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# Bioactive compounds and antioxidant activity in apple fruits cultivar Florina

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## Abstract

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The consumption of different apple cultivars contributes to improved human health by reducing the risk of cardiovascular disease and cancer. Apple fruit is a major source of phenolic compounds, dietary fibers (pectin and cellulose) and antioxidants. The current review demonstrates the nutritional potential of apple cultivar Florina and focused on the chemical composition and antioxidant potential of its fruits. Physicochemical characteristics such as moisture and ash content, phytochemical composition including sugar content, organic acids, phenolic acids (hydroxycinnamic acid), flavonols, dihydrochalcones, anthocyanins, mineral composition in apple cultivar Florina were summarized. Moreover, the present study evaluated the antioxidant potential of Florina apple fruits for healthy nutrition.

*Keywords:* apple cultivar; Florina; phytochemical compounds; phenolic compounds; antioxidant potential

## Introduction

Among the fruits production worldwide, apples are the second most produced tree fruit with 69 million metric tons/year (FAO). Moreover, in the human diet, apples (*Malus domestica* Borkh.) are popular amongst consumers because of their organoleptic characteristics (aroma, taste, and flavour). Apples constitute an important part of the human diet, as they are a source of sugars, dietary fibers pectin, vitamins (C and A), organic acids and various biologically active compounds (Wu et al., 2007). Apple fruit is a major source of phenolic compounds, because its consumption is widespread in many countries and it is available on the market for the whole year; therefore, it represents a major source of dietary antioxidants.

The chemical composition of apples has an influence on their quality and the health status of consumers. The chemical composition and the nutritional value of apples strongly depend on the variety, quality of the irrigation water and soils, climate conditions, farming practices, storage, and postharvest conditions (Cadar et al., 2014). There are information about many apple cultivars, but summarized data about some of them grown in Bulgaria are still absent. The current review focuses on gathering information about the chemical composition of fruits from Florina apple cultivar, grown worldwide.

The aim of the current study is to summarize the data about nutritional potential, phytocomponents and antioxidant potential of apple fruits from Florina.

### Characterization of Florina apple cultivar

The characteristics of apple fruit quality of Florina variety was assessed at the harvest time (Table 1).

**Table 1. Characteristics of apple fruits of Florina variety recorded over a 3-year period (2005-07) in 'Florina' (*Malus domestica*) apples at harvest time: fruit weight (g); flesh firmness (kg/0.5 cm$^2$) mean ± sem (Leccese et al., 2009)**

| Apple cultivar | Harvest period | Peel colour | Flesh colour | Fruit weight | Firmness, kg/0.5 cm$^2$ |
|---|---|---|---|---|---|
| Florina | 20-30 Sep | purple-red | Whitish | 169.2±15.4 | 8.8±1.0 |

Chemical composition of apple fruit is very complex, because it consists of numerous organic and inorganic compounds. The main chemical compounds that affect apple quality and nutritional properties were summarized (Table 2).

Florina apple cultivar was characterized as a dietary source of energy (Table 2). It was reported that Florina (Table 2) showed the highest TSS content (13.9°Brix) in comparison to Golden Delicious (13.7°Brix) and GoldRush (12.9°Brix). GoldRush had the highest TA values (6.55 meq/ 100 g fresh weight), twice as high as the other ones (Leccese et al., 2009). Soluble solids content is considered as a good indicator of the sugar content of apples and presumably of sweetness (Hoehn et al., 2003). In Florina cultivar its content is between 15.0 and 13.9 ± 0.5% (Table 2) which is considered as a high value in comparison to other apple cultivars. In addition, TSS, TA, and TSS/TA ratio as the major factors influencing taste and flavor of apples. Florina were shown to be much sweeter than GoldRush (Leccese et al., 2009).

**Monosaccharide content**

Sucrose, fructose and glucose are among the main soluble sugars in fruits, while malic, citric, and tartaric acids are the primary organic acids (Mahmood et al., 2012). The quality of apple fruits strongly depends on the proportion of these sugars (Wang et al., 2008). Wu et al. (2007) reported that fructose is the main sugar in apple fruits, which values can reach to 78 % of the total sugar content. The first substrate used during respiration is sucrose and during storage its level degrees while the content of glucose increases (Mezey & Mezeyová, 2018). Sturm et al. (1999) reported for seasonal variability of sugars in apple in different growing systems. Among 26 late ripening apple cultivars from Slovakia, fresh juice obtained from Florina cultivar demonstrated the lowest fructose (58 ± 10 g/L) and glucose content (13.4 ± 7.8 g/L) (Mezey & Mezeyová, 2018).

**Organic acids**

The organic acids found in Florina cultivar were summarized in Table 2, as malic acid was in the highest values

**Table 2. Nurtitional properties and bioactive compounds in fruits of Florina apple cultivar**

| Characteristics | Content | Reference |
|---|---|---|
| Dry matter content, % | 16.46<br>17.0 – 0.1 | Nour et al., 2010<br>Bouayed et al., 2011 |
| Soluble solids content, %<br>Brix (TSS) | 15.0<br>13.9 ± 0.5 | Nour et al., 2010;<br>Leccese et al., 2009 |
| Titratable acidity (TA), %<br>TA, meq malic acid 100 g/fresh weight | 0.201<br>2.64 ± 0.7 | Nour et al., 2010<br>Leccese et al., 2009 |
| Malic acid content, mg/100 g fresh weight | 749.1 | Nour et al., 2010 |
| Citric acid content, mg/100 g fresh weight | 31.1 | Nour et al., 2010 |
| Vitamin C, mg/100 g fresh weight | 12.00 | Gerhauser, 2008 |
| Protein, g/100 g fw | 0.3 | Gerhauser, 2008 |
| Fat, g/100 g fw | 0.6 | Gerhauser, 2008 |
| Carbohydrates, g/100 g fw | 11.4 | Gerhauser, 2008 |
| Total sugar, fw (sucrose, glucose and fructose) | 13.43 | Nour et al., 2010;<br>Mezey and Mezeyová, 2018 |
| Sugars/acids ratio (TSS/ TA) | 5.27 | Leccese et al., 2009 |
| Fibre, g/100 g fw | 2.0 | Gerhauser, 2008 |
| Pectin, g/100 g fw | 0.5 | Gerhauser, 2008 |
| Pectin content, yield % dw | 10-21 | Dranca and Oroian, 2018 |
| Uronic acid content, g/100 g | 84.25-93.90 | Dranca and Oroian, 2018 |
| Energy (kcal/kJ) | 54/227 | Gerhauser, 2008 |
| Total phenolics, mg gallic acid equivalents/100 g fw | 130.0– 2.7 | Bouayed et al., 2011 |
| Total flavonoids, mg catechin equivalents/100 g fw | 91.9– 1.8 | Bouayed et al., 2011 |
| Total anthocyanins, cyanidin 3-glucoside equivalents/100 g | 2.30– 0.10 | Bouayed et al., 2011 |

749.1 mg/100 g fresh weight (Nour et al., 2010). The main organic acid in apple fruits is malic acid, as its content is up to 90% of the total organic acids (Wu et al., 2007; Zhang et al., 2010). The sour taste of apples due to the presence and content of malic acid. In the cultivars with low amounts of malic acid, the sweet taste becomes predominant (Verberic et al., 2009). Mezey & Mezeyová (2018) reported that malic acid content measured in Florina cultivar has the lowest value 1.4 ± 1.9 g/L in comparison with other 25 late ripening varieties from Slovakia. In addition, tartaric, citric and ascorbic acids were present in relatively small amounts in apples compared to malic acid. The low values of the ascorbic acid content can be explained with its degradation during the storage of apples. The variation in organic acid content can affect to sensory properties and the glycemic index (Nour et al., 2010).

**Polyphenolic compounds**

Apple skins are a rich source of quercetin which is known to have strong antioxidant and anticancer activities. Different apple cultivars exhibit differing amounts of phytochemicals and antioxidant activity. Generally, five major polyphenolic groups are found in various apple cultivars: hydroxycinnamic acids, flavan-3-ols/ procyanidins, anthocyanins, flavonols, and dihydrochalcones. The flavan-3-ols can be found in their monomers (catechin and epicatechin), oligomers, and polymers (procyanidins); flavonols are often associated with sugar moieties (predominant sugar is galactose, glucose, rhamnose, arabinose, and xylose), whereas dihydrochalcones are mainly associated with glucose and xyloglucose. The complexity of the chemical profile and the variations are caused by growth period, growing season, geographic location and most importantly, genetic variation.

Some of the most important phytochemical compounds detected in Florina apple cultivar were summarized in Table 3. The presented data showed that anthocyanins and phloridzin are minor phenolic components of apple. Procyanidins, flavan-3-ols, and chlorogenic acid constitute the majority of the polyphenolics. The amount of flavonols is relatively consistent in different cultivars. The concentration of procyanidins/flavan-3-ols contribute to the in vitro antioxidant activity (Wojdyło et al., 2008).

Wojdyło et al.(2008) reported higher values for Florina apple 3.75 ±0.15 GAE g/fw (Table 3), than Bouayed et al. (2011) 130.0 – 2.7 mg gallic acid equivalents/100 g fw (Table 2). In addition the flesh tissue showed the lowest total phenolic values ranging from 0.3 to 0.84 mg GAEg fresh weight (Leccese et al., 2009). The last authors reported that highest mean total phenolic compounds content (3.75 ± 0.15 mg GAE g FW–1) was detected in the peel of the scab-resistant cultivars Florina and GoldRush when compared with Golden Delicious (1.72 ± 0.06 mg GAE g/ fresh weight).

**Table 3. Polyphenolic compounds in Florina apple cultivar (Wojdyło et al., 2008), [Data Expressed as mg/kg (Standard Error (n = 3)].**

| Phytochemical compounds | Content |
|---|---|
| **flavan-3-ols** | |
| (+)-catechin | 98.9±1.5 |
| (–)-epicatechin | 536.4±2.4 |
| procyanidin B2 | 674.2±2.9 |
| procyanidin B1 | 128.4±1.5 |
| procyanidin C1 | 345.5±2.1 |
| oligomeric procyanidins | 8117.3±11 |
| DPn, mean degree of polymerization | 4.6 |
| **hydroxycinnamic acid** | |
| chlorogenic acid | 234.7 ±1.4 |
| p-coumaroyloquinic acid | 03.6±0.1 |
| chlorogenic acid/ p-coumaroyloquinic acid | 65.2 |
| **Dihydrochalcones** | |
| phloretin 2′-xyloglucose | 3.8.2±0.7 |
| Phloridzin | 9.40±1.1 |
| **Flavonol** | |
| quercetin 3-rutinoside | 04.8±0.0 |
| quercetin 3-galactoside | 147.6±0.8 |
| quercetin 3-glucoside | 12.3±0.3 |
| quercetin 3-arabinoside | 63.4±1.4 |
| quercetin 3-xyloside | 96.4±1.2 |
| quercetin 3-rhamnoside | 223.9±1.3 |
| **Anthocyanins** | |
| cyanidin 3-galactoside | 72.3±1.3 |
| cyanidin 3-glucoside | 253.8±2.1 |
| **Total of polyphenols as sum** | 1119.2 |
| Total phenols in peel of Florina apple, mg GAE g/fw | 3.75 ±0.15 |

Oligomeric procyanidins in apple cultivar Florina characterized with mean degree of polymerization 4.6 (Wojdyło et al., 2008), that is indication to be used as cider apple in which the mean degree of polymerization ranges from 4.2 to 50.3 (Sanoner et al., 1999).

In general 5-Caffeoylquinic acid is the most abundant hydoxycinnamic acid in all apple cultivars. Hydroxycinnamic acid, especially p-coumaroylquinic acid was detected in fruits of Florina in concentration 3.6 mg/kg dw. The 5-caffeoylquinic acid (CQA)/p-coumaroylquinic acid ratio is important for juices and ciders production because CQA is considered to be a preferential natural substrate of the catecholase activity of polyphenol oxidase (Janovitz-Klapp et al., 1990).

Florina apple cultivar is characterized with red or partially dark red peels and as a result of this coloration is the content of cyanidin-3-galactoside and 3-glucoside was 72.3 nd 253.8 mg/kg dw (Wojdyło et al., 2008). Apple anthocyanins consist of two different cyaniding glycosides, as cyanidin-3-galactoside is more common than cyanidin-3-glucoside. According to Reay et al. (1999) the concentrations of anthocyanin in apple skins are due to the combination of low overnight temperatures and high level of sunshine hours during ripening. However, in some red apple cultivars four different cyanidin glycosides, additionally about 3-arabinosideand 3-galactoside were present in low concentrations (Vrhovsek et al., 2004), but in Florina cultivar, their levels are extremely high (Wojdyło et al., 2008).

Climatic differences registered over the 3-year period appeared to affect apple TAc and total phenolic content, particularly in the peel tissue of Florina cultivar. The overall results of this study indicate a possible substantial effect of the water availability during the summer period: drier seasons seem to enhance phenolic content.

**Antioxidant activity**

The antioxidant activity of Florina apple cultivar was summarized in Table 4.

Leccese et al. (2009) reported that total antioxidant activity in peel varied from 17.5 to 41 μmol TE/ g fresh weight, whereas in the flesh, the values ranged from 3.5 to 6 μmol TE/ g fresh weight. The highest mean antioxidant capacity was found in the scab resistant cultivars Florina and GoldRush, with changes related to the growing season.

In general, antioxidant activity in apples due to the presence of phenolic compounds. Wojdyło et al. (2008) reported for the linear regression between antioxidant activity evaluated by three methods and total phenolic content (Table 5). Moreover, total antioxidant activity values and total phenolic contents was analyzed both in the flesh and peel tissues (Leccese et al., 2009). A good relationship was found in the flesh as expressed by the relation $y = 3.8996x + 2.3325$ ($R^2 = 0.601$, $P < .0001$) and in the peel this was expressed by the relation $y = 6.088x + 8.720$ ($R^2 = 0.752$, $P < .0001$).

**Recommended daily intake**

Raw apple material contains high concentrations of phenolics and has beneficial effects on health because it reduces the risk of cancer and cardiovascular heart disease (Knekt et al., 1997). These data confirm the fact that regular consumption of apples enriches the diet in an important amount of polyphenolic compounds. Apples were identified as the only flavonoid-rich food that might be protective. There was a 27 and 28% lower risk of type 2 diabetes associated with the consumption of 2–6 apples/week or 1 apple per day, respectively, compared to no apple consumption (Hyson, 2011). Moreover, the World Health Organization has recommended that people should consume fruits, at least 5 times a day or 400 g of fruit and vegetables per day to reduce the risk of civilization diseases (Anonymous, 2003). If we eat one apple (approximately 150 g) each day, we may be able to get about 1 g of polyphenols with a significant amount of healthy antioxidant activity. The daily human consumption of polyphenols in the average diet has been estimated to be about 1 g.

**Table 5. Positive Correlation between Phenolic Compounds and Antioxidant Activity (Wojdyło et al., 2008).**

| Variables | ABTS | DPPH | FRAP |
|---|---|---|---|
| Total of polyphenols | 0.871 | 0.839 | 0.804 |
| Dihydrochalcones | 0.260 | 0.198 | 0.256 |
| Flavonols | 0.279 | 0.143 | 0.175 |
| Anthocyanins | 0.146 | 0.035 | 0.095 |
| Procyanidins | 0.690 | 0.591 | 0.633 |
| Hydroxycinnamic acid | 0.542 | 0.636 | 0.549 |

**Mineral composition**

Cadar et al. (2014) found significant amounts of several essential elements such as Ca, Cr, Fe, K, Mg, Mn, Na and Zn in an edible part of Florina cultivars grown in Cluj county, Romania. The consumption of representing minerals has good impact to the nutrition and a healthy status. These authors reported that Florina apples contained Cu (1.25 mg/kg), Zn (1.65 mg/kg), Mn (0.290 mg/kg), Fe (2.64 mg/kg), Ca (2634 mg/kg), Na (78.5 mg/kg), Mg (3400 mg/kg) and low levels of K 5523 mg/kg for dry weight. The detected levels of Pb and Cd into all apple samples were lower than the values set by European regulations (1881/2006/EC): Pb (0.10 mg/kg wet weight) and Cd (0.05 mg/kg wet weight) in fruits. In addition, Nour et al. (2010) detected 11 minerals in fifteen apple fruits cultivars grown in Romania. In Florina cultivar they found the following macro- and microelemets Na (0.28 mg/100

**Table 4. Antioxidant activity of Florina apple cultivar**

| | DPPH | ABTS | FRAP | References |
|---|---|---|---|---|
| Antioxidant activity, **μMTE**, 100 g dry weight | 15.4±2.4 | 85.9±2.8 | 21.1±5.0 | Wojdyło et al., 2008 |
| Antioxidant activity **μMTE**, 100 g fw | | 342±66 | 1.097±68 | Bouayed et al., 2011 |

g), K (160.85 mg/100 g), Ca (2.06 mg/100 g), Mg (6.41 mg/100 g), P (17.04 mg/100 g), Fe (0.25 mg/100 g), Mn (0.03 mg/100 g), Zn (0.06 mg/100 g), Cr (0.03 mg/100 g), Cu (0.07 mg/100 g) and Sr (0.02 mg/100 g) for fresh weight. Many of the mineral mean values such as sodium, potassium, magnesium, and iron were greater than the data from USDA National Nutrient Database for Standard Reference (2009). The mineral content has impact not only on consumers health, but also on apple fruit quality. Calcium and iron are macro elements which influence the consumption quality of fruits in a fresh state (Campeanu et al., 2009). Calcium plays a critical role in ripening and senescence processes (Marcelle, 1995). Apple fruit with low Ca status are sensitive to pathological diseases and have low storage potential (Nour et al., 2010).

## Conclusion

The current review presented valuable information about phytochemical compounds, antioxidant potential and mineral content in Florina apple cultivar. Due to important nutraceutical compounds apple from this cultivar can be considered as a potential source of antioxidants and mineral for healthy human nutrition. Moreover, the summarized information about the chemical composition of Florina apple cultivar evaluated the quality of producing crops and can useful for future characterization of apple production.

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