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THE EVOLUTION OF SOME CHEMICAL COMPOUNDS OF QUINCE (*Cydonia oblonga MILL.)* DURING GROWTH AND RIPENING

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ABSTRACT. *Variations of the main chemical components in quince fruits belonging to the 'Bereczki' cultivar were studied during growth and ripening. The dry matter content, the total soluble solids, the titratable acidity, the total phenolic content, the flavonoid content, and the antioxidant capacity of the fruit were determined. The highest dry matter content was recorded at the maturity of consumption, with the same upward trend observed in fruit content in soluble solids (TSS%). The titratable acidity of quince is increased constantly from the fruit setting (3.68 g malic acid/100 g fw) to the harvest maturity (14.07 g. malic acid/100 g fw). Quince is characterized by a high content of total phenolics, the highest values were recorded at fruit formation (117.92 mg/l). The same variation regarding the flavonoid content was observed, the highest values being obtained at the fruit formation (114.1 mg/l). The antioxidant activity in quince is more intense at the beginning of growth (fruit formation, immature fruit). Therefore, quince shall be grown in larger areas and used both fresh and processed because it is a source of biologically active compounds.*

KEYWORDS: *quince, total phenolics, flavonoids, antioxidant activity*

INTRODUCTION

Quince passes to the Romans as a symbol of Venus, the ancestor of the Roman people. In Romanian cuisine, the high pectin content of quince in combination with honey lays the foundations for all later jellies and jams. Apicius et al. (1991) talks about quinces kept entirely in honey and defrutum, a new wine boiled with spices and evaporated until it reaches half the initial quantity. Quinces (*Cydonia oblonga* Miller*, Rosaceae*) are large-sized seed

fruits (10-12 cm in diameter) and asymmetrical shapes and have a characteristic fragrance (Silva et al. 2004). Due to the complex chemical composition and the interaction between different components, the general antioxidant activity of the quince is high. Silva et al. (2004) compared the antioxidant activity of whole extracts (methanolic extracts) from quince with its two fractions. The phenolic fraction has always shown stronger antioxidant activity than the whole extracts. Fattouch et al. (2007) highlighted the antimicrobial effect of quince pulp and its extracts. As part of an ongoing study on the analysis of phenolic compounds in quince (Andrade et al. 1998, Silva et al. 2002), we have data on the screening of flavonoids in quince seeds. Sancheti et al. (2010) reported the antihyperglycemic, antihyperlipidemic and antioxidant effects of *Chanomeles sinensi*. It should also be noted that in the literature besides *C. oblonga* the name quince is also used for other plants such as the chinese quince (*Pseudocydonia sinensis Schneid*), the japanese quince (*Chaenomeles japonica*), or the flowering quince (*Chaenomeles speciosa (Dulce)* Nakai). The quince fruit (*Cydonia oblonga Miller*) is too acid and astringent; it is not very appreciated for fresh consumption, but it can be consumed and processed as jam, jelly, or stewed fruit (Szychowski et al. 2014). Quince has low-fat content and is an important natural source of phenolic acids and flavonoids (Wojdyło et al. 2013). Polyphenols are natural compounds found in quince, and manufactured products still contain significant amounts of polyphenols. Polyphenols may contribute to fruit bitterness, astringency, flavor, and oxidative activity (Pandey & Rizvi 2009). Antioxidants reduce oxidative damage to biomolecules and cells, being involved in the pathogenesis of certain types of cancer (Valko et al. 2006). In this paper, we aimed to study the evolution of some chemical characteristics of quinces during their growth and ripening.

MATERIALS AND METHODS

Plant material

To achieve the proposed goal, quince fruits belonging to the 'Bereczki' cultivar, organically grown on a private plantation in Dolj county, Romania, were studied. No chemical treatments have been carried out to control diseases and pests. Variety of great vigor, rustic, produces abundantly and constantly. It has a long vegetation period. The fruit is large or very large, ovoid-elongated, or pear-shaped, and has an

unevenly ribbed surface. The flesh is yellow, intensely aromatic, sweet-sour, and pleasant to the taste; consumption period: October - November.

During the growth and ripening of the fruits, samples were taken and analyzed from a chemical point of view. Fruit sampling started from fruit setting (May 5) and continued until consumption maturity (July 7-immature fruits; September 18-cessation of fruit growth; October 20-harvest maturity), the last sampling taking place after fruit harvest respectively, after 20 days of keeping them to complete the ripening (November 11-consumption maturity). In this way, five fruit sampling dates were established, and chemical analyses were performed. The dry matter content, the total soluble solids, the titratable acidity, the total phenolic content, the flavonoid content, and the fruit's antioxidant capacity were determined (Cosmulescu et al. 2018, Ionica et al. 2013). Experiments were executed in three repetitions, and the results were expressed as average ± standard error of the average repetitions.

Analytical methods

The dry matter content (DM) was determined by water evaporation from the analytical average sample kept in an oven (Memmert, Germany) at 105°C; the results were expressed in percent. The soluble solids content (TSS) was determined using a digital refractometer (Hanna Instruments, USA), and the results were expressed in percentage. The titratable acidity (TA) was determined by neutralizing the aqueous extract of quince with sodium hydroxide (0.1n) in the presence of phenolphthalein as an indicator. The results were expressed in g malic acid/100 g fm. The total polyphenolic content was determined using the Folin-Ciocalteu method (Singleton & Rossi 1965, Ionica et al. 2013). Folin-Ciocalteu reagent (2 N, Merck), gallic acid (99% purity, Sigma-Aldrich), and anhydrous sodium carbonate (99% SigmaAldrich) were used. One gram of quince homogenate was extracted with 15 mL of methanol in an ultrasonic bath for 60 minutes at ambient temperature. After extraction, the samples were centrifuged for 5 minutes at 4200 rpm, and the supernatants were filtered through polyamide membranes with a pore diameter of 0.45 pm and stored at -20°C. 100 µl of each methanol extract from quince were mixed with 5 ml distilled water and 500 µl Folin-Ciocalteu reagent. After 30 seconds to 8 minutes, 1.5 ml of sodium carbonate (20% v/v) was added. The reaction mixture was diluted with distilled water to a final volume of 10 ml. The preparation of the standard gallic acid solution followed the same procedure. Absorbance at 765 nm was measured on a Varian Cary 50 UV spectrophotometer (Varian Co., USA) after an incubation of 30 minutes at 40°C, and the results were expressed in mg gallic acid (GAE)/100 fw. The total flavonoid content was measured according to the colorimetric method (Zhishen et al. 1999). An aliquot of 1 ml of standard catechin solution at different concentrations (0-100 mg l, external calibration with n = 6 concentrations) or sample (methanolic quince extracts obtained for the determination of polyphenols) was placed in tubes of 10 ml containing 4 ml of water. 0.3 ml of 5% $NaNO_2$ was added. After 5 minutes, 0.3 ml of 10% $AlCl_3$ was added. At

6 minutes, 2 ml of 1 M NaOH was added. The mixture was immediately made up to a volume of 10 ml with distilled water and stirred vigorously. The absorbance of the mixture was determined at 510 nm. The total quince flavonoid content was expressed in mg/100 g of fresh weight.

Antioxidant activity (AOA) was measured in methanolic extract using the DPPH test (2,2-diphenyl-1-picrylhydrazyl). Methanol (Merck, Germany), DPPH (2,2-diphenyl-1-picrylhydrazyl) (Sigma Aldrich, Germany), and Trolox (Merck, Germany) were used. Sampling was performed according to the protocol for the total polyphenol content. The free radical scavenging capacity of DPPH free radical extracts was evaluated as described by Oliveira et al. (2008), with some modifications (Ionica et al. 2013). Each ethanolic quince extract (50 µl) was mixed with 3 mL of 0.004% (v/v) DPPH methanolic solution. The mixture was incubated for 30 minutes at room temperature in the dark, and the absorbance was measured at 517 nm on a Varian Cary 50 UV-VIS spectrophotometer. DPPH free radical scavenging capacity was calculated with reference to Trolox (6-hydroxy2,3,7,8-tetramethylchroman-2-carboxylic acid), which was used as a standard reference to transform the inhibitory capacity of each solution extract in Trolox mmol equivalent antioxidant activity/L. The radical was freshly prepared and protected from light. A methanol/water control was used in each analysis. All tests were performed in triplicate, and the results were expressed in mmol Trolox/100 g fw.

RESULTS AND DISCUSSIONS

Data regarding the fruit content in dry matter, total soluble solids, and titratable acidity of fruit during growth and ripening are presented in Table 1.

During the fruit growth, the dry matter content (DM%) increased continuously from fruit formation to maturity due to the accumulations and continuous synthesis of chemical compounds. The highest DM content was recorded at the maturity of consumption (31.19%), respectively, after the 20 days of storage to perfect the fruit's ripening (November 11). Against the background of the increase in DM content, the water content of the fruit decreased steadily, the largest decrease recorded during the ripening improvement in direct correlation with the DM. The results are consistent with those presented by Rop et al. (2011), who reported values of total dry matter content in several quince varieties between 13.73 and 21.84%. The same upward trend was observed in terms of fruit content in soluble solids (TSS%), the highest growth rate being recorded between July 9 (12.96%) and September 18 (15.95%), respectively, during the fruit ripening period.

Table 1. Variation of dry matter (%), soluble solids (%), and titratable acidity (g malic acid/100 g fw) of quinces during their growth and ripening

Date of sampling	May 28 (fruit setting)	July 9 (immature fruits)	September 18 (cessation of fruit growth)	October 20 (harvest maturity)	November 11 (consumption maturity)
DM	20.17±3.42	21.21±4.02	21.50±3.87	24.96±4.99	31.19±5.29
TSS	9.97±1.61	12.96±2.35	15.95±2.43	17.05±3.06	18.61±3.53
TA	3.68±0.62	5.36±0.96	6.03±1.11	14.07±2.67	9.71±1.64

During the period of maturity improvement, the growth rate of the soluble solids was the lowest and is most likely due to the solubility of substances with complex molecular structures, especially pectin. The data are consistent with those presented by Rop et al. (2011), who reported soluble solids content values for several quince varieties between 10.9 and 17.7%. Regarding the titratable acidity of quince, it constantly increased from the formation of the fruit setting (3.68 g. malic acid/100 g fw) to the harvest maturity (14.07 g. malic acid/100 g fw) after which decreased during the period of ripening improvement (20 days of storage). Data are consistent with those reported by Silva et al. (2005), highlighting the strong acidic character of quince compared to other fruits. Data regarding the total phenolic content, flavonoid content, and the antioxidant activity of the quince are presented in Table 2. Quince is characterized by a high content of total phenolics, the highest values were recorded at the fruit setting (May 28, 117.92 mg/l), which decreased sharply until the growth of fruit cessation (September 18, 22.16 mg/l), subsequently acquiring an upward trend until the consumption maturity (November 11, 65.08%). Therefore, the value of the total phenolic content of fruit at the consumption maturity is significantly lower than the value recorded at fruit formation.

Flavonoids are components of phenolic substances. Data showed the same variation regarding the flavonoid content of the quince, with the highest values obtained at the fruit setting (May 28; 114.1 mg/l) and the lowest at the cessation of fruit growth (September 18; 21.49 mg/l). As phenolic substances are components that give increased resistance to the fruit, it is understandable why they are in the largest amount in the early stages of their growth. It is also found that flavonoids are an important component of the total content in phenols, representing 96.68% of the total phenolics in the

formation of the fruit, respective 73.92% in the maturity of consumption. Our data are consistent with the literature (Stojanović et al. 2017, Fattouch et al. 2007, Wojdyło et al. 2013). Regarding the antioxidant activity, it is observed that the quince is distinguished by an intense activity throughout its growth and ripening. AOA is more intense at the beginning of growth (fruit setting, immature fruit), after which it suddenly decreases when the growth of the fruit stops. After that, it acquires an increasing rhythm until consumption maturity. The highest antioxidant activity is recorded in the fruit setting (May 28, 9.676 mmol Trolox/100 g fw.).

Table 2. Quince content in total phenolics (mg/l), flavonoids (mg/l), and antioxidant activity (mmol Trolox/100g fw) during their growth and ripening

Date of sampling	May 28 (fruit setting)	July 9 (immature fruits)	September 18 (cessation of fruit growth)	October 20 (harvest maturity)	November 11 (consumption maturity)
Total phenolics	117.92±22.40	75.61±12.85	22.16±3.54	53.23±8.51	65.08±11.06
Flavonoids	114.01±20.52	45.90±7.34	21.49±3.29	33.03±5.28	48.11±7.21
AOA	9.676±1.54	9.132±1.55	3.929±0.66	4.5600.72±	4.839±0.82

CONCLUSIONS

Quince is among the forgotten species. In the past, fruit pulp was mainly used to prepare various foods. This study demonstrates the positive effect that quinces can have on human health. Thus, we must emphasize the importance of using whole fruits for the benefit of total bioactive compounds. The data draw attention to the synergistic effects of quince polyphenols to be considered and clearly show that quince is characterized by high biological activity, given in particular phenolic substances. The content of flavonoids is relatively high, representing a significant fraction of phenolic substances. These compounds are found in the largest quantity at the formation of the fruit and in appreciable amounts at the maturity of consumption, making quince very valuable fruit from a chemical point of view. Quince shall be grown in larger areas and used both fresh and processed because it is an

important raw material for processing various foods and a source of biologically active compounds. Quince has a high antioxidant activity throughout the fruit's growth and development, demonstrating the presence of biologically active compounds.

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