducing antioxidant power)] was analyzed as recently described by Wojdyło *et al.,* (2016), and according to methods by Benzie and Strain (1996) and Re *et al.,* (1999), respectively.

3.5. Organic acids and sugars

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

3.6. Fatty acids

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

Fatty acids were in situ methylated according to Park and Goins (1994) with some modifications. Basically, 50 mg of quince seeds oil were transferred into a test tube together with 80 μL of C17:0n-hexane solution (20 mg mL^{-1}) as internal standard. Then, 100 μL of dichloride methane and 1 mL of 0.5 N NaOH in methanol were added and the tubes were heated in a water bath at 90°C for 10 min. One milliliter of BF_3 in methanol

were added and the mixture was left at room temperature (25°C) for 30 min. One milliliter of dis-tilled water and 600 µL of hexane were added and then fatty acid methyl esters (FAME) were extracted by vigorous shaking for about 1 min. Following centrifugation, the aliquots were dried with anhydrous Na_2SO_4 and the top layer was transferred into a vial flushed with nitrogen which was stored at −20°C until analyzed by GC-MS.

The identification and quantification of the fatty acids was performed on a gas chromatograph (GC-MS), Shimadzu GC-17A (Shimadzu Corporation, Kyoto, Japan), coupled with a Shimadzu mass spectrometer detector GC-MS QP-5050A. The GC-MS system was equipped with a TRACSIL Meta X5 column, 95% dimethyl-poysiloxane and 5% diphenyl-polysiloxane (Teknokroma S. Co. Ltd., Barcelona, Spain; 30 m × 0.25 mm i.d., 0.25 µm film thickness). Chromatographic conditions were identical to those previously described by Calín-Sánchez *et al.,* (2013).

3.7. Sensory analysis

Trained panelists from the Food Quality and Safety Group of the Miguel Hernández University, UMH (Alicante, Spain) participated in this study – seven for raw quinces and eight for died ones. Each of the panelists had more than 500 h of testing experience with a variety of food products. For the current study, the panelists received further orientation on fresh and processed quinces.

The evaluation of quince samples was carried out at UMH facilities using individual booths with controlled illumination (70–90 fc) and temperature (20 ± 2°C) during three different sessions; samples were evaluated in triplicate. The samples order for each panelist was randomized. The samples, 3 slices of raw quince fruit, were served into odor-free, disposable 150 mL covered plastic cups. All samples were served at room temperature and unsalted cracker sand distillated water were used to clean palates between samples. The quince samples (3 slices of dried quinces), were served in odor-free, disposable 100 mL plastic glasses with lids for the evaluation; additional samples were available if the panelists requested them.

For raw quinces, three sessions of 2 h were held for the samples evaluation. Quince samples were assessed using descriptive sensory analysis but only the most relevant sensory descriptors were assessed in this study: quince flavor, fruity flavor, sourness, sweetness, bitterness and astringency. A linear numerical scale was used, where 0 = no intensity and 10 = extremely strong intensity. Results are reported as the mean value ± standard error.

For dried quinces, also three sessions of 2 h were held for the samples evaluation; all 10 samples (coming from 10 drying treatments) were assayed in each session, with

about ~3 min between samples (~8–9 min per sample). Quince samples were assessed using descriptive sensory analysis and a total 16 attributes were evaluated and quantified:

- **appearance**: pulp color and color homogeneity;
- **flavor**: sourness, sweetness, bitterness, astringency, quince ID flavor, pineapple, apple/pear, fruity, burnt, aftertaste; and,
- **texture**: hardness, crunchiness, graininess, and fiberness.

A numerical scale, from 0 to 10 with increments of 0.5, was used, where 0 represents no intensity and 10 represents extremely strong intensity.

3.8. Statistical analyses

Statistical analyses were performed using SPSS 20.0 for Windows (SPSS Science, Chicago, IL, USA). A basic descriptive statistical analysis was followed by an analysis of variance test for mean comparisons. The method used to discriminate among the means was Fisher's Least Significant Difference (LSD) procedure at a 95.0% confidence level. Cluster analysis (CA) was also performed. Quality parameters and the concentrations of bioactive compounds were used for partial least square regression (PLS2) analysis with the intensity data of the main sensory attributes. Unscrambler version 9.7 (Camo Software, Oslo, Norway) was used to conduct PLSR.

For quince liquors article results are given as the mean ± standard deviation of, at least, two independent determinations. All statistical analyses were performed with Statistica version 10 (StatSoft, Krakow, Poland). First data was subjected to four-way (alcohol content, quince variety/ clone, presence of skin, and ratio quince:ethanol) analysis of variance (ANOVA); later data was also subjected to Duncan's test to compare the means. Differences were considered statistically significant at $p < 0.05$.

For quince drying manuscript statistical analyses were performed using SPSS 20.0 for Windows (SPSS Science, Chicago, IL, USA). A basic descriptive statistical analysis was followed by an analysis of variance (ANOVA) test for mean comparisons. The method used to discriminate among the means (Multiple Range Test) was the Tukey procedure at a 95.0% confidence level.

3.9. Liquor manufacturing

Extra pure ethanol (96% abv) was used for the manufacturing of the liquors. Ethanol was first adjusted to 60% abv for maceration with quince fruits. Three parameters were considered in this study: (i) quince cultivar/clone, (ii) fruits with or without skin, and (iii) ratio quince:ethanol (60% abv). As previously mentioned, 3 quince cultivars/clones were evaluated: Vranja, ALM3, and ZM2. Half of the quince fruits were manually peeled, and

maceration was conducted with whole or peeled fruits. Finally, two different quince:ethanol ratios were used: (i) 50:50 and (ii) 25:50. A total of 3 L of each quince liquor was macerated during 3 months at approximately 20 °C and in darkness, using 3 different 1 L glass jars (3 replications), and avoiding leaving headspace in the jars. After appropriate maceration period (3 months), the alcohol percentage was adjusted to 30% abv by proper addition of sucrose and distillate water; this alcohol level was selected to obtain products with similar characteristics to Spanish commercial liquors.

3.10. Identification of polyphenols by the LC-PDA-MS method

Identification and quantification of polyphenols from quince liquors was carried out using an Acquity ultraperformance LC system equipped with a photodiode detector (PDA; UPLC) with binary solvent manager (Waters Corp., Milford, MA, USA) series with a mass detector G2 QTOF Micro mass spectrometer (Waters, Manchester, UK) equipped with an electrospray ionization (ESI) source operating in negative modes. Separation of polyphenols was carried out using a UPLC BEH C18 column (1.7 µm, 2.1 x 100 mm; Waters Corp., Milford, MA, USA) at 30 °C.

Samples (5 µL) were injected, and elution was completed within 15 min using a sequence of elution modes: linear gradients and isocratic. The flow rate was 0.45 mL/min. The mobile phase was composed of solvent A (4.5% formic acid) and solvent B (100% of acetonitrile). The program began with isocratic elution with 99% A (0-1 min), and then a linear gradient was used until 12 min, lowering A to 0%; from 12.5 to 13.5 min, returned to the initial composition (99% A); and then held constant to re-equilibrate the column. Analysis was carried out using full scan, data-dependent MS scanning from m/z 100 to 1000. The mass tolerance was 0.001 Da, and the resolution was 5.000. Leucine enkephalin was used as the mass reference compound at a concentration of 500 pg/µL at a flow rate of 2 µL/min, and the $[M-H]^-$ ion at 554.2615 Da was detected over 15 min of analysis during ESI-MS accurate mass experiments, which was permanently introduced via the LockSpray channel using a Hamilton pump. The lock mass correction was ±1.000 for Mass Window. The mass spectrometer was operated in a negative ion mode and set to the base peak intensity (BPI) chromatograms and scaled to 12,400 counts per second (cps) (=100%). The optimized MS conditions were as follows: capillary voltage of 2500 V, cone voltage of 30 V, source temperature of 100 °C, desolvation temperature of 300 °C, and desolvation gas (nitrogen) flow rate of 300 L/h. Collision-induced fragmentation experiments were performed using argon as collision gas, with voltage ramping cycles from 0.3 to 2 V. The characterization of the single components was carried out via the retention time and the accurate molecular masses. Hydroxycinnamic acid, flavan-3-ols and flavonols compound were optimized to their estimated molecular masses $[M-H]^-$ in the negative

mode before and after fragmentation. The data obtained from LC–MS were subsequently entered into MassLynx 4.0 ChromaLynx Application Manager software. On the basis of these data, the software is able to scan different samples for the characterized substances.

3.11. Analysis of polyphenol compounds

Five milliliters of the quince liquors were centrifuged for 10 min at 15,000g at 4°C. The analytical column [UPLC BEH C18 column (1.7 µm, 2.1 x 100 mm; Waters Corp., Milford, MA, USA)] was kept at 30 °C by column oven, whereas the samples were kept at 4 °C. The mobile phase was composed of solvent A (4.5% formic acid) and solvent B (acetonitrile). Elution was the same gradient as LC/MS analysis. PDA spectra were measured over the wavelength range of 200-600 nm in steps of 2 nm. The runs were monitored at the following wavelengths: flavan-3-ols at 280 nm, hydroxycinnamates at 320 nm, and flavonol glycosides at 360 nm. Retention times (Rt) and spectra were compared with those of pure standards. Calibration curves at concentrations ranging from 0.05 to 5 mg/mL (R^2 6 0.9998) were made from (-)-epicatechin, (+)-catechin, procyanidin B1, B2 and C1, chlorogenic acid, neochlorogenic acid, 3,5-di-caffeoylquinic acid, quercetin and kaempferol -3-O-glucoside and -3-O-rutinoside. 4-p-Coumaroylquinic acid was expressed as caffeic acid, acylated quercetin and kaempferol were expressed as quercetin and kaempferol-3-Oglucoside, respectively. All analyses were run in duplicate. Results were expressed as mg/100 mL.

3.12. Identification and quantification of polyphenols in dried quinces

The quince extract for polyphenols analysis was prepared as described by Wojdyło *et al.,* (2016) and using the same analytical set up. Identification and quantification of polyphenols in the quince extracts were carried out using an ACQUITY Ultra Performance LCTM system. PDA spectra were measured in the wavelength range 200–600 nm. The runs were monitored at 280 nm for flavan-3-ols and 360 nm for flavonol glycosides. Calibration curves, in the range 0.05–5.00 mg mL^{-1} ($R^2 \geq 0.999$), were conducted using (+)-catechin, (−)-epicatechin, chlorogenic, neochlorogenic, and cryptochlorogenic acids, procyanidin B2 and C1, kaempferol-3-O-glucoside, and quercetin-3-O-glucoside. Kaempferol and quercetin derivatives were expressed as kaempferoland quercetin-3-O-glucoside, respectively.

3.13. Analysis of procyanidins by phloroglucinolysis method

Direct phloroglucinolysis of quince liquors was performed as described previously by Wojdyło, Oszmiański, and Bielicki (2013). Portions (0.5 mL) of liquors in 2 mL Eppendorf vials were freeze-dried (24 h; Alpha 1-4 LSC; Martin Christ GmbH, Osterode am Harz, Germany), then 0.8 mL of the methanolic solution of phloroglucinol (75 g/L) and ascorbic

acid (15 g/L) was added. After the addition of 0.4 mL of methanolic HCl (0.3 mol/L), the vials were closed and incubated for 30 min at 50 °C with continuous vortexing using a thermo shaker (TS-100; BIOSAN, Lithuania). The reaction was stopped by placing the vials in an ice bath, withdrawing 0.5 mL of the reaction medium and diluting with 0.5 mL of 0.2 mol/L sodium acetate buffer. Then, the vials were cooled in ice water and centrifuged immediately at 20,000g for 10 min at 4 °C.

The analysis of polymeric procyanidins compounds was carried out on a UPLC system Acquity (Waters Corp., Milford, MA, USA) consisting of a binary solvent manager, and fluorescence detector (FL). Empower 3 software was used for chromatographic data collection and integration of chromatograms. A partial loop injection mode with a needle overfill was set up, enabling 5 µL injection volumes when a 10 µL injection loop was used. Acetonitrile (100%) was used as a strong wash solvent and acetonitrile-water (10%) as a weak wash solvent. The analytical column BEH Shield C18 (2.1 mm x 50 mm; 1.7 µm) was kept at 15 °C by column oven, whereas the samples were kept at 4 °C. The flow rate was 0.45 mL/min. The mobile phase was composed of solvent A (2.5% acetic acid) and solvent B (acetonitrile). Elution was as follows: 0-0.6 min, isocratic 2% B; 0.6-2.17 min, linear gradient from 2% to 3% B; 2.17-3.22 min, linear gradient from 3% to 10% B; 3.22-5.00 min, linear gradient from 10% to 15% B; 5.00-6.00 min, column washing; and reconditioning for 1.50 min. The fluorescence detection was recorded at an excitation wavelength of 278 nm and an emission wavelength of 360 nm. The calibration curves, which were based on peak area, were established using (+)-catechin, (-)-epicatechin, and procyanidin B1 after phloroglucinol reaction as (+)-catechin- and (-)-epicatechin-phloroglucinol adduct standards. The average degree of polymerization was calculated as the molar ratio of all the flavan-3-ol units (phloroglucinol adducts + terminal units) to (-)-epicatechin and (+)-catechin, which correspond to terminal units. All incubations were done in duplicate. Results were expressed as milligrams per 100 mL.

3.14. Drying procedures

Just before drying, 2 kg of quince fruits were cut in slices of approximately 3 cm wide and pitted. The moisture content of fresh samples was 7.2 ± 0.3 kg kg^{-1} db (**d**ry **b**asis). Four dehydration technologies were used:

i) Convection (convective drying, CD), using a convective drier designed and built at the Agricultural Engineering Institute of Wrocław (Wrocław, Poland). Hot-air temperature during CD was adjusted at 50, 60, or 70 ± 1 °C, and the air velocity was 1.0 ± 0.1ms^{-1}.

ii) Vacuum-microwave drying (VMD), using a SM-200 drier, Plazmatronika S.A. (Wrocław, Poland). During VMD, the initial microwave power was set at 120 and

480 ± 2W (VMD120 and VMD480). However, the tests revealed that during drying at 480 W, sample temperature increased above 100 °C, after the moisture content of 1 kg kg^{-1} db, leading to burned samples. Therefore, before the samples reached this critical moisture content, the microwave power was reduced to 120W in the treatment VM480-120. In all VMD treatments, the pressure within the VMD chamber ranged between 4 and 6 kPa.

iii) Combined drying, consisting of an initial stage of CPD at 50, 60 or 70 ± 1 °C followed by a final stage of VMFD at 480–120 ± 2 W. VMFD started after 60, 70 or 90 min of CPD for 50, 60 or 70 °C, respectively; this is, when the moisture content of the material being dried was around 2 kg kg−1 db. In the case of combined CPD-VMFD the reduction of microwave power from 480 to 120W was applied before the samples reached the moisture content of 0.5 kg kg^{-1} db to prevent reaching excessive sample temperature. The continuation of VMFD at 480W until lower values of moisture content than the critical one for pure VMD was possible because the temperature of CPD samples was decreased until ambient temperature before VMFD.

iv) Freeze-drying (FD), using a freeze-drier Alpha 1-4 LSC, Martin Christ GmbH (Osterode am Harz, Germany). It was considered as the control treatment, because it is generally admitted that FD leads to dried products of the highest quality (Huang *et al.,* 2009). During FD, the pressure and temperature inside the drying chamber was 0.960 kPa and −60 °C, respectively, while the temperature of heating shelves reached 26 °C. Samples were kept in the drying chamber for 24 h.

These 4 drying technologies led to the final application of 10 drying treatments: 3CD (50, 60 and 70 °C), 3 VMD (120, 480 and 480–120 W), 3 combined methods (CPD-VMFD), and 1 control (FD). The proposed range of parameters determining the conditions of the different drying methods used resulted from the former experience during drying of different plant materials, such as garlic (Calín-Sanchez, Figiel, Wojdyło, Szarycz & Carbonell-Barrachina, 2014), pomegranates (Calín-Sanchez, Figiel, Szarycz *et al.,* 2014), apples (Chong *et al.,* 2014), sour cherries (Wojdyło, Figiel, Lech, Nowicka & Oszmiański, 2014), jujube (Wojdyło *et al.,* 2016), etc. It was found that using of temperatures and microwave powers below 50 °C and 240W in CD and VMD, respectively, caused ineffective drying in terms of time of the process, energy efficiency and quality of the dried product. On the other hand, application of temperatures over 70 °C and microwave powers over 480W led to negative changes of most quality attributes determined for the dried product.

The initial mass of all the samples to be dried was 60 ± 1 g, and all drying methods continued until the moisture content of the dried samples was below 0.1 kg kg^{-1} db to meet microbial safety requirements.

After drying of quince samples, approximately half of the dried product was posted by fast-courier to Spain for analyzing the sensory profiles, while the rest of the analyses were performed in Poland.

3.15. Modeling of drying kinetics

The drying kinetics was based on mass losses of quince samples. The moisture ratio (MR) is defined according to Eq. (1):

$$MR = \frac{M(t) - M_e}{M_0 - M_e}$$

where M(t), M0 and Me denote moisture content achieved after drying time t, initial moisture content, and equilibrium moisture content, respectively. The value of equilibrium moisture content (Me) usually is very low and can be omitted from Eq. (1) without a significant change in the value of MR (Dadali, Apar, & Özbek, 2007). The moisture content of the dried samples was determined by drying ground samples in a vacuum dryer (SPT-200, ZEAMiL Horyzont, Krakow, Poland) for 24 h at 60 °C until reaching a constant weight. The decrease in the moisture ratio, MR, during drying was described using five drying models (Table 1), which are commonly applied to predict the drying behavior of plant materials.

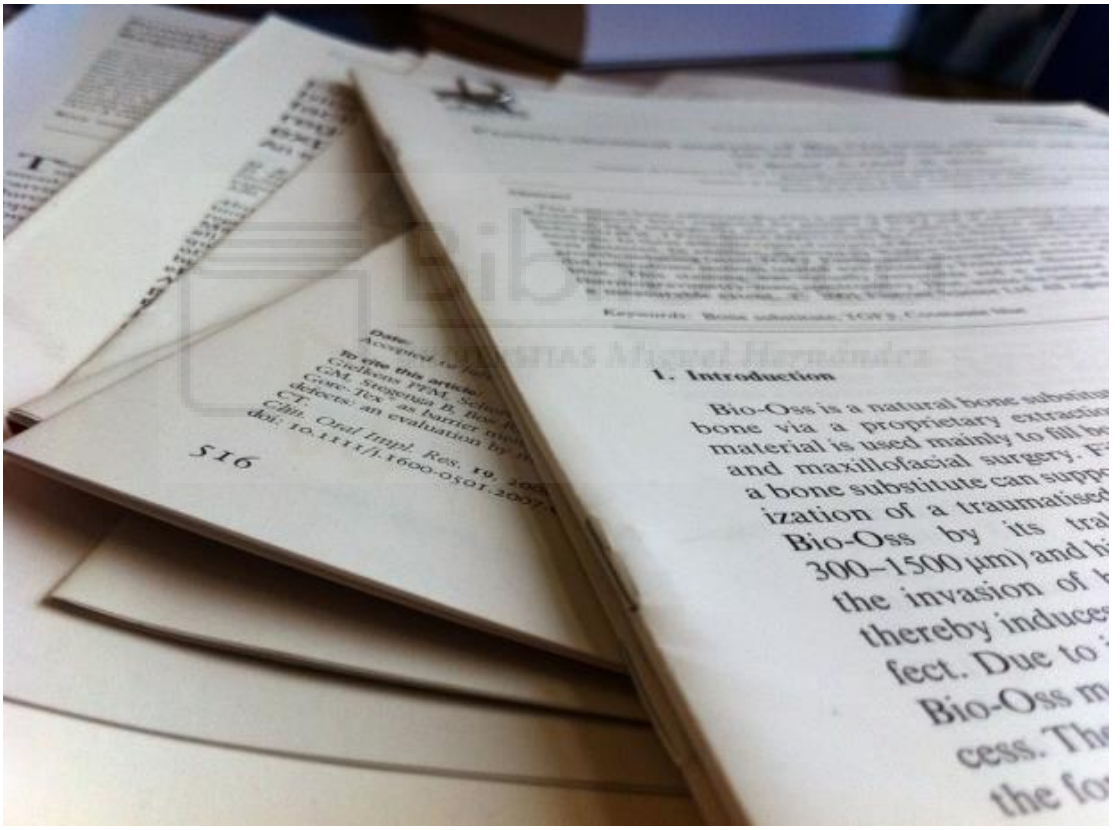
Table 1
Mathematical models applied to the experimental drying curves.

Model	Model equation	References
Modified Page	$MR = A \cdot e^{-k \cdot t^{B}}$	Rafie *et al.* (2010)
Henderson-Pabis	$MR = A \cdot e^{-k \cdot t}$	Henderson and Pabis (1961)
Logarithmic	$MR = A \cdot e^{-k \cdot t} + B$	Dandamrongrak, Young, and Mason (2002)
Midilli-Kucuk	$MR = A \cdot e^{-k \cdot t^{B}} + C \cdot t$	Midilli, Kucuk, and Yapar (2002)
Weibull	$MR = A - B \cdot e^{-k \cdot t^{C}}$	Babalis, Papanicolaou, Kyriakis, and Belessiotis (2006)

3.16. Temperature of dried samples

The temperature of the vacuum-microwave treated quince samples (VMD and VMFD) was measured using an infrared camera Flir i50 (Flir Systems Inc., Stockholm, Sweden), just after taking the samples out of the dryer, and only the maximum value was recorded. It is important to remember that during CD and FD, the material temperature never exceeds the temperature of hot air or heating plate, respectively.

Chapter 4.- Publications



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Technological aspects as the main impact on quality of quince liquors

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a b s t r a c t

Phytochemical profiles of 24 quince liquors were studied as the combination of technologically variant. Liquors were obtained after macerating quinces from three varieties (*Vranja*, *ALM3* and *ZM2*), with or without skin, at two ratios of quince:ethanol (50:50 and 25:75), and at two alcohol content (60% and 30%). Polyphenols were identified by LC-PDA-QTOF/MS and quantified by UPLC-PDA and UPLC-FL. A total of 18 polyphenolic compounds were identified and classified as 5 flavan-3-ols, 5 phenolic acids, and 8 flavonols. Flavan-3-ols were the most abundant group followed by hydroxycinnamates and flavonols. The highest contents of total polyphenols (~1000 mg/100 mL) and antioxidant activity (37.1 mmol Trolox/100 mL) were found in the liquors prepared using fruits with skin and 50:50 quince:ethanol ratio. The skin of quinces was the main source of phenolic acids and especially flavonols. The high antioxidant activity and polyphenolic content of quince liquor may be deemed as a promising new alcoholic beverage.

1. Introduction

Quince (*Cydonia oblonga* Miller) belongs to the Maloideae subfamily of the Rosaceae family, which includes commercially important fruits, such as apples and pears (Wojdyło, Oszmiański, & Bielicki, 2013). Quince fruits are mainly used in the manufacture of marmalade, jam, jelly, cakes, and liquors (Silva *et al.,* 2002; Silva, Andrade, Gonçalves, *et al.,* 2004; Silva, Andrade, Ferreres, *et al.,* 2005; Silva, Andrade, Martins, *et al.,* 2005; Silva, Andrade, Martins, Seabra, & Ferreira, 2006); the most popular quince product in Spain is a jam called "quince sweet". However, their consumption as fresh fruit is not too popular mainly due to the high and unpleasant intensities of sourness, bitterness, astringency and of woodiness in the most widely grown quince cultivars.

Quinces have received attention in the last ten years because of their high content in biologically active phytochemicals (proanthocyanidins, hydroxycinnamic acid etc.) and antioxidant capacity. Several studies have recently described antioxidant (Legua *et al.,* 2013), antimicrobial (Fattouch *et al.,* 2007; Silva & Oliveira, 2013), antiallergic (Shinomiya, Hamauzu, & Kawahara, 2009), antihemolytic (Costa *et al.,* 2009), and antiproliferative (Márcia, Silva, Renata, Patrícia, & Andrade, 2010) properties of quince phenolics (Wojdyło, Oszmiański, & Bielicki, 2013). Besides, quince has low fat content and it is an important source of organic acids, sugars, crude fiber and minerals, such as potassium, phosphorous and calcium (Rodríguez-Guisado *et al.,* 2009; Sharma, Joshi, & Rana, 2011; Shinomiya *et al.,* 2009).

The polyphenolic compositions of quince fruits (Wojdyło, Oszmiański, & Bielicki, 2013; Silva *et al.,* 2002), leaves (Oliveira *et al.,* 2007), jams (Silva, Andrade, Seabra, & Ferreira, 2001; Wojdyło, Oszmiański, Teleszko, & Sokół-Łetowska, 2013), juice (Wojdyło, Teleszko, & Oszmiański, 2014) and jellies (Silva *et al.,* 2000) have been properly studied. Besides, the effects of the manufacturing process on the composition and quality of final commercial products have been evaluated; for example, the effects of jam processing on the contents of phenolics, organic acids, and free-amino-acids were examined (Silva, Andrade, Valentão, *et al.,* 2004). However, there are no studies in the scientific literature dealing with detailed information on the polyphenolic profiles and antioxidant activity of quince liquors.

Herbs spirits have been made and consumed for centuries in different European countries, especially in cold regions. These liquors are generally prepared by macerating different aromatic herbs or/and fruits in fermented grape marc distillate, distilling

the fermented grape marc in the presence of herbs, adding herbal extracts to the distilled alcohol, or combining some of these methodologies (Vázquez-Araújo, Rodríguez-Solana, Cortés-Diéguez, & Domínguez, 2013).

In Spain there are several Geographical Designation of Spirits, e.g. Spirits and Traditional Liquors from Galicia, GDSTL from Galicia (http://www.orujodegalicia.org) and from Alicante (http://www.licoresdealicante.com). The products protected by these Geographical Designations must fulfill some requirements; for instance, and among others: (i) the liquors should be prepare using aromatic herbs typical and endemic of specific regions, (ii) the liquors must have between 20% and 40% alcohol by volume (abv), and (iii) the liquors need to meet certain sensory characteristics: translucent and clean appearance, color between pale yellow to dark brown, intense, fine, delicate, tasty and complex aroma, with floral and balsamic notes, and reminding the herb notes. Some of these Geo- graphical Designations are opening their spectrum of herbs and perhaps typical fruits could be included in a near future; for instance, the GDSTL of Galicia has very recently authorized the use of any kind of herb which is suitable for human consumption.

In this study, it was investigated how the varieties [one quince cultivar: *Vranja* and two quince clones: *ALM3* and *ZM2*] and technological aspects [(i) maceration in alcohol, (ii) use of fruits with or without skin, and (iii) the ratio of fruit to alcohol] affect the content of polyphenol compounds and antioxidant activity in quince liquors. The identities of polyphenolics were confirmed using LC–MS.

2. Materials and methods

2.1. Chemicals

2,2'-Azinobis(3-ethylbenzothiazoline-6-sulfonic acid (ABTS), 6- hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid (Trolox), 2,4,6-tri(2-pyridyl)-s-triazine (TPTZ), acetic acid, phloroglucinol, and methanol were purchased from Sigma–Aldrich (Steinheim, Germany). (-)-Epicatechin, (+)-catechin, procyanidin B1, B2 and C, quercetin and kaempferol -3-*O*-glucoside, -3-*O*-galactoside and -3-*O*-rutinoside were purchased from Extrasynthese (Lyon, France). Chlorogenic acid (3-caffeoylquinic acid), neochlorogenic acid (5-caffeoylquinic acid), cryptochlorogenic acid (4-caffeoylquinic acid), and 3,5-dicaffeoylquinic acid were purchased from TRANS MIT GmbH (Giessen, Germany). Acetonitrile for UPLC (Gradient grade) and ascorbic acid were from Merck (Darmstadt, Germany). UPLC grade water, prepared by using an HLP SMART 1000s system (Hydrolab, Gdańsk, Poland), was additionally filtered through a 0.22 lm membrane filter immediately before use. Extra pure ethanol (96% abv, alcohol by volume) was from Scharlau, (Barcelona, Spain).

2.2. Quince fruits

One quince cultivar (*Vranja*) and two clones (*ALM3* and *ZM2*) were used in this research; all of them were appropriate for food manufacturing and widely grown in Spain. The selected plant materials belong to the quince gene bank located at the experimental field station of the Universidad Miguel Hernández de Elche (Orihuela, Alicante, Spain). Trees were planted at a spacing of 4 x 3 m. The experiment was established in a randomized block design with four single-tree replications and grafted onto quince *BA-29* rootstock. Fruits were harvested at commercial ripening stage (total soluble solids > 15 °Brix and maturity index > 30) at the end of September and first October 2012, and 20 homogeneous fruits (based on color, size and absence of defects) were selected from each variety (5 fruits from each tree) and used for manufacturing of liquors; about 6 kg of fresh quinces per each variety was used in this study.

2.3. Liquor manufacturing

Extra pure ethanol [96% abv (alcohol by volume)] was used for the manufacturing of the liquors. Ethanol was first adjusted to 60% abv for maceration with quince fruits. Three parameters were considered in this study: (i) quince cultivar/clone, (ii) fruits with or without skin, and (iii) ratio quince:ethanol (60% abv). As previously mentioned, 3 quince cultivars/clones were evaluated: *Vranja*, *ALM3*, and *ZM2*. Half of the quince fruits were manually peeled, and maceration was conducted with whole or peeled fruits. Finally, two different quince:ethanol ratios were used: (i) 50:50 and (ii) 25:50. A total of 3 L of each quince liquor was macerated during 3 months at approximately 20 °C and in darkness, using 3 different 1 L glass jars (3 replications), and avoiding leaving headspace in the jars. After appropriate maceration period (3 months), the alcohol percentage was adjusted to 30% abv by proper addition of sucrose and distillate water; this alcohol level was selected to obtain products with similar characteristics to Spanish commercial liquors.

2.4. Identification of polyphenols by the LC-PDA-MS method

Identification and quantification of polyphenols from quince liquors was carried out using an Acquity ultraperformance LC system equipped with a photodiode detector (PDA; UPLC) with binary solvent manager (Waters Corp., Milford, MA, USA) series with a mass detector G2 QTOF Micro mass spectrometer (Waters, Manchester, UK) equipped with an electrospray ionization (ESI) source operating in negative modes. Separation of polyphenols was carried out using a UPLC BEH C18 column (1.7 lm, 2.1 x 100 mm; Waters Corp., Milford, MA, USA) at 30 °C.

Samples (5 µL) were injected, and elution was completed within 15 min using a sequence of elution modes: linear gradients and isocratic. The flow rate was 0.45 mL/min. The mobile phase was composed of solvent A (4.5% formic acid) and solvent B (100% of acetonitrile). The program began with isocratic elution with 99% A (0-1 min), and then a linear gradient was used until 12 min, lowering A to 0%; from 12.5 to 13.5 min, returned to the initial composition (99% A); and then held constant to re-equilibrate the column. Analysis was carried out using full scan, data-dependent MS scanning from *m/z* 100 to 1000. The mass tolerance was 0.001 Da, and the resolution was 5.000. Leucine enkephalin was used as the mass reference compound at a concentration of 500 pg/µL at a flow rate of 2 µL/min, and the $[M-H]^-$ ion at 554.2615 Da was detected over 15 min of analysis during ESI-MS accurate mass experiments, which was permanently introduced via the LockSpray channel using a Hamilton pump. The lock mass correction was ±1.000 for Mass Window. The mass spectrometer was operated in a negative ion mode and set to the base peak intensity (BPI) chromatograms and scaled to 12,400 counts per second (cps) (=100%). The optimized MS conditions were as follows: capillary voltage of 2500 V, cone voltage of 30 V, source temperature of 100 °C, desolvation temperature of 300 °C, and desolvation gas (nitrogen) flow rate of 300 L/h. Collision-induced fragmentation experiments were performed using argon as collision gas, with voltage ramping cycles from 0.3 to 2 V. The characterization of the single components was carried out via the retention time and the accurate molecular masses. Hydroxycinnamic acid, flavan-3-ols and flavonols compound were optimized to their estimated molecular masses $[M-H]^-$ in the negative mode before and after fragmentation. The data obtained from LC–MS were subsequently entered into MassLynx 4.0 ChromaLynx Application Manager software. On the basis of these data, the software is able to scan different samples for the characterized substances.

2.5. Analysis of polyphenol compounds

Five milliliters of the quince liquors were centrifuged for 10 min at 15,000*g* at 4 °C. The analytical column [UPLC BEH C18 column (1.7 µm, 2.1 x 100 mm; Waters Corp., Milford, MA, USA)] was kept at 30 °C by column oven, whereas the samples were kept at 4 °C. The mobile phase was composed of solvent A (4.5% formic acid) and solvent B (acetonitrile). Elution was the same gradient as LC/ MS analysis. PDA spectra were measured over the wavelength range of 200-600 nm in steps of 2 nm. The runs were monitored at the following wavelengths: flavan-3-ols at 280 nm, hydroxycinnamates at 320 nm, and flavonol glycosides at 360 nm. Retention times (R_t) and spectra were compared with those of pure standards. Calibration curves at concentrations ranging from 0.05 to 5 mg/mL ($R^2 \leq 0.9998$) were made from (-)-epicatechin, (+)-catechin, procyanidin B1, B2 and C1, chlorogenic acid, neochlorogenic acid, 3,5-di-caffeoylquinic acid, quercetin and kaempferol -3-*O*-glucoside and -3-*O*-rutinoside. 4-*p*-Coumaroyl- quinic acid was expressed as caffeic acid, acylated quercetin and kaempferol were expressed as quercetin and kaempferol-3-*O*- glucoside, respectively. All analyses were run in duplicate. Results were expressed as mg/100 mL.

2.6. Analysis of procyanidins by phloroglucinolysis method

Direct phloroglucinolysis of quince liquors was performed as described previously by Wojdyło, Oszmiański, and Bielicki (2013). Portions (0.5 mL) of liquors in 2 mL Eppendorf vials were freeze-dried (24 h; Alpha 1-4 LSC; Martin Christ GmbH, Osterode am Harz, Germany), then 0.8 mL of the methanolic solution of phloroglucinol (75 g/L) and ascorbic acid (15 g/L) was added. After the addition of 0.4 mL of methanolic HCl (0.3 mol/L), the vials were closed and incubated for 30 min at 50 °C with continuous vortexing using a thermo shaker (TS-100; BIOSAN, Lithuania). The reaction was stopped by placing the vials in an ice bath, withdrawing 0.5 mL of the reaction medium and diluting with 0.5 mL of 0.2 mol/L sodium acetate buffer. Then, the vials were cooled in ice water and centrifuged immediately at 20,000*g* for 10 min at 4 °C.

The analysis of polymeric procyanidins compounds was carried out on a UPLC system Acquity (Waters Corp., Milford, MA, USA) consisting of a binary solvent manager, and fluorescence detector (FL). Empower 3 software was used for chromatographic data collection and integration of chromatograms. A partial loop injection mode
with a needle overfill was set up, enabling 5 µL injection volumes when a 10 µL injection loop was used. Acetonitrile (100%) was used as a strong wash solvent and acetonitrile-water (10%) as a weak wash solvent. The analytical column BEH Shield C18 (2.1 mm x 50 mm; 1.7 µm) was kept at 15 °C by column oven, whereas the samples were kept at 4 °C. The flow rate was 0.45 mL/min. The mobile phase was composed of solvent A (2.5% acetic acid) and solvent B (acetonitrile). Elution was as follows: 0-0.6 min, isocratic 2% B; 0.6-2.17 min, linear gradient from 2% to 3% B; 2.17-3.22 min, linear gradient from 3% to 10% B; 3.22-5.00 min, linear gradient from 10% to 15% B; 5.00-6.00 min, column washing; and reconditioning for 1.50 min. The fluorescence detection was recorded at an excitation wavelength of 278 nm and an emission wavelength of 360 nm. The calibration curves, which were based on peak area, were established using (+)-catechin, (-)-epicatechin, and procyanidin B1 after phloroglucinol reaction as (+)-catechin- and (-)-epicatechin-phloroglucinol adduct standards. The average degree of polymerization was calculated as the molar ratio of all the flavan-3-ol units (phloroglucinol adducts + terminal units) to (-)-epicatechin and (+)-catechin, which correspond to terminal units. All incubations were done in duplicate. Results were expressed as milligrams per 100 mL

2.7. Analysis of antioxidant activity

The $ABTS^{\bullet+}$ activity, DPPH and ferric reducing ability of plasma (FRAP) assay were prepared as described previously by Wojdyło, Oszmiański, Teleszko, *et al.,* (2013). For all analyses, a standard curve was prepared using different concentrations of Trolox. All determinations were performed in triplicate using a Shimadzu UV-2401 PC spectrophotometer (Kyoto, Japan). The results were corrected for dilution and expressed in mmol Trolox/100 mL.

2.8. Statistical analysis

Results are given as the mean ± standard deviation of, at least, two independent determinations. All statistical analyses were performed with Statistica version 10 (StatSoft, Krakow, Poland). First data was subjected to four-way (alcohol content, quince variety/clone, presence of skin, and ratio quince:ethanol) analysis of variance (ANOVA); later data was also subjected to Duncan's test to compare the means. Differences were considered statistically significant at $p < 0.05$.

3. Results and discussion

3.1. Identification of phenolic compounds

As an initial step, quince liquors were analyzed by LC–MS-QTOF system. The LC–MS and mass spectral data obtained are summa- rized in Table 1. In total, 18 polyphenolic compounds found in quince liquors were identified.

Five compounds belonging to *flavan-3-ols* were detected in quince liquors, two monomers, two dimers and one trimer. (+)-Catechin and (-)-epicatechin, peaks 5 and 8 (R_t = 3.71 and 4.59 min, k_{max} = 278 nm) had $[M-H]^-$ at *m/z* 289 and MS/MS fragment at *m/z* 245. Peaks 3 and 7 (R_t = 3.40 and 3.91 min, k_{max} = 278 nm) were identified as procyanidin B1 and B2 using $[M-H]^-$ at *m/z* 577, and by MS/MS fragmentation of these peaks at *m/z* 289. Cochromatography with a standard was used to confirm the identity of these compounds. Apart from these compounds, one procyanidin trimer (compound 11) at R_t = 7.32 min with *m/z* 865 was identified in quince liquors. This procyanidin had the characteristic fragmentation pattern of a negatively charged molecular ion $[M-H]^-$ at *m/z* 577 and/or 289.

Five *hydroxycinnamates*, four derivatives of caffeoylquinic acid and one of coumaroylquinic acid, were detected as well. Peaks 1, 4 and 6 with k_{max} 325 nm had characteristic mass spectral data of $[M-H]^-$ at *m/z* 353 and MS/MS fragmentation at *m/z* 191 and 173. Those compounds at R_t 2.30, 3.45, and 3.82 min were identified as neochlorogenic, chlorogenic and cryptochlorogenic acid, respectively, after comparison with corresponding standards. Peak 2 (R_t = 3.11 min, k_{max} = 309 nm) was identified as 4-*O*-*p*-coumaroylquinic acid on the basis of mass spectral data. It had an $[M-H]^-$ at *m/z* 337, which fragmented on MS/MS to yield a major ion at *m/z* 173 and a minor peak at *m/z* 136. This fragmentation pattern has been shown to be characteristic of the 4-isomer of *p*-coumaroyl- quinic acid (Clifford, Johnston, Knight, & Kuhnert, 2003). This identification of 4-*O*-*p*-coumaroylquinic acid in quince products is supported by previous report of this compound in apples (Alonso-Salces *et al.,* 2004). Peak 14 with R_t = 8.18 min and k_{max} = 326 nm gave a characteristic $[M-H]^-$ at *m/z* 515, which fragmented on MS/MS to the precursor ion at *m/z* 353; this information confirmed the 3-regiochemistry of the caffeoyl substituent (Alonso-Salces *et al.,* 2004) and it was identified as 3,5-di-*O*- caffeoylquinic acid.

Quercetin and kaempferol derivatives are the *flavonols* previously found in quince fruits (Fattouch et al., 2007; Silva,

Table 1
Identification of phenolic compounds in quince liquors in $[M-H]^-$, retention time [R_t] and k_{max} with LC–MS-QTOF and MS/MS.

Peak	Name	R_t (min)	k_{max} (nm)	MS $[M-H]^-$ (m/z)	MS/MS $[M-H]^-$
1	Neochlorogenic acid	2.30	325	353	191
2	4-*O*-*p*-Coumaroylquinic acid	3.11	309	337	173/136
3	Procyanidin B1	3.40	278	577	289
4	Chlorogenic acid	3.45	325	353	191
5	(+)-Catechin	3.71	278	289	245
6	Cryptochlorogenic acid	3.82	325	353	173
7	Procyanidin B2	3.91	278	577	289
8	(-)-Epicatechin	4.59	278	289	245
9	Quercetin-3-*O*-galactoside	7.10	243; 352	463	301
10	Quercetin-3-*O*-rutinoside	7.20	243; 352	609	301
11	Procyanidin C1	7.32	278	865	577/289
12	Quercetin-3-*O*-glucoside	7.34	243; 352	463	301
13	Kaempferol-3-*O*-galactoside	8.01	264; 345	447	285
14	3,5-di-*O*-Caffeoylquinic acid	8.18	326	515	353/136/182
15	Kaempferol-3-*O*-rutinoside	8.30	264; 345	593	285
16	Kaempferol-3-*O*-glucoside	8.51	264; 345	447	285
17	Quercetin glucoside acylated by *p*-coumaric	10.79	242; 352	609	463/301/136
18	Kaempferol glucoside acylated by *p*-	12.02	265; 345	593	285

Andrade, Ferreres, *et al.*, 2005; Silva, Andrade, Martins, *et al.*, 2005) and leaves (Oliveira *et al.*, 2007). These compounds exhibit UV-vis absorption maxima at about 352 nm for quercetin and at 345 nm for kaempferol derivatives (Table 1). Peaks 9, 12 and 17 had characteristic MS/MS fragment at m/z 301. Peaks 9 and 12 with R_t = 7.10 and 7.34 min, respectively, had characteristic mass at m/z 463 and MS/MS fragment at m/z 301. The loss of 162 amu equates to the loss of a hexose sugar. Comparison of the retention times of these peaks and those of standards allowed their identification as quercetin-3-*O*-galactoside and quercetin-3-*O*-glucoside, respectively. Peak 10 (R_t = 7.20 min, k_{max} = 352 nm) was identified as quercetin-3-*O*-rutinoside on the basis of $[M-H]^-$ at m/z 609 and MS/MS fragment at m/z 301. Four peaks were identified as kaempferol derivatives according to their UV spectra and MS fragmentation leading to the kaempferol aglycone at m/z 285 in a negative mode. Peak 13 was identified as kaempferol-3-*O*-galactoside with m/z 447 and an MS/MS fragment at 285 obtained after the loss of 162 amu (galactose moiety). Peaks 15 and 16 had $[M-H]^-$ at m/z 593 and 447 with a fragment at m/z 285 (loss of 308 and 162 amu: two and one hexose moiety) and were identified as kaempferol-3-*O*-rutinoside and kaempferol-3-*O*-glucoside, respectively.

Peaks 17 and 18 were also identified as quercetin and kaempferol derivatives according to their mass spectrum with a distinctive main fragment at m/z 463/301 and 285, respectively. However, these compounds had a maximum absorption at shorter wavelength (314 nm), which on the other hand indicated acylation of the sugar moiety on this flavonol with hydroxycinnamic acid (Marks, Mullen, & Crozier, 2007). An analogous relationship was observed for compound 18. MS in the negative mode gave the base peak at m/z 593 and MS/MS main fragment at m/z 285 (loss m/z 308 matching to a *p*-coumaroylglucoside moiety), which corresponds to kaempferol glucoside acylated by *p*-coumaric acid and peak 17 at m/z 609 and MS/MS main fragment at m/z 301 (loss m/z 308: *p*-coumaroylglucoside moiety), which corresponds to quercetin glucoside acylated by *p*-coumaric acid. These compounds were identified previously by Wojdyło, Oszmiański, and Bielicki (2013) and Wojdyło, Oszmiański, Teleszko, *et al.*, (2013) in Polish quinces and quince-based products, e.g. jams.

3.2. Quantification of phenolic compounds

Regarding the obtained quantification results, Fig. 1 shows the differences among the total phenolic determined by UPLC in the final quince liquors. The total phenolic ranged from 149 to 1008 mg/100 mL of liquor. The content of total phenolic compounds was significantly ($p < 0.05$) affected by the quince variety

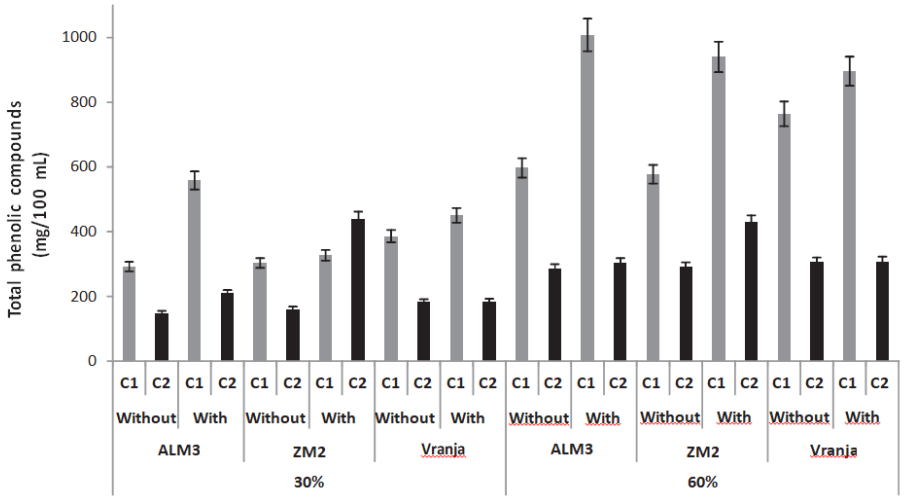

Fig. 1. Total phenolic (mg/100 mL) compounds in quince liquors. C1 and C2 mean quince:ethanol ratio of 50:50 and 25:75, respectively. "Without" and "with" mean liquors macerated using quince fruits without or with skin. 30% and 60% indicate the final alcohol percentage of the quince liquors; error bars indicate the standard deviation of the mean.

and the technological aspects [alcohol content (30% or 60%), ratio fruit:ethanol (C1 or C2), and maceration using fruits with or without skin. The highest contents of total phenolic compounds were found in the liquors prepared using *Vranja* and *ZM2* fruits (means of 434 and 433 mg/100 mL, respectively) compare to a mean content of 425 mg/100 mL in *ALM3* liquors. Liquors prepared from fruits with skin had about 1.4 times more phenolic com- pounds than liquors prepared only using the pulp of quinces (means of 504 and 358 mg/100 mL, respectively). The liquors obtained using the ratio 50:50 of quince:ethanol were characterized by higher total polyphenols content than those of 25:75 liquors (means of 592 and 270 mg/100 mL, respectively) because quince fruits are a rich source of polyphenols (Wojdyło, Oszmiański, & Bielicki, 2013; Wojdyło, Oszmiański, Teleszko, *et al.*, 2013). As expected, liquors with 60% alcohol content had significantly ($p < 0.05$) higher content of phenolic compounds than liquors containing 30% alcohol content (means of 558 and 303 mg/100 mL, respectively); this is normal because 30% liquors were obtained after dilution of 60% alcohol liquors with sucrose and distillate water.

The relatively high contents of total phenolic compounds finally found in the commercial liquors (30% alcohol) could be related to the fact that ethanol was a good extracting solvent for phenolic compounds from plants (Roby, Sarhan, Selmin, & Khalel, 2013). Abad-García *et al.*, (2007) conducted a study to optimize the extraction of phenolic compounds from fruits. These authors concluded that with increasing ethanol concentration increased efficiency of extraction of all the groups of polyphenolic compounds due to two factors: the polarity of the alcohol and its polyphenoloxidase (PPO) inhibition property. Later Chew *et al.*, (2011), Xu, Bao, Gao, Zhou, and Wang (2012) showed that ethanol concentration should be between 40% and 60% and the yield of the process depends also on the ratio of solvent to sample, temperature and extraction time. In grape wine high level of phenolic compounds was reported after long prefermentative maceration of mash because these com- pounds are mainly located in the grape skins (Ramey, Bertrand, Ough, Singleton, & Sanders, 1986). These are the reasons why a high alcohol content, 60%, and the factor with or without skin were used for the maceration of quince fruits.

The total polyphenol content found in commercial quince liquors, 30% alcohol content (303 mg/100 mL) was an order of magnitude above the values reported in other promising herb liquors (Vázquez-Araújo *et al.*, 2013). These authors reported values within the range 20.5–33.2 mg gallic acid equivalents/ 100 mL. Similar values to the ones found in quince liquor were also reported by Mena, Gironés-Vilaplana, Martí, and García-Viguera

Table 2
Content of flavan-3-ols (mg/100 mL) in quince liquors.

Alcohol (%)	Variety	Skin	Conc.[t]	PP[t]	PB1[t]	C[t]	PB2[t]	E[t]	PC1[t]	Total flavan-3-ols	DP[t]
30	*ALM3*	Without	C1	11.5	36.8	3.13	27.6	8.82	189	277	1.7
			C2	17.6	7.80	6.98	4.50	86.2	24.3	147	2.3
		With	C1	32.8	120	27.5	23.6	128	47.1	378	2.1
			C2	22.9	25.7	10.7	7.51	57.1	21.8	146	3.9
	ZM2	Without	C1	21.6	33.7	3.80	30.6	101	72.0	262	1.7
			C2	20.4	18.9	13.9	7.67	45.1	39.4	145	3.5
		With	C1	31.0	32.4	19.8	14.2	31.2	30.9	159	1.9
			C2	66.7	53.6	42.8	29.5	70.6	79.0	342	1.3
	Vranja	Without	C1	20.5	84.8	6.12	23.9	167	49.9	352	2.9
			C2	17.9	40.8	2.41	11.7	75.7	22.6	171	3.2
		With	C1	20.0	115	4.04	31.5	143	46.7	361	2.6
			C2	23.5	40.5	1.16	9.58	57.3	13.5	145	3.9
60	*ALM3*	Without	C1	16.2	95.8	10.3	62.0	272	112	569	2.4
			C2	11.4	25.6	9.25	15.0	172	49.6	283	3.1
		With	C1	34.3	185	55.0	40.6	248	101	664	1.5
			C2	17.0	29.0	1.23	18.1	115	nd[t]	180	2.0
	ZM2	Without	C1	22.0	74.2	10.8	69.0	193	137	506	1.7
			C2	15.6	21.8	19.6	31.9	88.7	84.1	262	1.9
		With	C1	50.8	128	11.2	121	138	161	610	1.3
			C2	21.8	28.5	19.2	39.3	63.2	63.8	236	1.5
	Vranja	Without	C1	12.8	182	10.0	64.9	330	96.0	696	1.8
			C2	10.4	49.9	15.1	12.6	151	46.4	286	2.2
		With	C1	15.3	239	8.28	74.6	287	92.8	716	1.7
			C2	12.7	45.5	12.7	16.4	118	27.8	233	2.1
		Alcohol									
			30	20.0b[¥]	50.9b	11.9b	18.5b	80.9b	53.0b	241b	1.9b
			60	25.5a	92.0a	15.2a	47.1a	181a	80.9a	437a	2.6a
		Variety									
			ALM3	20.5b	65.7b	15.5b	24.9c	136b	68.1b	330b	2.4ab
			ZM2	31.3a	48.9c	17.6a	42.9a	91.3c	83.3a	315c	1.9b
			Vranja	16.6c	99.7a	7.48c	30.6b	166a	49.4c	370a	2.6a
		Skin									
			Without	16.5b	56.0b	9.27b	30.1b	141a	76.8a	330b	2.4a
			With	29.1a	86.9a	17.8a	35.5a	121b	57.1b	348a	2.2a
		Concentration									
			C1	24.1a	111a	14.2a	48.6a	171a	94.5a	462a	1.9b
			C2	21.5b	32.3b	12.9b	17.0b	91.7b	39.4b	215b	2.6a

[t] C1 and C2 mean quince:ethanol ratio of 50:50 and 25:75, respectively.

[t] PP = polymeric procyanidins; C = (+)-catechin; E = (-)-epicatechin; PB1 = procyanidin B1; PB2 = procyanidin B2; PC1 = procyanidin C1; DP = degree of polymerization; nd = not detected.

[¥] Mean values followed by different letters are statistically different at $p < 0.05$.

(2012) in pomegranate wine, range between 200 and 400 mg/ 100 mL. However, the content of these compounds in final product strongly depend on variety (Mena *et al.,* 2012).

The major polyphenolic groups in quince liquors were flavan- 3-ols (mean of 339 mg/100 mL for all studied samples) followed by hydroxycinnamic acids (mean of 141 mg/100 mL) and flavonols (93.4 mg/100 mL). The composition and contents of the polyphenols detected in the quince liquors were similar to those previously reported in fresh quinces from different cultivars and in quince-based products (Silva *et al.,* 2002; Wojdyło, Oszmiański, & Bielicki, 2013; Wojdyło, Oszmiański, Teleszko, *et al.,* 2013; Wojdyło, Teleszko, & Oszmiański, 2014). Flavan-3-ols, hydroxycinnamic acid and flavonols represented, respectively, 59.1%, 24.6% and 16.3% of total polyphenols in quince commercial liquors; however, their contents were strongly influenced by cultivar and technological factors.

Table 2 presents the results from UPLC-PDA and UPLC-FL analysis of individual catechins, dimeric, trimeric and polymeric procyanidins in the different types of liquors. It can be noted that there is marked difference in the levels of monomers, dimers, trimers and polymeric procyanidins among the different liquor-making technologies. As expected, the contents of these compounds were higher in the 60% liquors (437 and 241 mg/100 mL, respectively) than in the commercial-like 30% liquors. Besides, the contents of flavan-3-ols were always higher in liquors with a ratio quince:ethanol 50:50, this is with higher proportion of fruit compared to alcohol (462 and 215 mg/100 mL, for ratio 50:50 and 25:75, respectively). Additionally the content of flavan-3-ols was dependent on quince variety, with *Vranja* liquors having the highest total content of flavan-3-ols but not for all compounds; for instance *ZM2* liquors had higher contents of polymeric procyanidins, (+)-catechin, procyanidin B2, and procyanidin C1. The factor "skin" influenced the individual contents of flavan-3-ols but not too much the total content (348 compared to 330 mg/100 mL in liquors macerated with quince fruits with and without skin, respectively). These results agreed well with those obtained previously by Sun, Spranger, Roque Do Vale, Leandro, and Belchior (2001) who studied Tinta Miuda red wines, and concluded that the concentration of each galloylated procyanidin is dependent on the winemaking technology.

In general, it can be seen that quince liquors contained higher concentrations of monomeric and dimeric flavan-3-ols than of polymeric proanthocyanidins. This pattern is completely the oppo- site of that previously reported in quince juices (Wojdyło, Teleszko,& Oszmiański, 2014); in the case of juices, polymeric procyanidins were more abundant than monomeric and dimeric catechins. Probably during maceration of quince fruits in ethanol, (-)-epicatechin and (+)-catechin dimers and trimers experienced depolymerization

Table 3
Content of hydroxycinnamic acids (in mg/100 mL) in quince liquors.

Alcohol (%)	Variety	Skin	Conc.[t]	NA[t]	4-*p*-COU[t]	ChA[t]	CA[t]	3,5-CA[t]	Total hydroxycinnamic
30	*ALM3*	Without	C1	4.65	0.56	7.89	0.90	0.03	14.1
			C2	0.26	0.06	0.38	0.14	0.00	0.84
		With	C1	14.9	1.42	51.6	3.86	0.76	72.5
			C2	5.15	0.41	12.3	1.06	0.22	19.1
	ZM2	Without	C1	11.1	1.30	23.6	2.03	0.05	38.0
			C2	4.41	0.43	8.07	0.69	0.01	13.6
		With	C1	27.1	3.06	65.4	4.60	0.24	100
			C2	7.79	0.80	23.4	1.50	0.07	33.6
	Vranja	Without	C1	11.4	2.09	16.1	2.67	0.04	32.4
			C2	4.35	0.67	4.63	0.84	nd[t]	10.5
		With	C1	20.8	4.16	32.3	5.85	0.13	63.2
			C2	8.91	1.56	12.8	1.78	0.10	25.1
60	*ALM3*	Without	C1	9.17	0.56	15.6	0.76	0.07	26.1
			C2	0.21	0.43	0.37	0.06	0.01	1.07
		With	C1	29.0	2.25	99.7	5.93	0.32	137
			C2	5.76	0.26	24.7	1.83	0.52	33.0
	ZM2	Without	C1	21.3	0.69	45.5	2.33	0.27	70.0
			C2	6.89	0.83	17.2	0.57	0.03	25.5
		With	C1	55.2	2.65	135	5.75	0.10	199
			C2	12.3	0.82	47.1	2.47	0.13	62.9
	Vranja	Without	C1	22.8	4.86	33.2	5.95	0.01	66.8
			C2	6.47	0.88	9.79	1.62	nd	18.8
		With	C1	41.4	7.30	65.3	12.4	0.22	127
			C2	15.1	1.82	28.4	3.99	0.21	49.4
		Alcohol							
			30	10.1b[¥]	1.38b	21.5b	2.16b	0.14a	37.9b
			60	18.8a	1.95a	43.5a	3.63a	0.16a	69.9a
		Variety							
			ALM3	8.63c	0.74c	26.6b	1.82c	0.24a	40.4c
			ZM2	18.3a	1.32b	45.6a	2.49b	0.11b	69.7a
			Vranja	16.4b	2.92a	25.3c	4.38a	0.09b	51.6b
		Skin							
			Without	8.58b	1.11b	15.2b	1.55b	0.04b	28.8b
			With	20.3a	2.21a	49.8a	4.25a	0.25a	79.0a
		Concentration							
			C1	22.4a	2.58a	49.3a	4.42a	0.19a	80.8a
			C2	6.46b	0.75b	15.8b	1.38b	0.11a	27.0b

[t] C1 and C2 mean quince:ethanol ratio of 50:50 and 25:75, respectively.

[t] NA = neochlorogenic acid; 4-*p*-COU = 4-*p*-coumaroylquinic acid; ChA = chlorogenic acid; CA = cryptochlorogenic acid; 3,5-CA = 3,5-*O*-dicaffeoylquinic acid; nd = not detected.

[¥] Mean values followed by different letters are statistically different at $p < 0.05$.

and were converted into their elementary units. A similar effect has previously been observed in other alcoholic products or blueberry products (Brownmiller, Howard, & Prior, 2009).

The mean degree of polymerization (DP; number of flavan-3-ol units) affects the physicochemical properties of procyanidins (Hamauzu, Yasui, Inno, Kume, & Omanyuda, 2005). The DP of the polymeric fraction in quince liquors was always lower than 4 (Table 2), with *Vranja* liquors having the highest value (2.6) of all studied quince varieties. Additionally technologically variant had a significance impact on DP value. The DP of the polymeric fraction in quince fruit was from 8.3 to 11.2, with a mean value of 9.7 (Wojdyło, Oszmiański, & Bielicki, 2013), and in quince juices it ranged from 2.5 to 13.5 (Wojdyło, Teleszko, & Oszmiański, 2014). Therefore, the degree of polymerization was significantly lower in juices compared to fresh fruits and in liquors than in juices. The lower DP value means that quince liquors are characterized by lower astringency than their main ingredient, quince fruits. Bitterness and astringency in fruits and fruit-based products depend on the flavanol contents, DP, and the residual pectin (Vidal *et al.*, 2004).

Considering the three groups of phenolic compounds (flavan-3-ols, hydroxycinnamic acids, flavonols), hydroxycinnamates were found as the second most abundant group in the quince liquors. The main compounds in this group were: chlorogenic acid > neochlorogenic acid > cryptochlorogenic acid > 4-*p*-coumaroylquinic acid > 3,5-*O*-dicaffeoylquinic acid (Table 3). Hydroxycinnamic acids were found at the highest level in *ZM2* liquors (total content of 69.7 mg/100 mL) followed by *Vranja* (51.6 mg/100 mL) and finally *ALM3* (40.4 mg/100 mL). The concentration of this chemical group also increased when fruits were macerated with skin (79.0 mg/100 mL compared to only 28.8 mg/100 mL in products without skin) and at with the highest proportion of fruits, ratio 50:50 fruit:ethanol (80.8 mg/100 mL compared to only 27.0 mg/ 100 mL in products prepared using the ratio 25:75).

It is not surprising to note that liquors after maceration with skinned fruits contained the highest concentrations of the major flavonols, such as quercetin and kaempferol derivatives. These results clearly indicate the greater contribution of skin to the flavonols composition of quince liquors compared to that of the fruit pulp. The content of flavonols has been proved to be significantly higher in the skin than in the pulp of quince fruits (Silva *et al.*, 2002; Silva, Andrade, Valentão, *et al.*, 2004). The contents of flavonols in liquors made with or without skin were 79.78 and 1.50 mg/100 mL of liquors, respectively (Table 4); this is the content was more than 50 times higher in the skin-macerated liquors. The effect of maceration with or without quince skin was particularly evident in the case of quercetin-3-*O*-rutinoside (62.0 and 0.54 mg/100 mL, respectively) and quercetin-3-*O*-glucoside. As expected, 60% liquors prepared with the higher proportion of fruits (C1) had higher flavonols contents that 30% liquors prepared using the 25:75 quince:ethanol ratio. Finally it is also very interesting to

Table 4
Content of flavonols (in mg/100 mL) in quince liquors.

Alcohol (%)	Variety	Skin	Conc.[t]	Q-GAL[t]	Q-RUT[t]	Q-GLU[t]	K-GAL[t]	K-RUT[t]	K-GLU[t]	Q-GLU-*p*-CUM[t]	K-GLU-*p*-CUM[t]	Total flavonols
30	*ALM3*	Without	C1	nd	0.33	0.05	0.09	nd	nd	0.55	nd	1.01
			C2	0.03	0.25	nd	nd	nd	nd	0.15	nd	0.43
		With	C1	5.18	84.6	11.5	1.24	1.30	2.03	0.54	0.65	107
			C2	2.15	34.8	5.00	0.31	0.64	0.82	0.16	0.15	44.1
	ZM2	Without	C1	0.04	0.35	0.06	0.33	0.42	0.65	0.32	1.05	3.22
			C2	0.01	0.26	0.04	0.04	0.14	0.23	0.22	0.54	1.49
		With	C1	3.48	52.2	6.17	0.32	0.64	3.65	0.83	0.46	67.7
			C2	3.00	49.8	7.72	0.68	1.01	1.24	0.36	0.20	64.0
	Vranja	Without	C1	nd[t]	0.51	nd	0.26	0.32	0.46	0.03	0.41	2.00
			C2	nd	0.24	nd	0.20	0.23	0.12	0.03	0.15	0.97
		With	C1	0.84	18.1	2.82	0.23	0.51	2.56	0.47	0.69	26.2
			C2	0.39	8.83	1.53	0.13	0.35	1.18	0.11	0.47	13.0
60	*ALM3*	Without	C1	nd	0.94	nd	nd	nd	nd	nd	1.04	1.98
			C2	nd	0.73	nd	nd	nd	nd	nd	nd	0.73
		With	C1	10.1	163	22.5	2.19	3.16	3.8	1.22	0.59	207
			C2	4.36	70.9	10.3	0.83	1.56	1.96	0.55	nd	90.4
	ZM2	Without	C1	nd	0.57	nd	nd	nd	nd	nd	0.33	0.90
			C2	0.87	1.06	0.13	0.96	0.05	nd	nd	nd	3.07
		With	C1	7.14	106	12.9	0.87	1.48	1.73	0.90	nd	131
			C2	6.04	101	15.9	1.44	2.28	2.49	0.68	nd	130
	Vranja	Without	C1	nd	0.81	nd	nd	nd	nd	nd	0.75	1.56
			C2	nd	0.48	nd	nd	nd	nd	nd	nd	0.48
		With	C1	1.65	36.5	6.16	0.50	1.02	5.22	1.86	nd	52.9
			C2	0.79	18.5	3.41	0.26	0.73	nd	1.06	nd	24.8
		Alcohol										
			30	1.26b[¥]	20.9b	2.91b	0.32b	0.46b	1.08b	0.31b	0.39a	27.6b
			60	2.58a	41.7a	5.93a	0.59a	0.86a	1.27a	0.52a	0.23b	53.7a
		Variety										
			ALM3	2.72a	44.5a	6.17a	0.58a	0.83a	1.08c	0.40a	0.31a	56.6a
			ZM2	2.57b	38.9b	5.36b	0.58a	0.75b	1.25a	0.41a	0.32a	50.1b
			Vranja	0.46c	10.5c	1.74c	0.20b	0.40c	1.19b	0.45a	0.31a	15.2c
		Skin										
			Without	0.08b	0.54b	0.03b	0.16b	0.10b	0.12b	0.11b	0.36a	1.50b
			With	3.76a	62.0a	8.82a	0.75a	1.22a	2.23a	0.73a	0.27a	79.8a
		Concentration										
			C1	2.37a	38.7a	5.18a	0.50a	0.73a	1.68a	0.56a	0.13b	50.2a
			C2	1.47b	23.9b	3.66b	0.41b	0.58b	0.67b	0.28b	0.50a	31.1b

[t] C1 and C2 mean quince:ethanol ratio of 50:50 and 25:75, respectively.

[t] Q = quercetin; K = kaempferol; GAL = galactoside; GLU = glucoside; RUT = rutinoside; *p*-CUM = acylated by *p*-coumaric acid; nd = not detected.

[¥] Mean values followed by different letters are statistically different at $p < 0.05$.

Table 5
Antioxidant activity (mmol Trolox/100 mL) in quince liquors.

Alcohol (%)	Cultivar	Skin	Concentration	ABTS	DPPH	FRAP
30	*ALM3*	Without	C1[t]	2.93	4.07	2.79
			C2	2.87	2.51	1.11
		With	C1	3.08	9.76	12.7
			C2	2.94	5.28	3.59
	ZM2	Without	C1	2.98	6.21	6.88
			C2	2.94	4.27	2.71
		With	C1	3.00	7.69	7.08
			C2	3.16	11.5	17.8
	Vranja	Without	C1	2.94	4.74	3.62
			C2	2.92	3.58	1.32
		With	C1	2.97	7.05	6.89
			C2	2.90	4.44	2.48
60	*ALM3*	Without	C1	2.96	6.00	6.00
			C2	2.91	3.51	1.13
		With	C1	3.25	14.7	26.1
			C2	3.04	8.17	8.62
	ZM2	Without	C1	3.06	9.78	14.3
			C2	3.01	6.52	6.31
		With	C1	3.35	16.0	37.1
			C2	3.11	11.23	15.3
	Vranja	Without	C1	3.01	7.02	8.15
			C2	2.94	5.28	4.03
		With	C1	3.09	10.6	15.3
			C2	2.94	6.81	6.30
		Alcohol				
			30	2.97b[t]	5.92b	5.74b
			60	3.06a	8.80a	12.4a
		Variety				
			ALM3	3.08a	6.75b	7.75b
			ZM2	3.00ab	9.14a	13.4a
			Vranja	2.96b	6.19b	6.01b
		Skin				
			Without	2.96b	5.29b	4.86b
			With	3.07a	9.42a	13.3a
		Concentration				
			C1	3.05a	8.63a	12.2a
			C2	2.97b	6.09b	5.89b

[t] C1 and C2 mean quince:ethanol ratio of 50:50 and 25:75, respectively.

[t] Mean values followed by different letters are statistically different at $p < 0.05$.

remark that *Vranja* liquors had significantly lower total flavonols content (15.2 mg/100 mL) than *ZM2* (50.1 mg/100 mL) and *ALM3* (56.6 mg/100 mL) liquors.

3.3. Antioxidant activity

To conduct a complete evaluation of the antioxidant activity of a specific product, such as quince liquor, two or more analytical methods should be used to achieve appropriate information. Consequently, three *in vitro* assays, $ABTS^{\bullet+}$, DPPH and FRAP, were used to properly evaluate the antioxidant activity of varietal quince liquors (Table 5). The $ABTS^{\bullet+}$ method seems less sensitive than the DPPH and FRAP assays to the changes observed in the antioxidant activity of quince liquors; for instance, values in the $ABTS^{\bullet+}$ method varied in a narrow range, 2.87–3.35 mmol Trolox/100 mL.

In this study, positive correlations were observed among the total polyphenol content and the antioxidant activity measured by the by $ABTS^{\bullet+}$ ($R^2 = 0.6297$), DPPH ($R^2 = 0.6535$) and FRAP ($R^2 = 0.6602$) assays. These positive correlations showed that most of the antioxidant activity of quince liquors comes from their content in polyphenolic compounds.

In general, liquors from *ZM2* fruits showed significantly ($p < 0.05$) higher antioxidant potential than those of *ALM3* and *Vranja* fruits (e.g. 13.43, 7.75, and 6.01 mM Trolox/100 mL in the FRAP assay, respectively). This significant impact of fruit cultivar on antioxidant activity has also been previously described by other authors in other fruits and it was attributed to their phytochemical composition (Mena *et al.*, 2012; Vázquez-Araújo *et al.*, 2013). As expected the antioxidant activity was higher in 60% liquors prepared using a higher proportion of quince fruits (ratio 50:50 quince:ethanol). Besides, the use of fruits with skin during maceration significantly improved the antioxidant activity of the liquors, according to all methods assayed. Kelebek, Selli, Canbas, and Cabaroglu (2009), Pérez-Gregorio, Regueiro, Alonso-González, Pastrana-Castro, and Simal-Gándara (2011) show that winemaking processes could severely alter the antioxidant activity of fruit wine. Additionally quince liquors kept very high antioxidant activity values in the commercial samples (those adjusted to 30% alcohol content): 29.7, 59.2, and 57.4 mmol Trolox, in the $ABTS^{\bullet+}$, DPPH and FRAP assays, respectively. Mena *et al.*, (2012) reported values of antioxidant activity in pomegranate wine by two methods, $ABTS^{\bullet+}$, DPPH; their results moved in the ranges 18–40 and 7– 20 mmol Trolox. The values of the antioxidant activity of quince liquors proved to be higher than that of pomegranate wine, especially when DPPH data is used. The high values of the antioxidant activity of the quince liquor suggest the promising potential of these new alcoholic beverages.

4. Conclusion

The polyphenolic compounds and antioxidant activity together with influence of variety and manufacturing factors were moni-

tored in quince liquors. Liquors prepared using fruits from the Spanish clone ZM2 had the highest antioxidant activity (3.00, 9.14 and 13.43 mmol Trolox/100 mL in $ABTS^{\bullet+}$, DPPH and FRAP assays, respectively). This high antioxidant activity was linked to their high content of hydroxycinnamic acids (69.7 mg/100 mL) and flavonols (50.1 mg/100 mL). However, the quince variety leading to the highest contents of flavan-3-ols was *Vranja* (370 mg/ 100 mL), while *ALM3* fruits were richer in flavonols. The ratio 50:50 of quince fruit:ethanol and the use of fruits with skin is highly recommended to obtain quince liquors with the highest content of polyphenolic compounds and antioxidant activity. The skin of quince fruits is the main source of hydroxycinnamic acids and especially flavonols; more than 50 times higher content of flavonols (79.8 mg/100 mL) were found in liquors from whole fruits as compared with those obtained using peeled quinces. It has been clearly proven that the polyphenols content in this type of product is largely responsible for their antioxidant capacity. Finally, the high values of the antioxidant activity and polyphenolic compounds of the quince liquor suggest the promising potential of these new alcoholic beverages.

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Kinetics, biocompounds, antioxidant activity, and sensory attributes of quinces as affected by drying method

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A B S T R A C T

Quinces are attracting interest due to their health and nutritional benefits. Drying kinetics, bioactive compounds, antioxidant activity, and the main sensory parameters were determined in dried quinces, cultivar *Leskovač*, as affected by the drying method. The highest total polyphenols content was observed in dried samples obtained after freeze drying and convective drying at 50 °C. The best drying treatment, considering only sensory attributes, was vacuum-microwave drying at 480 W, because it led to intermediate dark color and high intensities of basic tastes and key flavor attributes. The studied parameters were finally used to recommend convective drying at 60 °C as the most appropriate drying method for quinces, because it had a high content of total phenolic compounds (2nd best treatment out of 10), a good sensory profile, was cheap, and caused no negative effects on nutritional or sensory parameters; the only disadvantage was its long drying time.

1. Introduction

Quince (*Cydonia oblonga* Miller) fruits are not fully appreciated as fresh products because of pulp hardness and fiberness, bitterness, and especially their astringency. But when ripe, they are highly demanded for manufacturing marmalades, jams, jellies, and cakes (Silva *et al.*, 2005). Quinces have low fat content and are an important source of organic acids, sugars, crude fiber, and minerals (K, P, and Ca), as well as other health-promoting constituents, such as phenolic compounds (Fattouch *et al.*, 2007; Wojdyło, Oszmianski, & Bielicki, 2013). They are known to have hypoglycemic, antiinflammatory, anticarcinogenic, antimicrobial, antiallergic, and antiulcerative properties, and act as a tonic for heart and brain (Fattouch *et al.*, 2007; Shinomiya, Hamauzu, & Kawahara, 2009).

In recent years, consumers' preferences seemed to have changed towards higher consumption of processed fruit products, especially fruit snacks. Up to now, dehydration is the most commonly used method to extend fruits and vegetables shelf life. Drying is used for the reduce moisture content of fruits and vegetables, aiming to an efficient preservation and long storage; this improved storage is based on the prevention of microorganisms' development. Another advantage is cheaper and easier transport due to reduced weight and volume (Tzampelikos, Vouros, Bardakas, Filios, & Margaris, 2014; Wojdyło, *et al.*, 2016). However, the drying of fruits is a complex process, which involves simultaneous heat and mass transfer in transient conditions. The knowledge of the heat and mass transfer mechanisms related to the process and the role of the drying parameters has a direct impact on the improvement of the dehydrated product quality (Tzampelikos *et al.*, 2014).

Freeze-drying (FD) is supposed to be the best drying method be- cause it produces high quality dried items, with sensory and nutritional properties resembling those of the fresh products, and finally with good rehydration capacity. However, it is very expensive and slow, has a high-energy consumption, and requires big investment due to the need of modern and expensive refrigeration and vacuum systems (Huang, Zhang, Yan, Mujumdar, & Sun, 2009). On the other hand, convective drying (CD) is still the most popular drying method in food industry because it is cheap and requires simple equipment. However, it has several disadvantages: (i) long times are necessary and high temperatures can be reached, (ii) significant degradation of key color and flavor compounds and functional constituents can be lost due to contact with hot air, (iii) the products can suffer severe shrinkage, resulting in tissue collapse (Figiel, Szumny, Gutiérrez-Ortíz, & Carbonell-Barrachina, 2010), and (iv) if fossil-fuel is used to produce hot air, it can adversely

affect climate change.

A modern method, vacuum-microwave drying (VMD) is supposed to overcome the disadvantages of CD (Lin, Durance, & Scaman, 1998). The main advantage of this innovative method is that the applied energy is absorbed by all water molecules in the food; this is, the energy is ap- plied to the whole product and not only to its surface. This drying method creates a puffing phenomenon, which is responsible for a porous texture of dried material (Sham, Scaman, & Durance, 2001). The VMD technique has been successfully used to dehydrate many fruits and vegetables, including cranberries (Sunjka, Rennie, Beaudry, & Raghavan, 2004), strawberries (Krulis, Kuhnert, Leiker, & Rohm, 2005), and tomatoes (Durance and Wang, 2002), among others.

The use of a combined method consisting of a first step of CD (convective pre-drying, CPD) followed by a second step of VM (vacuum- microwave finish drying, VMFD) seems to be a good idea. The CPD stage reduces significantly and fast the initial moisture content of the fruits, without risking their bioactive compounds, and then the VMFD takes the moisture content down to a targeted value, which is ideal for the safe and long storage of the dried products (Durance and Wang, 2002). This combined method has been successfully used to dehydrate jujubes (Wojdyło *et al.*, 2016), pomegranates (Calín-Sanchez, Figiel, Wojdyło, Szarycz & Carbonell-Barrachina, 2014) and apples (Chong, Figiel, Law, & Wojdyło, 2014).

The aim of this study was to check which of the 10 proposed drying methods (CD at 50, 60, 70 °C; VMD at 120, 480, 480–120 W; CPD-VMFD at 50, 60, 70 °C during CPD and 480–120 W during VMFD) was more appropriate for quinces. The suitability of the drying methods was evaluated by analyzing the following parameters: drying kinetics (total drying time and maximum temperature reached), phenolic composition, antioxidant capacity, and key sensory attributes.

2. Materials and methods

2.1. Plant material

Fresh quince fruits (*Cydonia oblonga* Miller, cultivar *Leskovač*) were harvested from the Medical Garden of Wrocław Medical Academy (Wrocław, Poland). 2 kg of quinces were randomly harvested at commercial ripening as determined by fruit color, and change of peel from hairy to waxy appearance (avoiding injured and sunburned fruits) and were processed in October 2013.

2.2. Drying procedures

Just before drying, 2 kg of quince fruits were cut in slices of approximately 3 cm wide and pitted. The moisture content of fresh samples was 7.2 ± 0.3 kg kg^{-1} db (dry basis). Four dehydration technologies were used:

(i) *Convection* (convective drying, CD), using a convective drier designed and built at the Agricultural Engineering Institute of Wrocław (Wrocław, Poland). Hot-air temperature during CD was adjusted at 50, 60, or 70 ± 1 °C, and the air velocity was 1.0 ± 0.1 m s^{-1}.

(ii) *Vacuum-microwave drying* (VMD), using a SM-200 drier, Plazmatronika S.A. (Wrocław, Poland). During VMD, the initial microwave power was set at 120 and 480 ± 2 W (VMD120 and VMD480). However, the tests revealed that during drying at 480 W, sample temperature increased above 100 °C, after the moisture content of 1 kg kg^{-1} db, leading to burned samples. Therefore, before the samples reached this critical moisture content, the microwave power was reduced to 120 W in the treatment VM480-120. In all VMD treatments, the pressure within the VMD chamber ranged between 4 and 6 kPa.

(iii) *Combined drying*, consisting of an initial stage of CPD at 50, 60 or 70 ± 1 °C followed by a final stage of VMFD at 480–120 ± 2 W. VMFD started after 60, 70 or 90 min of CPD for 50, 60 or 70 °C, respectively; this is, when the moisture content of the material being dried was around 2 kg kg^{-1} db. In the case of combined CPD- VMFD the reduction of microwave power from 480 to 120 W was applied before the samples reached the moisture content of kg kg^{-1} db to prevent reaching excessive sample temperature. The continuation of VMFD at 480 W until lower values of moisture content than the critical one for pure VMD was possible because the temperature of CPD samples was decreased until ambient temperature before VMFD.

(iv) *Freeze-drying* (FD), using a freeze-drier Alpha 1-4 LSC, Martin Christ GmbH (Osterode am Harz, Germany). It was considered as the control treatment, because it is generally admitted that FD leads to dried products of the highest quality (Huang *et al.*, 2009). During FD, the pressure and temperature inside the drying chamber was 0.960 kPa and −60 °C, respectively, while the temperature of heating shelves reached 26 °C. Samples were kept in the drying chamber for 24 h.

These 4 drying technologies led to the final application of 10 drying treatments: 3CD (50, 60 and 70 °C), 3 VMD (120, 480 and 480–120 W), 3 combined methods (CPD-VMFD), and 1 control (FD). The proposed range of parameters determining the conditions of the different drying methods used resulted from the former experience during drying of different plant materials, such as garlic (Calín-Sanchez, Figiel, Wojdyło, Szarycz & Carbonell-Barrachina, 2014), pomegranates (Calín-Sanchez, Figiel, Szarycz *et al.*, 2014), apples (Chong *et al.*, 2014), sour cherries (Wojdyło, Figiel, Lech, Nowicka & Oszmiański, 2014), jujube (Wojdyło *et al.*, 2016), etc. It was found that using of temperatures and micro- wave powers below 50 °C and 240 W in CD and VMD, respectively, caused ineffective drying in terms of time of the process, energy efficiency and quality of the dried product. On the other hand, application of temperatures over 70 °C and microwave powers over 480 W led to negative changes of most quality attributes determined for the dried product.

The initial mass of all the samples to be dried was 60 ± 1 g, and all drying methods continued until the moisture content of the dried samples was below 0.1 kg kg^{-1} db to meet microbial safety requirements.

After drying of quince samples, approximately half of the dried product was posted by fast-courier to Spain for analyzing the sensory profiles, while the rest of the analyses were performed in Poland.

2.3. Modeling of drying kinetics

The drying kinetics was based on mass losses of quince samples. The moisture ratio (*MR*) is defined according to Eq. (1):

$$MR = \frac{M(t) - M_e}{M_0 - M_e} \quad (1)$$

where $M(t)$, M_0 and M_e denote moisture content achieved after drying time t, initial moisture content, and equilibrium moisture content, respectively. The value of equilibrium moisture content (M_e) usually is very low and can be omitted from Eq. (1) without a significant change in the value of *MR* (Dadali, Apar, & Özbek, 2007). The moisture content of the dried samples was determined by drying ground samples in a vacuum dryer (SPT-200, ZEAMiL Horyzont, Krakow, Poland) for 24 h at 60 °C until reaching a constant weight. The decrease in the moisture ratio, *MR*, during drying was described using five drying models (Table 1), which are commonly applied to predict the drying behavior of plant materials.

2.4. Temperature of dried samples

The temperature of the vacuum-microwave treated quince samples (VMD and VMFD) was measured using an infrared camera Flir i50 (Flir

Table 1
Mathematical models applied to the experimental drying curves.

Model	Model equation	References
Modified Page	$MR = A\,e^{-k\,t^{B}}$	Rafie *et al.*, (2010)
Henderson-Pabis	$MR = A\,e^{-k\,t}$	Henderson and Pabis (1961)
Logarithmic	$MR = A\,e^{-k\,t} + B$	Dandamrongrak, Young, and Mason (2002)
Midilli-Kucuk	$MR = A\,e^{-k\,t^{B}} + C\,t$	Midilli, Kucuk, and Yapar (2002)
Weibull	$MR = A - B\,e^{-k\,t^{C}}$	Babalis, Papanicolaou, Kyriakis, and Belessiotis (2006)

Systems Inc., Stockholm, Sweden), just after taking the samples out of the dryer, and only the maximum value was recorded. It is important to remember that during CD and FD, the material temperature never exceeds the temperature of hot air or heating plate, respectively.

2.5. *Identification and quantification of polyphenols*

The quince extract for polyphenols analysis was prepared as de- scribed by Wojdyło *et al.*, (2016) and using the same analytical set up. Identification and quantification of polyphenols in the quince extracts were carried out using an ACQUITY Ultra Performance LC^{TM} system. PDA spectra were measured in the wavelength range 200–600 nm. The runs were monitored at 280 nm for flavan-3-ols and 360 nm for flavonol glycosides. Calibration curves, in the range 0.05–5.00 mg mL^{-1} ($R^2 \geq 0.999$), were conducted using (+)-catechin, (−)-epicatechin, chlorogenic, neochlorogenic, and cryptochlorogenic acids, procyanidin B2 and C1, kaempferol-3-*O*-glucoside, and quercetin-3-*O*-glucoside. Kaempferol and quercetin derivatives were expressed as kaempferol- and quercetin-3-*O*-glucoside, respectively.

2.6. *Antioxidant activity (ABTS^{+} and FRAP methods)*

The antioxidant activity [ABTS^{+} and FRAP (ferric reducing anti- oxidant power)] was analyzed as recently described by Wojdyło *et al.*, (2016), and according to methods by Benzie and Strain (1996) and Re *et al.*, (1999), respectively.

2.7. *Sensory analysis*

Eight highly trained panelists (> 500 h of experience) from Universidad Miguel Hernández de Elche (UMH) participated in this study (Meilgaard, Civille, & Carr, 2007). They have been trained for a variety of fruits and fruit-based products, including fresh quinces (Szychowski, Munera-Picazo, Szumny, Carbonell-Barrachina, & Hernández, 2014). For the current study, the panelists received further orientation on fresh and dried quinces.

The evaluation of quince samples was carried out at UMH facilities using individual booths with a combination of natural and non-natural (fluorescent light, 70–90 fc) and temperature (20 ± 2 °C) during three different sessions. Samples were evaluated in triplicate and the samples order for each panelist was randomized.

The quince samples (3 slices of dried quinces), were served in odor- free, disposable 100 mL plastic glasses with lids for the evaluation; additional samples were available if the panelists requested them. All samples were served at room temperature and unsalted crackers and distillated water were used to clean palates between samples.

Three sessions of 2 h were held for the samples evaluation; all 10 samples (coming from 10 drying treatments) were assayed in each session, with about ~3 min between samples (~8–9 min *per* sample). Quince samples were assessed using descriptive sensory analysis and a total 16 attributes were evaluated and quantified:

- *appearance*: pulp color and color homogeneity;
- *flavor*: sourness, sweetness, bitterness, astringency, quince ID flavor, pineapple, apple/pear, fruity, burnt, aftertaste; and,
- *texture*: hardness, crunchiness, graininess, and fiberness.

A numerical scale, from 0 to 10 with increments of 0.5, was used, where 0 represents no intensity and 10 represents extremely strong intensity.

2.8 *Statistical analyses*

Statistical analyses were performed using SPSS 20.0 for Windows (SPSS Science, Chicago, IL, USA). A basic descriptive statistical analysis was followed by an analysis of variance (ANOVA) test for mean comparisons. The method used to discriminate among the means (Multiple Range Test) was the Tukey procedure at a 95.0% confidence level.

3. Results and discussion

3.1. *Drying kinetics*

The changes in the moisture ratio (*MR*) of quince samples dehydrated by CD at 50, 60 or 70 °C, VMD at 120, 480 and 480–120 W, and by the combined CPD-VMFD consisted of CPD at 50, 60 and 70 °C, followed by MVFD at reduced magnetron power of 480–120 W were presented in Fig. 1A, B and C, respectively. Parameters of models de- scribing the drying kinetics of quinces dehydrated using all these protocols were summarized in Table 2. The modified Page, Midilli-Kucuk, and Weibull were found as the best models taking into account the highest values of R^2 (means of 0.9914, 0.9948, and 0.9904, respectively) and the lowest values of RSME (0.0137, 0.0122, and 0.0271, respectively). However, among them, the modified Page model has the simplest form and has been widely used in other fruits and vegetables and allows easy comparison. This same model was used to predict the drying behavior of many plant materials, such as pomegranates (Calín-Sanchez *et al.*, 2014), pumpkin slices (Alibas, 2007), and apples (Doymaz, 2010). A basic information concerning influence of different drying conditions on drying time, maximum temperature, and final moisture content of quince fruits dehydrated by particular methods was summarized in Table 3.

In the initial stage of CD, a fast loss of water, down to approximately 2 kg kg^{-1} db was observed, regardless of the drying temperature applied (Fig. 1). The second stage caused a reduction in the speed of water removal from quince samples due to a significantly lower drying rate. Increasing the temperature of hot air from 50 to 70 °C decreased the drying time from 300 to 240 min (Table 3). This decrease in the drying time, agreed with the increase of the drying constant *k* of modified Page model, from 0.0076 to 0.0120 (Table 2). The drying time of quince slices was significantly lower than that required to dry other fruits until similar final moisture content, but similar decreases in the drying time was observed when increasing the temperature of hot air. For example, increasing the temperature of hot air from 50 to 70 °C decreased the drying time from 2400 to 840 min in sour cherries (Wojdyło *et al.*, 2014), from 1395 to 225 min in pomegranate arils (Calín-Sanchez *et al.*, 2014), and from 1210 to 450 min in jujubes (Wojdyło *et al.*, 2016).

On the other hand, the increase in microwave power from 120 to 480 W decreased VMD time of quince slices from 120 to 34 min; a similar trend was reported for VMD of jujubes, with drying time being reduced from 112 to 30 min (Wojdyło *et al.*, 2016). Even though the application of VMD in its pure form significantly reduced the drying time, in general the combined CPD-VMFD is recommended for industrial application due to practical and economic reasons (Hu, Zhang, Mujumdar, Xiao, & Jin-cai, 2006). The increase in CPD temperature from 50 to 70 °C decreased the total drying time of the CPD-VMFD quinces from 135 to 112 min.

The final moisture content of dried products was in the range from 1.6 to 0.10 kg kg^{-1} db, depending on the drying conditions applied.

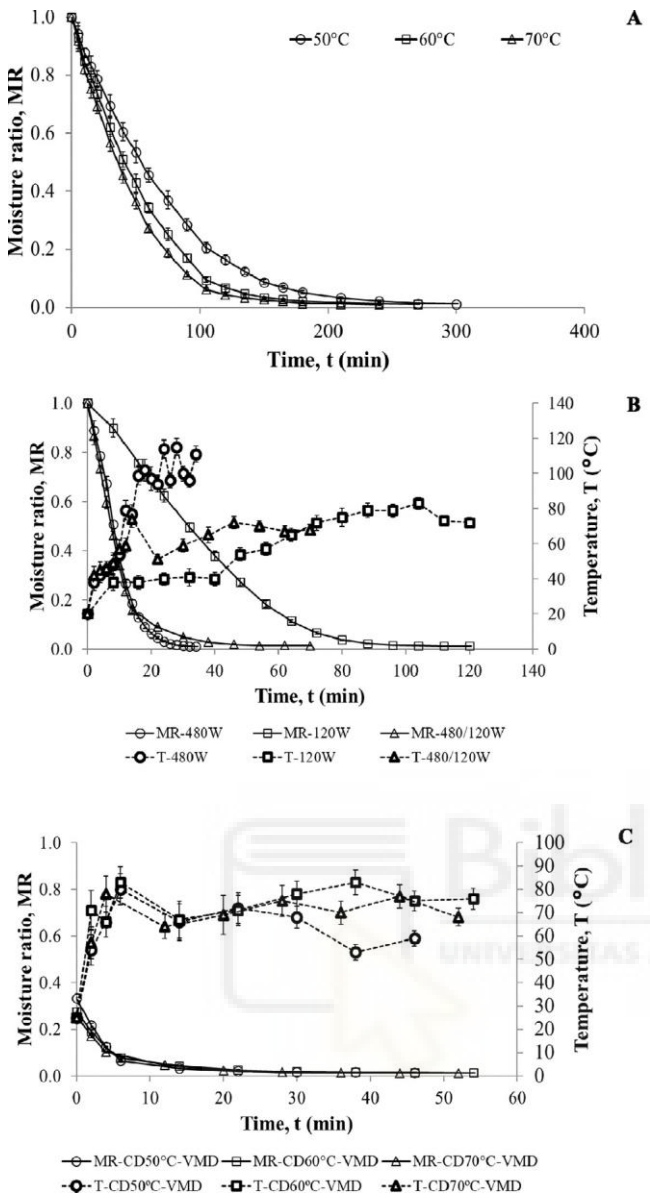

Fig. 1. Drying kinetics of quince samples dehydrated by: CD at temperature 50, 60 and 70 °C (A), VMD at microwave power 120, 480 W and reduced 480–120 W (B), and combined CPD-VMFD at CPD temperature 50, 60 and 70 °C and reduced VMFD power 480–120 W (C); MR, t, and T stand for moisture ratio, time, and temperature, respectively.

This low moisture content guaranteed the microbiological safety of the dried product.

3.2. *Temperature of dried material*

The maximum temperature of the quince slices dried by FD and CD reached the temperature of heating plate, 26 °C, and the temperature of the hot air (50, 60 or 70 °C). In the case of the VMD treatment, the maximum temperature of samples depended on the balance of the energy generated by water molecules inside the material under micro- wave radiation and the energy necessary for water evaporation. For VMD the highest value of the maximum temperature was 115 °C, and it was reached in samples dried at 480 W; whereas the lowest value, 72 °C, was recorded for samples dried at an adjusted power, 480–120 W, reduced microwave power (Fig. 1B). On the other hand, in the combined methods, CPD-VMFD at different CPD temperatures, the maximum temperatures reached were statistically equivalent, and reached a mean of 80 ± 1 °C (Fig. 1C).

3.3. *Identification and quantification of polyphenols compounds in dried quinces*

For fresh quinces of the *Leskovač* variety, Wojdyło *et al.*, (2013) identified 26 polyphenolic compounds, whereas in the current study only 22 were identified by comparing the UV–vis spectra, λ_{max}, MS spectra, and retention times to those of authentic standards (Table 4). The four compounds not identified in the dried quinces were: procyanidin dimer, quercetin-3-*O*-robinoside, quercetin-3-*O*-glucoside, and kaempferol-3-*O*-galactoside. Thus, it is possible that the drying of quinces decreased the complexity of the phenolic profile, especially quercetin and kaempferol derivatives (Table 4) but a different situation will be found for the phenolic content.

Statistical analysis showed that the drying method did not influence the polyphenolic profile (the same compounds were found in all dried quinces), but it affected the amount of each phenolic compound, except for compounds C21 and C22 (Table 5). The total content of phenolic compounds followed the same trend previously reported for phenolic acids, with the mean of all CD, VMD, and CPD-VMFD samples reaching 5183 mg 100 g^{-1} dm, a significantly higher value than that reported in fresh quinces, 3437 mg 100 g^{-1} dm (Wojdyło *et al.*, 2013).

The predominant phenolic family in the dried quinces, independently of the drying method, was flavan-3-ols, with procyanidin B2 (C4) and (−)-epicatechin (C8) being the most abundant compounds. In general, all drying methods induced a higher content of polymeric procyanidins (C6, C7, C12, C13, C14, C17) as compared to FD, being the combined method CPD70-VMFD the one reaching the highest value (2266 mg 100 g^{-1} dm). The higher content of polymeric procyanidins in CD, VMD, and CPD-VMFD could be related to their higher astringency as compared to the control treatment, FD (Wojdyło *et al.*, 2013).

The second major group of polyphenolic compounds in dried quinces was the hydroxycinnamic acids [derivatives of caffeoylquinic acid, especially 5-*O*-caffeoylquinic acid (C3), 3-*O*-caffeoylquinic acid (C1), and 4-*O*-caffeoylquinic acid (C5)]. Individual polyphenols varied greatly among the drying method tested; thus, 5-*O*-caffeoylquinic acid (C3) ranged between 774 and 1325 mg 100 g^{-1} dm in CD70 and CD50 samples, respectively, while 3-*O*-caffeoylquinic acid (C1) ranged be- tween 573 and 1169 mg 100 g^{-1} dm in the same treatments. Comparing these results with those previously obtained by Wojdyło *et al.*, (2013) in fresh fruits of the *Leskovač* variety, all drying methods evaluated increased the content of these phenolic acids. The concentrations of the phenolic acids, especially 5-O-caffeoylquinic acid (C3) may be important when fruits are processed into more complex products, because these compounds are considered to be a preferential natural substrate of the catecholase activity of the polyphenol oxidase. Therefore, the relative concentrations of these compounds could influence the oxidation processes and color development during manufacturing of quince-based products. Besides, they are also considered as flavor precursors and, thus, they can also influence the flavor of the processed products, such as jams or dried products (Guyot, Marnet, Sanoner, & Drilleau, 2003).

The total content of phenolic compounds followed the same trend previously reported for phenolic acids, with the mean of all CD, VMD, and CPD-VMFD samples reaching 5183 mg 100 g^{-1} dm, a significantly higher value than that reported in fresh quinces, 3437 mg 100 g^{-1} dm (Wojdyło *et al.*, 2013). This behavior did not agree with those previously reported in other products, in which total phenolic compounds significantly decreased after the drying process; this was the case of garlic (Calín-Sanchez *et al.*, 2014), jujubes (Wojdyło *et al.*, 2016), among others.

The results obtained in this study showed that the total content of phenolics compounds followed the order FD ≫ CD ≥ CPD- VMFD ≥ VMD, with the treatment CD50 leading to the highest total content of phenolic compounds after the control treatment, FD. Those results could be affected by many complex factors. For instance, CD

Table 2
Parameters of models describing the drying kinetics of quinces as affected by the drying method.

Model	Drying method	Drying conditions	Parameters				Statistics	
			A	*k*	*B*	*C*	RMSE	R^2
Modified Page	CD	50 °C	1.000	0.0076	1.140		0.0108	0.9990
		60 °C	1.000	0.0092	1.170		0.0127	0.9986
		70 °C	1.000	0.0120	1.140		0.0120	0.9987
	VMD	120 W	1.000	0.0037	1.520		0.0124	0.9986
		480 W	1.000	0.0282	1.530		0.0129	0.9984
		480–120 W	1.000	0.0513	1.320		0.0232	0.9950
	CPD-VMFD	50 °C – 480–120 W	0.334	0.2420	0.994		0.0169	0.9728
		60 °C – 480–120 W	0.278	0.3010	0.692		0.0129	0.9761
		70 °C – 480–120 W	0.260	0.3150	0.675		0.0096	0.9858
Henderson-Pabis	CD	50 °C	1.000	0.0139			0.0246	0.9948
		60 °C	1.000	0.0181			0.0282	0.9933
		70 °C	1.000	0.0211			0.0248	0.9948
	VMD	120 W	1.000	0.0269			0.0671	0.9594
		480 W	1.000	0.1030			0.0646	0.9612
		480–120 W	1.000	0.1030			0.0397	0.9855
	CPD-VMFD	50 °C – 480–120 W	0.334	0.2410			0.0157	0.9773
		60 °C – 480–120 W	0.271	0.1850			0.0158	0.9652
		70 °C – 480–120 W	0.251	0.1560			0.0151	0.9661
Logarithmic	CD	50 °C	1.000	0.0140	0.0001		0.0252	0.9945
		60 °C	1.000	0.0183	0.0001		0.0290	0.9929
		70 °C	1.000	0.0212	0.0001		0.0255	0.9944
	VMD	120 W	1.000	0.0271	0.0001		0.0695	0.9562
		480 W	1.000	0.1050	0.0001		0.0666	0.9585
		480–120 W	1.000	0.1080	0.0149		0.0499	0.9853
	CPD-VMFD	50 °C – 480–120 W	0.320	0.2700	0.0164		0.0091	0.9921
		60 °C – 480–120 W	0.259	0.2210	0.0178		0.0076	0.9917
		70 °C – 480–120 W	0.241	0.230	0.0158		0.0082	0.9896
Midilli-Kucuk	CD	50 °C	1.000	0.0080	1.13	−0.0001	0.0111	0.9989
		60 °C	1.000	0.0090	1.17	−0.0001	0.0130	0.9986
		70 °C	1.000	0.0120	1.15	−0.0001	0.0124	0.9987
	VMD	120 W	1.000	0.0039	1.51	−0.0001	0.0126	0.9985
		480 W	1.000	0.0268	1.56	0.0003	0.0122	0.9986
		480–120 W	1.000	0.0492	1.34	0.0004	0.0197	0.9968
	CPD-VMFD	50 °C – 480–120 W	0.333	0.2090	1.12	0.0005	0.0110	0.9881
		60 °C – 480–120 W	0.277	0.2520	0.831	0.0003	0.0102	0.9847
		70 °C – 480–120 W	0.259	0.284	0.763	0.0002	0.0079	0.9899
Weibull	CD	50 °C	1.000	14.49	1.41	−0.677	0.0358	0.9890
		60 °C	1.000	16.05	1.27	−0.796	0.0408	0.9860
		70 °C	1.000	13.94	1.27	−0.785	0.0390	0.9869
	VMD	120 W	1.000	28.90	1.30	−1.01	0.0370	0.9876
		480 W	1.000	11.13	1.16	−1.28	0.0377	0.9867
		480–120 W	1.000	7.30	1.06	−1.20	0.0403	0.9850
	CPD-VMFD	50 °C – 480–120 W	0.331	2.74	0.323	−1.39	0.0063	0.9960
		60 °C – 480–120 W	0.275	2.54	0.271	−1.11	0.0038	0.9979
		70 °C – 480–120 W	0.258	2.18	0.258	−1.03	0.0034	0.9981

drying, especially at lower temperatures effectively preserved polyphenolic compounds (especially phenolic acids), even drying time was longer. Additionally, while drying of quinces by CPD-VMFD and VMD promoted higher contents of a different family, flavonols. This behavior may be due to the fact that a large percentage of phenolic compounds are bound to cellular structures, and during CD there is a release of these bound phytochemicals from the matrix. Wojdyło *et al.*, (2014) showed that content of phenolic acids in the dried sour cherry samples ranged from 74% to 99% of the initial value in fresh fruits; they showed that phenolic acids were more stable during drying than the remaining polyphenols. Similar effects have been observed for quince drying.

Additionally, it was observed that the flavonols content of processed quinces compared with those of the FD samples increased (Table 5). The probable effect of temperature and microwave effects in causing such a change is the breakdown of the cells in the skin and the ex- traction of these compounds on the outside. This effect is beneficial for human health because quercetin has powerful antioxidant properties and protects the body from free radical.

3.4. *Antioxidant activity (AA) of dried quince*

In a previous study with quince liquors, the FRAP method proved to be more efficient than the $ABTS^+$ in describing differences among quince cultivars and manufacturing conditions; however, both methods were capable to measure the changes in the AA of dried quinces and showed similar trends. No statistically significant correlation was found between total polyphenolic content and the AA measured neither by the $ABTS^+$ ($R^2 = 0.3849$) nor the FRAP ($R^2 = 0.4096$) assays. This lack of correlation seemed to imply that other compounds (e.g. Maillard reaction products) than phenolics played a key role in the AA of dried quinces, or/and (ii) the contribution of polyphenols in intermediate stages of oxidation have greater antioxidant power than initially even though this is temporary. Maillard reaction leads to the formation of new compounds, often by a chain-breaking mechanism, with higher AA, especially one of the intermediary products, hydroxymethylfurfural (HMF). The higher the Maillard reaction products content, the higher the AA (Piga, Del Caro, & Corda, 2003). Madrau *et al.*, (2009) also showed that in apricots, cultivar *Cafona*, despite the marked reduction

Table 3
The drying time, maximum temperature and final moisture content of dried quinces as affected by the drying method.

Drying method	Drying conditions	Drying time (min)			Maximum temperature	Final moisture content
		CD	VMD	Total	(°C)	(kg kg^{-1} db)
ANOVA†		***	**		***	NS
CD	50 °C	300a†	0	300a	50e	0.08a
	60 °C	270b	0	270b	60d	0.07a
	70 °C	240c	0	240c	70c	0.06a
VMD	120 W	0	120a	120d	83b	0.09a
	480 W	0	34d	34g	115a	0.08a
	480–120 W	0	70b	70f	72c	0.10a
CPD-VM-FD	50 °C – 480–120 W	90d	46c	136d	80b	0.10a
	60 °C – 480–120 W	70e	54c	124d	83b	0.09a
	70 °C – 480–120 W	60f	52c	112e	78bc	0.08a

† NS = not significant F ratio ($p < 0.05$); *, **, and ***, significant at $p < 0.05$, 0.01, and 0.001, respectively. ‡Treatment means of the ANOVA test (values are the mean of 3 replications). Values followed by the same letter, within the same column, were not significant different ($p < 0.05$), Tukey's multiple-range test.

Table 4
LC–MS QTof analysis of main phenolic compounds in dried quinces.

	Name	R_t (min)	λ_{max} (nm)	MS $[M-H]^-$ (m/z)	MS/MS $[M-H]^-$ (m/z)
C1	3-*O*-Caffeoylquinic	2.31	325	353	191
C2	4-*O*-*p*-acid	3.13	309	337	173/136
C3	5-*O*-Caffeoylquinic	3.48	325	353	191
C4	Procyanidin B2	3.73	278	577	289
C5	4-*O*-Caffeoylquinic	3.86	325	353	173
C6	Procyanidin tetramer	3.95	278	1153	577/289
C7	Procyanidin trimer	4.14	278	865	577/289
C8	(-)-Epicatechin	4.61	278	289	245
C9	*p*-Coumaroylquinic derivatives	4.73	310	337	136
C10	Caffeoylquinic	4.96	324	353	136
C11	Caffeoylshikimic acid	5.01	323	335	179
C12	Procyanidin trimer	5.07	278	865	577
C13	Procyanidin trimer	5.48	278	865	577/289
C14	Procyanidin dimer	5.56	278	577	289
C15	Quercetin-3-*O*-galactoside	7.12	243; 352	463	300
C16	Quercetin-3-*O*-rutinoside	7.24	243; 352	609	301
C17	Procyanidin dimer	7.36	278	577	289
C18	3,5-di-Caffeoylquinic acid	8.21	326	515	353/136/182
C19	Kaempferol-3-*O*-rutinoside	8.35	264; 345	593	285
C20	Kaempferol-3-*O*-glucoside	8.54	264; 345	447	285
C21	Quercetin glucoside acylated by *p*-acid	10.83	242; 352	609	463/301/136
C22	Kaempferol glucoside acylated by *p*-acid	12.08	265, 345	593	285

in phenols, which are in general responsible for the AA in most fruits and vegetables, the chain-breaking activity considerably increased in dried apricots leading to higher AA; while this behavior was not found in another apricot cultivar, *Pelese*.

As expected, the FD samples were those having the higher AA, followed by samples dried using VMD (Fig. 2). The application of CD or CPD significantly reduced the AA of dried quinces. In general and for both AA assays, the treatments can be ordered from the highest to the lowest AA values as follows: FD > VMD > CD≈CPD-VMFD. Within the VMD treatments, those showing the better behavior regarding AA were VMD at 480 W followed by VMD at 120 W. Those results could be affected by many complex factors, as suggested Wojdyło *et al.*, (2014). The lowest antioxidant capacity of the samples dried by CD and CPD-VMFD resulted from intensive oxidation occurred during their relatively long exposure to hot air. The VMD effectively reduced this oxidation effect mainly due to the significantly shorter processing time at a lower air pressure. Another possible explanation was that the poly- phenols in an intermediate state of oxidation can exhibit higher radical scavenging efficiency than the non-oxidized ones, although a sub- sequent loss in the antioxidant properties has been found for advanced enzymatic oxidation steps (Nicoli, Anese, & Parpinel, 1999). Yet, the mechanism of antioxidant capacity changes during VMD of quinces needs more consideration.

3.5. *Sensory analysis*

The first fact that needs to be discussed is that FD was properly selected as the control treatment, because the FD samples were characterized by a yellow (intensity = 0) and homogeneous (9.0) color, intense sour taste (8.5) with very low levels of bitterness (0.7) and astringency (0.3), with very intense quince ID flavor (7.7), and inter- mediate notes of fruity (5.3) and pome fruits (4.5), and no off-flavors being detected (burnt) (Table 6).

A general study of the sensory profiles of the dried samples showed that:

3.5.1. CD preserved well the flavor of the quince samples, by producing the highest mean intensity of the key flavor attributes, such as sourness (5.8, mean of all CD treatments), quince ID (4.9), pome fruits (3.3), and fruity (2.9) notes, but they were also characterized by the presence of a measurable off-flavor intensity, burnt (1.3), and also by the darkest color (7.3).

3.5.2. VMD could be considered as the best general method, because it led to intermediate color intensity (pale brown, 4.8, mean of all VMD treatments), with intermediate values of sourness (4.9), quince ID (4.5), pome fruits (2.9), and fruity (2.5) notes, and with low intensity of the burnt note (0.5).

3.5.3. The combined method, CPD-VMFD, was able to improve the color (4.2, pale green) and to minimize the intensity of the off-flavor burnt (0.2), but decreased the intensity of the key flavor attributes as compared to the CD treatment. The mean intensities of sourness, quince ID, pome fruits, and fruity notes for the VMD samples were 5.3, 4.1, 2.5, and 2.2, respectively.

Samples dried using CD were the darkest ones, with an increase in temperature leading to even darker color; a similar trend was observed with the microwave power in the VMD treatments, but with the adjusted method, VMD 480-120 reducing the browning of the samples. The combination of CPD-VMFD led to the best color of the samples, when air at 60 or 70 °C was used in the CPD step.

The best drying treatment, considering only sensory attributes, could be VMD at 480 W, because it led to intermediate dark color (5.8), but with intensity of basic tastes and flavor attributes very close to those of the control sample, FD. This sample was characterized by high intensity of sourness (7.2), high intensities of the flavor notes: quince ID (5.7), pome fruits (4.3), and fruity (3.8) (Table 6). However, if color is considered as a key attribute or the absence of off-flavors is required, the selection of the best method could be different. Therefore, the final conclusion can be that it is not easy to select the best drying method in a general manner, but it is possible to select the best conditions for each of the drying treatments. In this way, the recommended treatments to dry quince slices were: CD at 60 °C, VMD at 480 W, and CPD at 70 °C – VMFD. This selection was made according to samples being as close as

Table 5
Quantification of individual phenolic compounds (mg 100 g^{-1} dm) in dried quinces as affected by the drying method.

Compound	ANOVA†	FD	CD50	CD60	CD70	VMD120	VMD480	VMD480-120	CPD50-VMFD	CPD60-VMFD	CPD70-VMFD
C1	***	791 d‡	1169 a	1059 b	573 e	929 c	787 d	770 d	787 d	963 c	969 c
C2	***	111 cd	151 a	142 a	88 e	142 a	130 b	109 d	122 bc	151 a	145 a
C3	***	1224 bc	1325 a	1155 d	774 f	1206 bcd	1176 cd	1027 e	1072 e	1243 b	1300 a
C4	***	15,384 a	1020 b	392 b	201 b	442 b	136 b	22 b	90 b	239 b	85 b
C5	***	86 bc	118 a	110 a	54 d	75 c	87 c	76 c	79 c	84 c	106 ab
PP(C6,7,12-14,17)	***	1066 h	2075 bc	1921 d	1375 g	1816 ef	2016 c	2162 b	1874 de	1751 f	2266 a
C8	***	1212 a	315 b	219 c	220c	94 e	70 e	97 de	128 d	343 b	23 f
C9	**	72 a	69 a	64 ab	42 d	71 a	57 bc	53 c	58 bc	64 ab	55 bc
C10	***	76 ab	77 ab	74 ab	50 d	74 ab	66 bc	57 cd	81 a	61 cd	81 a
C11	**	68 ab	60 b	70 ab	74 a	68 ab	70 ab	66 ab	60 b	64 ab	74 a
C15	***	22 bc	20 bc	17 bc	14 c	39 a	40 a	25 b	25 b	35 a	16 bc
C16	***	26 bc	27 bc	24 bc	17 c	28 bc	36b	35b	30 bc	53 a	26 bc
C18	***	57 de	81 a	68 bc	52 de	50 e	61 cd	72 ab	75 ab	70 abc	77 ab
C19	***	115 def	129 de	104 ef	90 f	195 b	223 a	168 c	162 c	241 a	131 d
C20	***	26 def	30 de	25 ef	18 f	39 bc	43 ab	35 bcd	33 cde	51 a	19 f
C21	NS	17	16	16	20	24	21	16	17	24	20
C22	NS	26	19	29	30	22	23	21	25	26	23
Total	***	20,379a	6702 b	5488 c	3691 d	5314 c	5042 c	4810 c	4719 c	5464 c	5416 c

† NS = not significant F ratio ($p < 0.05$); *, **, and ***, significant at $p < 0.05$, 0.01, and 0.001, respectively. ‡Treatment means of the ANOVA test (values are the mean of 3 replications). Values followed by the same letter, within the same row, were not significant different ($p < 0.05$), Tukey's multiple-range test.

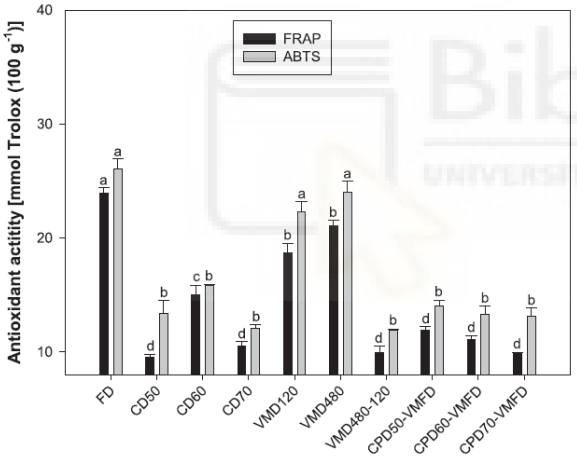

Fig. 2. Antioxidant activity of dried quinces as affected by the drying method.

possible to the profiles of the FD sample.

4. Conclusions

Fresh quinces were dried using convective (CD), vacuum-micro- wave (VMD), a combined method (CPD-VMFD: convective pre-drying followed by vacuum-microwave finish drying), and freeze drying (FD) as the control method. The quince drying kinetics was successfully described by the modified Page model. Twenty-two phenolic com- pounds were identified and quantified in dried quinces, with flavan-3-ols predominating, especially polymeric procyanidins, and procyanidin B2, followed by hydroxycinnamic acid, mainly 5-*O*-cafeeoylquinic and 3-*O*-caffeoylquinic acids. In general, a treatment that led to good results and that is the recommended drying method was CD at 60 °C; it showed the second total content of phenolics (5488 mg 100 g^{-1}), the second best sensory profile (e.g. quince ID 5.7, fruity 2.7, burnt 0,0), inter- mediate antioxidant activity, and its industrial set up is cheap and simple, although long drying time (270 min) was needed.

Table 6
Descriptive sensory analysis of dried quinces as affected by the drying method.

Attribute	ANOVA†	FD	CD50	CD60	CD70	VMD120	VMD480	VMD480-120	CPD50-VMFD	CPD60-VMFD	CPD70-VMFD
Pulp color	***	0.0 g‡	6.5 b	7.5 a	8.0 a	4.8 d	5.8 c	3.8 e	6.5 b	3.2 f	2.8 f
Homogeneity	***	9.0 a	4.8 g	5.0 g	5.2 g	8.0 b	6.3 cd	7.2 bc	5.3 fg	6.8 cd	6.2 ef
Sour	***	8.5 a	6.2 abc	5.7 abc	5.5 bc	4.3 bc	7.2 ab	3.3c	3.7 c	7.0 ab	5.3 bc
Sweet	NS	2.3	2.8	3.2	2.2	2.3	2.7	2.2	2.2	2.8	2.7
Bitter	NS	0.7	0.5	0.5	0.7	0.8	0.5	0.3	0.5	0.3	0.5
Astringent	**	0.3	1.5 a	1.2 a	1.0 a	1.2 a	1.0 a	1.2 a	1.2 a	0.7 ab	1.7 a
Quince ID	**	7.7 a	4.2 b	5.7 ab	5.0 ab	5.0 ab	5.7 ab	2.8 b	3.3 b	4.8 ab	4.0 b
Pineapple	NS	3.2	2.3	2.5	2.7	2.7	2.8	1.2	1.8	2.3	1.8
Pome fruits	*	4.5 a	2.8 abc	3.3 abc	3.8 ab	2.8 abc	4.3 ab	1.5 c	1.7c	3.3 abc	2.5 bc
Fruity	*	5.3 a	2.8 ab	2.7 ab	3.2 ab	2.3 ab	3.8 ab	1.3 b	1.5 b	3.3 ab	1.8 b
Hay	NS	0.0	0.3	0.0	0.3	0.5	0.2	0.8	0.2	0.3	0.0
Woody	NS	0.2	0.5	0.0	0.5	0.5	0.2	0.5	0.2	0.7	0.0
Burnt	***	0.0 b	0.0 b	0.0 b	3.8 a	0.8 b	0.7 b	0.0 b	0.3 b	0.2 b	0.0 b
Aftertaste	NS	2.8	3.0	2.7	2.7	2.7	3.3	2.5	2.7	3.5	2.2
Hardness	NS	0.2	3.7	3.3	4.2	3.5	5.5	2.0	1.8	3.5	3.0
Crunchiness	**	0.0 b	0.3 b	0.8 b	1.5 ab	0.3 b	4.0 a	0.2 b	0.7 b	0.3 b	0.2 b
Graininess	NS	0.0	0.7	0.7	1.3	1.7	0.7	0.5	0.7	1.0	1.3
Fiberness	NS	3.2	4.0	2.8	4.3	4.5	3.0	3.8	4.0	4.0	4.2

† NS = not significant F ratio ($p < 0.05$); *, **, and ***, significant at $p < 0.05$, 0.01, and 0.001, respectively. ‡Treatment means of the ANOVA test (values are the mean of 7 trained panellists). Values followed by the same letter, within the same row, were not significant different ($p < 0.05$), Tukey's multiple-range test.

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Chapter 5.-
Results and discussion

5.1. Quince Liquors (publication 1, *Food Chemistry*, 2015)

In total, **18 polyphenolic compounds** found in quince liquors were identified by LC-MS-QTOF system. Five compounds belonging to flavan-3-ols were detected in quince liquors, two monomers, two dimers and one trimer. (+)-Catechin, (-)-epicatechin, procyanidin B1 and B2 and procyanidin trimer. Five hydroxycinnamates, four derivatives of caffeoylquinic acid and one of coumaroylquinic acid, were detected as well. Neochlorogenic, chlorogenic and cryptochlorogenic acid, 4-O-p-coumaroylquinic acid and 3,5-di-Ocaffeoylquinic acid. quercetin-3-O-galactoside, quercetin-3-O-glucoside, quercetin-3-O-rutinoside, kaempferol-3-O-galactoside, kaempferol-3-O-rutinoside, kaempferol-3-O-glucoside, kaempferol glucoside acylated by p-coumaric acid, quercetin glucoside acylated by p-coumaric acid.

The **total phenolic content** determined by UPLC ranged from 149 to 1008 mg 100 mL^{-1}. The content of total phenolic compounds was significantly ($p < 0.05$) affected by the quince variety and the technological aspects [alcohol content (30% or 60%), ratio fruit:ethanol (C1 or C2), and maceration using fruits with or without skin. Liquors prepared from fruits with skin had about 1.4 times more phenolic compounds than liquors prepared only using the pulp of quinces. The liquors obtained using the ratio 50:50 of quince:ethanol were characterized by higher total polyphenols content than those of 25:75 because quince fruits are a rich source of polyphenols. As expected, liquors with 60% alcohol content had significantly ($p<0.05$) higher content of phenolic compounds than liquors containing 30% alcohol content. This is normal because 30% liquors were obtained after dilution of 60% alcohol liquors with sucrose and distillate water.

Consequently, three *in vitro* assays, ABTS, DPPH and FRAP, were used to properly evaluate the **antioxidant activity** of varietal quince liquors. The ABTS method seems less sensitive than the DPPH and FRAP assays to the changes observed in the antioxidant activity of quince liquors. In this study, positive correlations were observed among the total polyphenol content and the antioxidant activity measured by the by ABTS (R^2=0.6297), DPPH (R^2=0.6535) and FRAP (R^2=0.6602) assays. These positive correlations showed that most of the antioxidant activity of quince liquors comes from their content in polyphenolic compounds.

5.2. Quince Drying (publication 2, *Food Chemistry*, 2018)

The **drying kinetics** was based on mass losses of quince samples. The moisture ratio (MR) is defined according to Eq:

$$M_R = (M(t)-M_e)/M_0-M_e$$

where, *M(t)*, M_0 and M_e denote moisture content achieved after drying time *t*, initial moisture content, and equilibrium moisture content, respectively. The value of equilibrium moisture content (M_e) usually is very low and can be omitted from the previous equation without a significant change in the value of M_R.

The changes in the moisture ratio (M_R) of quince samples dehydrated by CD at 50, 60 or 70 °C, VMD at 120, 480 and 480–120 W, and by the combined CPD-VMFD consisted of CPD at 50, 60 and 70 °C, followed by MVFD at reduced magnetron power of 480–120W were analyzed.

The modified Page, Midilli-Kucuk, and Weibull were found as the best models taking into account the highest values of R^2 (means of 0.9914, 0.9948, and 0.9904, respectively) and the lowest values of RSME (0.0137, 0.0122, and 0.0271, respectively). However, among them, the **modified Page model** has the simplest form and has been widely used in other fruits and vegetables and allows easy comparison.

The CD drying time of quince slices was significantly lower than that required to dry other fruits until similar final moisture content, but similar decreases in the drying time was observed when increasing the temperature of hot air.

Even though the application of VMD in its pure form significantly reduced the drying time, in general the combined CPD-VMFD is recommended for industrial application due to practical and economic reasons. The increase in CPD temperature from 50 to 70 °C decreased the total drying time of the CPD-VMFD quinces.

The maximum temperature of the quince slices dried by **FD** and **CD** reached the temperature of heating plate, **26 °C**, and the temperature of the hot air **(50, 60 or 70 °C)**. In the case of the VMD treatment, the maximum temperature of samples depended on the balance of the energy generated by water molecules inside the material under microwave radiation and the energy necessary for water evaporation.

Statistical analysis showed that the drying method did not influence the polyphenolic profile (the same compounds were found in all dried quinces), but it affected the amount of almost all phenolic compounds. The **predominant phenolic family** in the dried quinces, independently of the drying method, was **flavan-3-ols**, with procyanidin B2 and

and (−)-epicatechin. In general, all drying methods induced a higher content of polymeric procyanidins. The second major group of polyphenolic compounds in dried quinces was the hydroxycinnamic acids.

The results obtained in this study showed that the **total content of phenolics compounds followed the order FD≫CD≥CPDVMFD≥VMD**, with the treatment **CD50** leading to the highest total content of phenolic compounds after the control treatment, FD. Those results could be affected by many complex factors.

Additionally, it was observed that the flavonols content of processed quinces compared with those of the FD samples increased. The probable effect of temperature and microwave effects in causing such a change is the breakdown of the cells in the skin and the extraction of these compounds on the outside. This effect is beneficial for human health because quercetin has powerful antioxidant properties and protects the body from free radical.

No statistically significant correlation was found between total polyphenolic content and the AA measured neither by the $ABTS^{+}$ (R^2=0.3849) nor the FRAP (R^2=0.4096) assays. This lack of correlation seemed to imply that other compounds (e.g. Maillard reaction products) than phenolics played a key role in the AA of dried quinces, or/and (ii) the contribution of polyphenols in intermediate stages of oxidation have greater antioxidant power than initially even though this is temporary. Maillard reaction leads to the formation of new compounds, often by a chain-breaking mechanism, with higher AA, especially one of the intermediary products, hydroxymethylfurfural (HMF).

As expected, the FD samples were those having the higher AA, followed by samples dried using VMD. In general and for both AA assays, the treatments can be ordered from the highest to the lowest **AA values as follows: FD > VMD > CD≈CPD-VMFD**.

The best drying treatment, considering only **sensory attributes**, could be VMD at 480 W, because it led to intermediate dark color (5.8), but with intensity of basic tastes and flavor attributes very close to those of the control sample, FD. This sample was characterized by high intensity of sourness (7.2), high intensities of the flavor notes: quince ID (5.7), pome fruits (4.3), and fruity (3.8).

Chapter 6.- Conclusions / Conclusiones

CONCLUSIONS

The aim of this study was to analyze fresh quinces and, then, try to use different methods of preservation of the fruit as a processed product – liquors and dried fruits. The important factor of these two processed products was to keep as high as possible the level of antioxidant activity and polyphenolic content to preserve their health benefits. Liquors seems as a promising new alcoholic beverage because of its high antioxidant activity and polyphenolic content. In dried quinces it was hard to find correlation between total phenolic content and antioxidant activity. It can be caused by other compounds that played key role in the antioxidant activity. One possibilities are Maillard reaction products. The main conclusions regarding raw quinces, quince-based liquors and dried quince fruits were:

1. PUM clone fruits are better suited for preparation of functional quince-based products because of their high TPC and TAA (e.g. 5810 mg gallic acid kg^{-1} peel and 5430 mg Trolox kg^{-1} peel).
2. Other clones, such as OHM14, ZM6 and OHM13 are appropriate for fresh consumption because of their equilibrated levels of sourness and sweetness and their high quince flavor.
3. The ratio 50:50 of quince fruit:ethanol, and the use of fruits with skin is highly recommended to obtain quince liquors with the highest content of polyphenolic compounds and antioxidant activity.
4. The quince drying kinetics was successfully described by the modified Page model.
5. Twenty-two phenolic compounds were identified and quantified in dried quinces, with flavan-3-ols predominating, especially polymeric procyanidins, and procyanidin B2, followed by hydroxycinnamic acid, mainly 5-O-cafeeoylquinic and 3-O-caffeoylquinic acids.
6. In general, a treatment that led to good results and that is the recommended drying method was CD at 60 °C; it showed the second total content of phenolics (5488 mg 100 g^{-1}), the second best sensory profile (e.g. quince ID 5.7, fruity 2.7, burnt 0,0), intermediate antioxidant activity, and its industrial set up is cheap and simple, although long drying time (270 min) was needed.

CONCLUSIONES

El objetivo de este estudio fue analizar membrillos frescos y, después, emplear distintos métodos de conservación para obtener productos procesados: licores y frutas secas. La meta principal fue mantener, lo más alto posible, el nivel de actividad antioxidante y el contenido polifenólico de estos dos productos procesados, para preservar sus beneficios para la salud. Los licores resultaron ser una nueva bebida alcohólica prometedora debido a su alta actividad antioxidante y su contenido polifenólico. En el caso de los membrillos secos, fue difícil encontrar una correlación entre el contenido fenólico total y la actividad antioxidante. Esto puede ser debido a otros compuestos que jugaron un papel clave en la actividad antioxidante; una de las posibilidades, son los productos de la reacción de Maillard. Las conclusiones principales obtenidas en el estudio llevado a cabo con membrillos crudos, licores a base de membrillo y membrillos secos fueron las siguientes:

1. Las frutas del clon PUM son más adecuadas para la preparación de productos funcionales a base de membrillo, debido a su alto TPC y TAA (por ejemplo, 5810 mg de ácido gálico kg^{-1} de piel y 5430 mg Trolox kg^{-1} de piel).
2. Otros clones, como OHM14, ZM6 y OHM13 son más apropiados para el consumo en fresco, debido a sus niveles equilibrados de acidez y dulzura y su intenso sabor a membrillo.
3. Para obtener licores de membrillo con mayor contenido de compuestos polifenólicos y actividad antioxidante, la proporción más recomendable es la de 50:50 (membrillo:etanol) y el empleo de frutas con piel.
4. La cinética de secado del membrillo fue descrita con éxito siguiendo el modelo de Page modificado.
5. Se identificaron y cuantificaron 22 compuestos fenólicos en membrillos secos, siendo los principales los flavan-3-oles, especialmente procianidinas poliméricas y procianidina B2, seguidos por ácidos hidroxicinámicos, principalmente ácidos 5-*O*-cafeoilquínico y 3-*O*-cafeoilquínico.
6. En general, el tratamiento por el que se obtuvieron los mejores resultados y, por lo tanto, el método de secado recomendado para este tipo de fruta fue CD (secado convectivo) a 60 °C; por este método se obtuvo la segunda concentración más alta de compuestos fenólicos (5488 mg 100 g^{-1}), el segundo mejor perfil sensorial (por ejemplo, membrillo-ID 5,7, afrutado 2,7, quemado 0,0), una actividad antioxidante intermedia y su implantación en la industria es simple y barata, aunque requiere de un largo tiempo de secado (270 min).

Chapter 7.- Future Research

After this PhD dissertation one thing has been demonstrated, quinces are interesting fruits from nutritional and if proper processing is done, there are many more options than just to prepare "*dulce de membrillo*". Then, the most important research lines for the cultivation of quinces are:

- To convince farmers in conducting proper cultivar selection based on how they want to use the final fruits.
- To see how quince trees respond to deficit irrigation strategies, as the climate change is limiting the resources and especially water.
- To keep seeking for new quince-based products, which are adapted to Spanish and international markets and respond to consumer demands and needs.

Chapter 8.- References

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