APPLE POLYPHENOLS AND THEIR CHANGES IN THE TECHNOLOGICAL PROCESS

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Abstract: This paper summarizes the information on the occurrence of phenolic compounds in appleand juice, with special reference to their health related properties. As phytochemical molecules belonging to polyphenols are numerous, we will focus on the main apples phenolic compounds with special reference to changes induced by apple cultivar, breeding approaches, fruit postharvest and transformation into juice.
Key words: apples, polyphenols, antioxidants, phenolic compounds, apple juice.

Introduction

One class of molecules that has significant health properties is that of polyphenols. In general terminology, they are considered as a: "*Structural class of mainly natural, organic chemicals compounds characterized by the presence of large multiples of phenol structural units*". Polyphenols are usually divided into several different groups (simple phenols, benzoic acids, phenyl propanoids, and flavonoids) on the basis of the number of carbon atoms in conjunction with the structure of the basic phenolic skeleton [4].

They originate from the plant aromatic pathway, starting with amino acids of the shikimate pathway and culminating in molecules produced by the phenyl propanoid and flavonoid pathways. The coordinated induction-regulation of these pathways leads to the production of several thousand different molecules. Their positive effects on human health were first proposed in 1936 [3], and the scientific consensus is now common as proven by the remarkable increase in the number of scientific publications where the "polyphenols" term appears (Fig. 1). The polyphenols are induced in plants under oxidative stress conditions and support the activity of other important cellular antioxidant compounds such as glutathione, α-tocopherol, ascorbic acid, and enzymes such as peroxidase, and superoxide dismutase. Phenolic compounds accumulated in plant organs (roots, stems, leaves, flowers, fruits, *etc*.), according to species characteristics, and are usually more abundant in the epidermal tissue of the organs, such as in the peel of fruit. This preferential localization is set in relation with effect of light on the phenolic metabolism, as well as, with the protective role of phenolic compounds against ultraviolet radiations and other abiotic and biotic stressors.

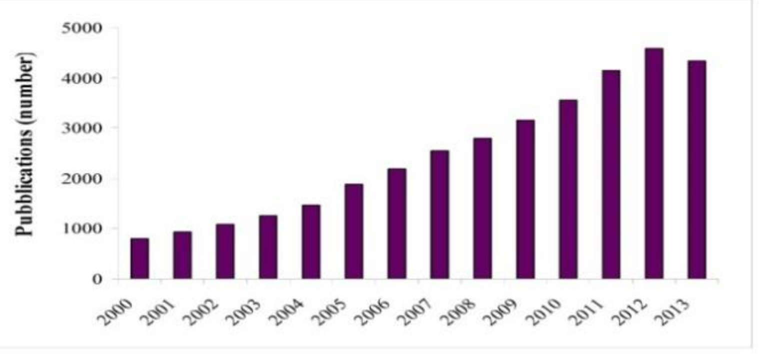

Fig. 1. *Number of publications, which include polyphenol research, since 2000.*
Publications registered in the ScienceDirect database where the keyword "polyphenols" is used. The 2013 data are related to the period of January–mid-July.

The aim of this article is to revise the scientific literature on the biochemical and antioxidant characterization of apple fruit at harvest, and the possible strategies and solutions for maintaining these properties. As phytochemical compounds could undergo relevant modifications during fruit storage and processing in juice, these aspects will be analyzed and discussed.

Apples – the object of study

Apples are one of the most commonly consumed fruits in the world. In 2017, world apple production was estimated at around 77 millions of tons according to Food and Agriculture Organization stats. Apple are eaten both raw and as processed products, such as cider, juice, and puree. Although apples are one of the most consumed fruits, the total phenolic contents of 62 fruits using the Folin-Ciocalteu method showed values ranging from 11.88 (*Pyruscommunis* L.) to 585.52 (*Ziziphusjujuba*Mill.) mg GAE/100 g of wet weight. In this wide range, apples belonging to green-delicious, red-delicious, and rose-red cultivars showed intermediate values of 68.29, 73.96, and 70.57 mg GAE/100 g of wet weight, respectively. Specific studies aimed at comparing total polyphenols in commercial and ancient apple cultivars were performed by P. Iacopini and A. Minnocci [1]. These studies showed that cultivar effects can be relevant as total polyphenol content range between 56 and 221 mg GAE/100 g of wet weight in Gala and Panaia red cultivars, respectively (Figure 2). These results prove that the genetic variability within apple germplasm can provide significant genetic variation for polyphenol traits.

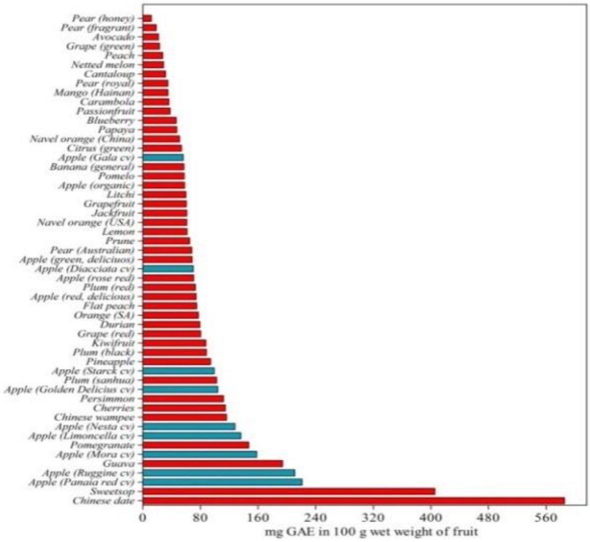

Fig. 2. *Total phenolic content in different fruits and apple cultivars.*

Phenolic Compounds in Apple

Apples contain a variety of phenolic compounds and, using liquid chromatography-mass spectrometry (LC-MS) or gas chromatography mass spectrography (GC-MS) analysis methods, it is possible to detect several polyphenolic molecules, such as (+)-catechin and (−)-epicatechin (flavan-3-ols or flavanols), phloridzin (dihydrochalcone glycosides), quercetin (flavonols), cyaniding (anthocyanidins), cyanidin-3-*O*-galactoside (anthocyanins), chlorogenicacid (phenolic acids), and hydroxycinnamates (p-coumaric acid). In general, the polyphenolic contents per fruit ranges between 19.6 and 55.8 (flavan-3-ols), 17.7–33.1 (flavonols), and 10.6–80.3 (chlorogenic acid) mg per 100g apple; the lowest values were recorded for phloridzin (1.0–9.3 mg per 100g apple) and anthocyanin (0.1–6.5 mg per 100g apple). Total phenolic, flavonoid, and anthocyanin contents in four apple varieties (Rome Beauty, Idared, Cortland, and Golden Delicious) were compared in flesh and peel . The total phenolic contents of the peel were highest in Idared and Rome Beauty (588.9 and 500.2 mg of GAE/100 g of peel, respectively) and drop to 75.7 and 93.0 (mg of GAE/100 g of flesh, respectively). For flavonoids, the Idared peel contains 303.2 mg of catechin equivalents/100 g, corresponding to six times higher concentrations than in flesh. Anthocyanins were detected only in peel, ranging from trace amount in Golden Delicious (yellow/green peel) to 26.8 mg of cyanidin 3-glucoside equivalents/100 g of peel in Idared.

Deeper characterization of apples polyphenol molecules associated with their localization in peel, flesh, and seeds, prove that peel, and also seeds, are rich in these compounds. A schematic representation of concentration ranges of specific polyphenols in peel, peel and flesh and seeds, is presented in Figure 3. In addition, seeds are usually discharged when eating apple fruit, the peel (which represents a small portion of the whole fruit weight) can provide a significant fraction of the phenolics, becoming an important donor of these compounds as confirmed by the literature. Flesh and peel values for (+)-catechin, (−)-epicatechin, phloridzin, quercetin, cyanidin-3-*O*-galactoside ranges between 0.45–3.4, 5.18–18.40, 0.64–9.11, 0.10–0.22, and not detectable-3.11 mg per 100 g fresh weight, respectively [1].

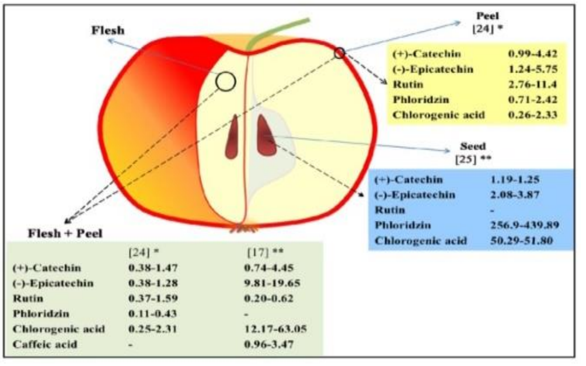

Fig. 3. *Polyphenol molecule concentrations ranges in seed, peel and peel + flesh*

Stability of Phenols in Apple Fruit during Postharvest and in Juice

The drying process together with the rise of temperature and processing time could diminish the phenolic compounds content and antioxidant activity of apples. High temperatures (especially 70 °C) destroy some of the phenolic compounds. The main phenolic compounds identified and quantified in dried apples (*Malusdomestica*) waschlorogenic acid, p-coumaric acid, phloretin-2’-O-glucoside, phloretin-2’-O-xyloglucoside, (+)-catechin, (-)-epicatechin, procyanidins. The total phenolics content in fresh apple was 224.82 mg/100 g of product. Procyanidins were the most predominant phenolic group and contributed to 73.68% of total phenolics content. The total content of procyanidins ranged from 165.64 mg/100 g product in fresh apple to 67.51, 44.05, and 32.26 mg/100 g product in dry apple after it was exposed to 14 h of hot-air drying process at 50°C, 60°C, and 70°C, respectively. p-Coumaric and chlorogenic acids during drying process were successively degraded. Dihydrochalcones content decreased with the rise of temperature and the time of processing. After 14 hours of drying at 60°C and 70°C, 100% loss of compounds belonging to dihydrochalcones occurred in apples.

Apple showed the lowest antioxidant which is attributed to vitamin C and phenolic compounds such as flavonoids and phenolic acids. Vitamin C was found to account for 65-100% of the antioxidant potential of beverages derived from the citrus fruits, but less than 5% of apple and other non-citrus fruit juices. The reaction of enzymatic browning is the major factor responsible for the loss (up to 83%) of the antioxidant activity in apple juice. Thermal treatment caused a significant decrease in antioxidant capacity and polyphenol concentration in apple juice (t = +105 ° C and +125 ° C). Apple jams and marmalades held at +4 ° C have a higher anthocyanin content and a total antioxidant capacity, than those stored at +20 ° C, while there is no significant difference between dark and light storage.

Freezing is an important method used to retain fruit quality during long-term storage. A storage temperature of –18ºC is typically used to reduce the chemical and biological spoilage of foods and to extend their shelf life. However, freezing causes cell breakage, allowing enzymatic reactions to occur. Therefore, anthocyanins and other phenolic compounds can degrade during freezing and more extensively during thawing, due to their interaction with oxidative enzymes. The general loss of antioxidant capacity begins as soon as cell integrity is broken and enzymes such as esterases, glycosidases and carboxylates can catalyze transformations and degradation of phenolic compounds.

Among these treatments, blanching can be used to inactivate enzymes that cause detrimental changes during frozen storage. The blanching could prevent the oxidative degradation of phenolic antioxidants during storage. However, as water-soluble phenols may be leached into water during blanching, steam blanching is preferred. For processed apple products, the most popular is apple juice. During its production, only a fraction of phenolic compounds are extracted, while the other remains in the pomace. Due to the fact that peel and seeds are discharged during juice production, phenolic compounds such as quercetin glycosides and dihydrochalcones, are found in small amounts in apple juice, [2].

Materials and Methods

The main objective of the research was fresh apples, and namely the determination of polyphenols in apples (as raw material) and in apple juice (finished product), and total phenol content in different fruits and varieties of apples (Figure 2).

Apples are characterized by the following organoleptic indices:

External appearance and consistency – whole fruit, slices or fruit slices, elastic when pressed. **Color** - light red to dark red, with yellow tones. **Taste and smell** - specific to the fruit variety, with no foreign taste and smell.

Results

The total content of polyphenols according to the Folin - Chocolate method for apples belonging to green – delicious, red – delicious, red - red cultivars showed intermediate values of 68.29; 73.96 and 70.57 mg GAE / 100 g wet weight. The deeper characterization of apple polyphenol molecules, associated with their location in the peel, flash and seeds, demonstrates that the peel and seeds are rich in these compounds. According to consumers' needs, apples are processed into clear apple juice, but many components with high antioxidant potential are lost during this process. Freezing is a good method of preserving the physicochemical properties of products, using the blanching method in advance. Vitamin C also contributes to the inactivation of PFO by lowering the pH, chelation of Cu, Fe ions and reducing oxygen availability. Thermal treatment and drying process considerably reduce the phenolic compounds content and antioxidant activity of apples.

Discussions

The analysis of these results has shown that the total content of polyphenols largely depends on apple variety, maturation stage, environmental factors, production techniques and apple storage conditions. The deeper characterization of apple polyphenol molecules, associated with their location in the peel, flesh and seeds, demonstrated that the peel and seeds are rich in these compounds. In addition, seeds are usually thrown when apples are consumed, the peel which accounts a small part of the total weight of the fruit, can provide a significant fraction of phenols, becoming an important donor of these compounds.

According to consumers' needs, apples are processed into clear apple juice, but many components with high antioxidant potential are lost during this process.

Conclusions

Based on the apple polyphenol data we have reviewed in this paper; some schematic conclusion could be drawn:

• the total content of polyphenols depends on the storage conditions of apples and the factors that influence the process of browning.

• Phenolic compound characterization in whole apple fruit is well established, while their fate during transformation in juice need to be improved in order to better clarify the losses of these compounds and suitable strategies for their optimal conservation.

• genomic revolution and biotechnological applications will boost genetic improvement of elite apple genotypes by enabling the introduction of highly specific polyphenolic traits.

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