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Compositional Characteristics of Fruits of several Apple (*Malus domestica* Borkh.) Cultivars

Violeta NOUR[1)], Ion TRANDAFIR[2)], Mira Elena IONICA[1)]

[1)] *University of Craiova, Faculty of Horticulture, 13 A. I. Cuza Street, Craiova, Dolj, Romania; vionour@central.ucv.ro*

[2)] *University of Craiova, Faculty of Chemistry, 107 Calea Bucuresti Street, Craiova, Dolj, Romania; nelutrandafir@yahoo.com*

Abstract

Fifteen apple cultivars grown in Valcea Research Station, Romania were evaluated in terms of fruit quality. Some selected compositional characteristics such as dry matter, total soluble solids, total sugar, titratable acidity, malic, citric and ascorbic acids and minerals content were investigated. Malic, citric and ascorbic acids were determined by a reversed-phase HPLC method. Sodium, calcium, magnesium, phosphorus, iron, manganese, copper, aluminium, chromium, zinc and strontium contents were determined by inductively coupled plasma-mass spectrometry following a microwave digestion while potassium content was determined by flame atomic absorption spectrometry. Large differences between cultivars were found for the contents of particular biochemical and mineral compounds. The dry matter content ranged between 12.49% ('Prima') and 20.09% ('Red Boskoop') while the total sugar content varied between 9.5% ('Cadel') and 15.03% ('Red Boskoop'). The highest titratable acidity was found in 'Red Boskoop' (0.771%), while in 'Starkrimson' the titratable acidity was only 0.101%. The respective ranges of malic and citric acid contents of the tested samples were: 522.2-1993.7 mg/100 g and 3.5-49.1 mg/100 g. The ascorbic acid content was on average 6.18 mg/100 g. Potassium was the most accumulated nutrient in fruits. The potassium content was comprised between 82.25 mg/100 g ('Mutzu') and 160.85 mg/100 g ('Florina'). Calcium follows, with variation limits between 1.70 mg/100 g ('Starkrimson') and 8.74 mg/100g ('Prima') while iron content varied between 0.19 mg/100 g ('Ionagold') and 0.40 mg/100 g ('Cadel' and 'Early Red'). The observed differences in composition are of such magnitude that they may affect both nutritional and sensory properties.

Keywords: apple cultivars, biochemical characteristics, mineral content

Introduction

The Apple (*Malus x malus*) is one of leading fruits which is being grown in temperate region of the world. Its beautiful appearance, crispy flesh, pleasant flavour and sweet taste attract the consumers and fetch high price (Asif Ali *et al.*, 2004).

The attractiveness of fruit to consumers is determined by visual attributes that include appearance, size, uniformity, colour and freshness, as well as non-visual attributes such as taste, aroma, flavour, firmness (texture), nutritional value and healthiness. Among these attributes, firmness and aroma appear to be the most important for consumers. Sugars, organic acids and phenolic compounds all contribute to the aroma of apples (Mikulič Petkovšek *et al.*, 2009).

Apple is mostly taken fresh and it ripens from late summer to winter. It is eaten through all the seasons. Quality of fruit is made of its external and internal (morphological-physical, biochemical and organoleptic) factors. With its quality it has to correspond to wishes of many consumers so that it can satisfy most of their needs, preferences, tastes and habits.

Chemical composition of apple fruit is very complex. It consists of numerous organic and inorganic compounds and macro biogenic and micro biogenic elements. Most represented are sugars, acids, pectin, tannins, starch, cellulose, vitamins, enzymes and phytohormones, while most represented chemical elements are nitrogen, phosphorus, potassium, calcium, sulphur, iron and magnesium. Organic compounds' content in fruit depends on fruit cultivar, ripeness, physiological condition of a tree as well as soil and weather conditions (Markuszewski and Kopytowski, 2008).

Fruits which in time of optimal ripe have most of the stated compounds in harmony are of great nutritive value, because in our regular diet we have a deficiency in compounds and elements that are in apple (Skendrović Babojelić *et al.*, 2007).

Apples are a part in all food diets and its therapeutic value is well known for different illnesses (determines the absorption of gastric secretions, the elimination of toxins, has diuretic effect). Firmness and sugar content are important quality attributes that directly influence consumers on purchasing fresh apple fruit. Organic acids are an important component of fruit flavor and, together with soluble sugars and aromas, contribute to the overall organoleptic quality of fresh apple fruits. Malic acid is the predominant organic acid in apple fruits (Campeanu *et al.*, 2009). Malic acid is the major component of apple that is founding to

maintain the liver in a healthy condition and it help in digestion process. The content of organic acids might be also of interest in that certain acids may lead to a lowering of the postprandial blood glucose and insulin responses. Available data concerning the glycaemic properties of apples do not include information regarding the carbohydrate composition or acid content (Suni *et al*., 2000).

Apples, and especially apple peels, have been found to have a potent antioxidant activity and can greatly inhibit the growth of liver cancer and colon cancer cells. The total antioxidant activity of apples with the peel was approximately 83 μmol vitamin C equivalents, which means that the antioxidant activity of 100 g apples (about one serving of apple) is equivalent to about 1500 mg of vitamin C. However, the amount of vitamin C in 100 g of apples is only about 5.7 mg. Vitamin C in apples contributed less than 0.4% of total antioxidant activity (Boyer and Liu, 2004). Lee *et al*. (2003) found that the average concentration of ascorbic acid among six apple cultivars was 12.8 mg/100 g fruit.

Apples contain a large concentration of flavonoids, as well as a variety of other phytochemicals, and the concentration of these phytochemicals may depend on many factors, such as cultivar, harvest, storage and processing of the apples. The concentration of phytochemicals also varies greatly between the apple peels and the apple flesh (Lee *et al*., 2003). Consumers are becoming more interested in the content of the health-promoting compounds in fruit because of their antioxidant activity (Robards *et al*., 1999).

The aim of these experiments was to compare some nutritional characteristics of fruits from different apples cultivars grown in Valcea Research Station. Fifteen apple cultivarss, harvested at commercial maturity, were analysed, paying special attention to the level of mineral substances, ascorbic, malic and citric acids.

Materials and methods

Plant material

This experiment was carried out in 2009. Fruits of fifteen apple cultivars differing in season type (**'Arlet', 'Ionagold'**, 'Cadel', 'Aura', 'Prima', 'Early Red', 'Red Booskop', 'Generos', 'Pătul', 'Idared', 'Golden Delicios', 'Granny Smith', 'Starkrimson', 'Florina', 'Mutzu') were randomly harvested at optimal ripening time from collection orchard of the Valcea Research Station (SCDP Valcea), located in Sub-Carpathian area in Oltenia (45°6′17″N, 24°22′32″E), with temperate climate. Harvested apples were stored in normal atmosphere at 1-3°C and 85% of relative humidity. In December, fruit chemical analyses were done. Experiment comprised 20 apples of each cultivar.

Analytical methods

The apples were evaluated on the basis of their dry matter at 105°C, soluble solids content, titratable acidity, ascorbic acid content, organic acids profile (malic and citric acids) and mineral content.

Soluble solids were measured in the juice pressed from the whole fruit. Soluble solids concentration was measured using a digital refract meter and the results were expressed as percentages. The total sugar content was determined by the Schoorl method and the results are expressed as g/100 g fresh matter, and the titratable acidity is expressed as g malic acid/100 g fresh matter being determined by titration of a known amount of water extract of apple fruits with 0.1 N NaOH using phenolphthalein as indicator.

Determination of malic, citric and ascorbic acids

For the analysis of organic acids the whole fruit without core was taken. 5 g of apple fruits was homogenized to puree and diluted to 100 ml with 0.1 N HCl. After 30 minutes the extraction solution was centrifuged at 4200 rpm for 10 minutes. The supernatant was filtered through 0.2 μm pore size filter.

Organic acids contents were determined by reversed-phase HPLC on a Surveyor Thermo Electron system equipped with a Diode Array Detector (DAD) using a Hypersil Gold aQ column (25 cm x 4.6 mm) with a particle size of 5 μm. A 50 mM water solution of KH_2PO_4 buffer at pH 2.8 was used as the mobile phase. The column temperature was kept at 10°C and the flow rate at 0.7 mL/min. Detection of malic and citric acids were by absorbance at 214 nm while detection of ascorbic acid was at 254 nm. All the results were expressed in mg/100 g.

Determination of mineral content

Sodium (Na), calcium (Ca), magnesium (Mg), phosphorus (P), iron (Fe), manganese (Mn), copper (Cu), aluminium (Al), chromium (Cr), zinc (Zn) and strontium (Sr) were determined by using the ICP-MS method previously described by Cosmulescu *et al*. (2009), after mineralisation in a microwave oven, while potassium (K) content was determined by flame atomic absorption spectrometry, using as an excitation source the cavitar cathode lamp for potassium.

For the microwave digestion, quantities of approximately 2.5 g sample were introduced into the TFM vessels, after that 5 ml nitric acid 65% and 2 ml hydrogen peroxide 30% were added. The heating programme is given in table 1. Reagent blanks were included in each series of digestions. After cooling them down, the vessel content was transferred to a 50 ml volumetric flask and make up to the mark with ultrapure water.

Tab. 1. Conditions for microwave digestion

Step	1	2	3	4	5	6
Temperature (°C)	80	80	120	120	200	Cooling
Power (W)	200	200	400	400	600	0
Run time (min)	5	2	15	2	10	20

A commercial ICP-MS system (Perkin-Elmer Elan9000), an atomic absorption spectrometer in flame (Avanta PM) and Milestone digestion microwave system were used. The experimental operating parameters are presented in Tab. 2. Etalon standards from multi-element stock solutions ICP-MS calibration STD 3 and mono-element 1000 ppm K were obtained.

Tab. 2. ICP-MS and the atomic absorption spectrometer in flame operating conditions

ICP-MS, model Elann9000	
Rf power(W)	1000
ICP torch	fassele type
Torch injector	ceramic alumina
Nebulizer	Tip cross flow
Nebulizer gas flow (l/min)	0.93
Spray chamber	
Sweeps/reading	20
Reading/replicate	2
Number of replicates	5
Atomic absorption spectrometer in flame Model AvantaPM	
Optics	Double fascicle
Flame	Air –Acetylene

All analyses were performed in triplicate, with a maximum error of less than 5%. All results were expressed in mg/100 g fruit.

Results and discussion

The analytical data from the apple cultivars are summarised in table 3. The average dry matter content of all cultivars investigated was close to 15.5%. The minimum dry matter contents were found in 'Prima' (12.49%) and 'Cadel' (12.91%), whereas the greatest amounts were found in fruits of 'Red Boskoop' cultivar (20.09%). For comparison, Mitre *et al*. (2009) have reported similar values of the dry matter content for 'Golden Delicious' (14.7%) and higher dry matter content for 'Starkrimson' (14.68%) grown in Central Transylvania, Romania.

Soluble solids content is a good indicator of sugar content of apples and presumably of sweetness (Hoehn *et al*., 2003). Soluble solids content varied between 10.8% ('Prima') and 16.5% ('Red Boskoop'). High values of soluble solids content were registered also in 'Early Red' (16.3%) and 'Florina' (15.0%) cultivars.

The sugar content varied between 9.5% and 15.03%, high contents of sugar were registered in 'Red Boskoop' (15.03%) and 'Early Red' (14.81%).

Titratable acidity may be an important tool in predicting taste of apples (Harker *et al*., 2002). This may be important during the assessment of fruit quality, since consumers often have distinct preferences for acid or sweet tasting apples (Daillant-Spinnler *et al*., 1996). The average value of titratable acidity was 0.265%. The highest titratable acidity was found in 'Red Boskoop' (0.771%), while in 'Starkrimson' the titratable acidity was only 0.101%.

Malic acid represents the major organic acid in apple fruits and its content is correlated, to a high extent, with titratable acidity (Markowski *et al*., 2009). Fruits from 'Red Boskoop', 'Granny Smith', and 'Patul' were most abundant in malic acid. The average content of malic acid for the fifteen apple cultivar was 919 mg/100 g. Veberic and Stampar (2005) found an average malic acid content accounting up to 835 mg/100 g in a study of twelve apple cultivars collected from orchards with either organic or integrated production of Slovenia.

Citric acid was present in lower quantities relatively to malic acid. The average content of citric acid was 21.47 mg/100 g. For comparison, Veberic and Stampar (2005) reported an average of 29 mg/100 g. Apple cultivars with higher content of citric acid were 'Starkrimson' (49.1 mg/100 g) and 'Early Red' (47.8 mg/100 g) while 'Patul' (7.7 mg/100 g) and 'Aura' (3.5 mg/100 g) presented the lowest contents.

The ascorbic acid contents were low (average 6.18 mg/100 g) with the exception of 'Red Boskoop' (18.7 mg/100 g) and 'Idared' (11.4 mg/100 g) in which the ascorbic acid content exceeded 10 mg/100 g. These low values may be explained by the decrease of the ascorbic acid content during the storage of apples.

Mineral content of apple cultivars

Apples are considered a good source of dietary minerals. The mineral composition of fifteen apple cultivars is given in Tab. 4. In these data, we can observe that potassium, magnesium, phosphorus and calcium showed the highest levels of concentration. In average, the order depending on content of elements/100 g of fresh weight, was as follows: K>Mg>P >Ca> Na> Fe> Zn> Cu> Mn> Cr> Sr> Al. Large differences between cultivars were found for the contents of particular mineral compounds.

Potassium was the most accumulated nutrient in fruits, followed by P and Mg, regardless of the cultivar. Most K accumulation in apple fruits was also observed by Nachtigall and Dechen (2006). The potassium content was comprised between 82.25 mg/100 g ('Mutzu' cultivar) and 160.85 mg/100 g ('Florina' cultivar), with a very significant difference, compared to the average value (112.3 mg/100g). A low content of this element could determine

Tab. 3. Basic composition of fifteen apple fruits cultivars

Apple cultivar	Dry matter total content (%)	Soluble solids content (%)	Total sugar (%)	Titratable acidity (%)	Malic acid content (mg/100 g)	Citric acid content (mg/100 g)	Ascorbic acid content (mg/100 g)
'Arlet'	16.26	14.2	12.58	0.168	718.4	37.5	4.7
'Ionagold'	14.96	14.3	12.69	0.201	678.1	10.1	3.5
'Cadel'	12.91	11.3	9.50	0.235	725.4	12.6	4.3
'Aura'	14.81	13.3	11.63	0.168	717.1	3.5	5.2
'Prima'	12.49	10.8	8.97	0.151	701.8	15.9	6.8
'Early Red'	16.66	16.3	14.81	0.134	637.7	47.8	3.6
'Red Boskoop'	20.09	16.5	15.03	0.771	1993.7	16.3	18.7
'Generos'	15.45	14.2	12.58	0.235	871.7	18.9	8.2
'Patul'	18.71	15.1	13.86	0.435	1250.2	7.7	2.6
'Idared'	14.04	13.0	11.31	0.268	893.9	13.8	11.4
'Golden Delicious'	14.72	13.2	11.52	0.302	973.5	7.9	3.8
'Granny Smith'	14.89	13.1	11.41	0.435	1274.1	26.4	4.2
'Starkrimson'	13.41	11.9	10.14	0.101	522.2	49.1	3.8
'Florina'	16.46	15.0	13.43	0.201	749.1	31.1	5.6
'Mutzu'	16.83	14.1	12.48	0.168	637.3	23.5	6.3
Average	15.513	13.753	12.129	0.265	919.059	21.473	6.18
Standard error	0.535	0.425	0.457	0.044	109.395	3.692	1.063
Standard deviation	2.070	1.645	1.768	0.171	394.431	14.299	4.118
Confidence level 95%	1.146	0.911	0.979	0.095	238.352	7.919	2.280
LSD5%	1.625	1.292	1.388	0.134	293.157	11.226	3.233

Tab. 4. Mineral concentration of fifteen apple fruits cultivars (mg/100 g fresh weight)

Apple cultivar	Na	K	Ca	Mg	P	Fe	Mn	Zn	Al	Cr	Cu	Sr
'Arlet'	7.65	110.26	7.08	10.00	6.77	0.38	0.04	0.26	0.04	0.02	0.05	0.03
'Ionagold'	1.37	85.32	1.99	5.08	6.18	0.19	0.02	0.19	0.00	0.01	0.04	0.01
'Cadel'	8.21	99.88	6.89	10.87	5.80	0.40	0.05	0.23	0.02	0.03	0.05	0.03
'Aura'	7.65	98.44	7.34	10.79	3.78	0.37	0.05	0.22	0.02	0.02	0.03	0.03
'Prima'	7.95	99.98	8.74	11.63	6.51	0.38	0.04	0.25	0.00	0.02	0.05	0.05
'Early Red'	8.92	116.11	7.45	11.84	7.76	0.40	0.05	0.25	0.07	0.04	0.05	0.03
'Red Boskoop'	6.29	123.16	6.24	10.38	8.57	0.34	0.04	0.22	0.00	0.02	0.04	0.03
'Generos'	1.55	102.03	2.98	6.72	7.25	0.24	0.05	0.21	0.00	0.02	0.04	0.02
'Patul'	1.58	102.20	2.76	6.95	7.91	0.23	0.04	0.20	0.00	0.02	0.06	0.01
'Idared'	1.49	101.03	3.73	6.08	7.53	0.21	0.04	0.21	0.00	0.03	0.05	0.04
'Golden Delicious'	1.36	134.35	2.04	5.16	8.00	0.20	0.03	0.22	0.00	0.02	0.05	0.01
'Granny Smith'	1.40	108.82	3.75	6.11	6.27	0.21	0.06	0.21	0.00	0.03	0.03	0.03
'Starkrimson'	0.49	159.85	1.70	6.81	8.14	0.24	0.04	0.06	0.00	0.02	0.05	0.01
'Florina'	0.28	160.85	2.06	6.41	17.04	0.25	0.03	0.06	0.00	0.03	0.07	0.02
'Mutzu'	0.26	82.25	1.75	5.02	4.55	0.21	0.04	0.07	0.00	0.09	0.03	0.01
Average	3.763	112.30	4.433	7.99	7.471	0.283	0.041	0.191	0.01	0.028	0.046	0.024
Standard error	0.893	6.062	0.656	0.665	0.766	0.021	0.003	0.018	0.005	0.005	0.003	0.003
Standard deviation	3.459	23.477	2.539	2.578	2.968	0.083	0.010	0.069	0.020	0.019	0.011	0.012
Confidence level 95%	1.916	13.001	1.406	1.427	1.643	0.046	0.005	0.038	0.011	0.010	0.006	0.007
LSD5%	2.716	18.431	1.993	2.023	2.329	0.065	0.008	0.054	0.016	0.014	0.009	0.010

some problems in terms of the quality of apples, especially during the storage of apples for a long time (Campeanu *et al*., 2009).

Significant differences were observed among cultivars for phosphorus and magnesium concentrations. Thus, six cultivars ('Cadel', 'Red Boskoop', 'Aura', 'Arlet', 'Early Red'

Tab. 5. Mineral content of apples, raw, with skin (mg/100g) reported in the literature*

Minerals	Ca	Fe	Mg	P	K	Na	Zn	Cu	Mn
Value (mg/100 g)	5.80	0.123	5.07	10.87	107.25	0.72	0.043	0.027	0.035

*Sources: USDA National Nutrient Database for Standard Reference, Release 22 (2009)

and 'Prima') presented magnesium concentration higher than phosphorus concentration. Also, only 'Mutzu', 'Ionagold' and 'Golden Delicious' cultivars presented magnesium content around the value reported in literature (tab. 5), all the other values beeing higher. Except 'Florina' with 17.04 mg P/100 g, all the other cultivars presented phosphorus concentrations inferior in relation with the content reported in literature but similar with the ones reported by Nachtigall and Dechen (2006).

Calcium (Ca) follows, with variation limits between 1.70 mg/100 g ('Starkrimson') and 8.74 mg/100g ('Prima'), the recorded average value being 4.43 mg/100g, inferior in relation to the average reported in the literature (5.80 mg/100 g, Tab. 5). Calcium and iron are macro elements with a secondary part in plant development but which influence the consumption quality of fruits in a fresh state (Campeanu *et al*., 2009).

According to Wojcik (2004), apple fruit with low Ca status are sensitive to pathological diseases, even if they are stored in controlled atmosphere storage. Moreover, fruit poor in Ca have low storage potential because Ca plays a critical role in ripening and senescence processes (Marcelle, 1995).

Jager and Putter (1999) did not find high correlations between fruit mineral content and fruit quality at harvest and after storage, although firmness at harvest was negatively correlated with N content and positively correlated with P content and Mg content. Generally, however, apple fruit quality is reduced by high N, low Ca, high K, high Mg, and low P concentrations in fruit tissue (Bramlage, 1993).

Iron content in apples varied between 0.19 mg/100g in 'Ionagold' cultivar and 0.40 mg/100 g in 'Cadel' and 'Early Red' cultivars, with an average of 0.28 mg/100 g.

The obtained values for Mn and Cu in the analyzed apple cultivars compared to the data from USDA National Nutrient Database for Standard Reference (Tab. 5), are complying with variation limits. However, the average content in zinc (Zn) was higher in the studied cultivars. The average copper content was higher than the average reported by USDA National Nutrient Database but in accordance with the data reported by Nachtigall and Dechen (2006). Average values under 0.03 mg/100 g weight were recorded for the next elements: chromium (Cr), strontium (Sr) and aluminum (Al).

Conclusions

The present study shows considerable variation in biochemical characteristics and mineral content between cultivars. 'Red Boskoop' was the best graded cultivar based on the high contents of dry matter, soluble solids, sugar, malic and ascorbic acid. High values of the dry matter content were registered in 'Early Red', 'Mutzu' and 'Florina' cultivars.

The average content of malic acid for the fifteen apple cultivar was 919 mg/100 g. It was noticed a great range of the malic acid content i.e. between 522.2 mg/100 g in 'Starkrimson' cultivar and 1993.7 mg/100 g in 'Red Boskoop'. The variation in organic acid content may have implications for both sensory properties and the glycaemic index.

Potassium was the most accumulated nutrient in fruits, followed by P and Mg, regardless of the cultivar. 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.

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