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Bioactive Compounds and Volatile Profile Dynamics During Fruit Growth of Several Plums Cultivars

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ABSTRACT

The therapeutic value of plums is provided by the contained bioactive compounds, but in consumers choice an essential role is played by the product flavour in which volatile compounds are important contributors. The content in bioactive compounds, the antioxidant activity as well as the volatile profile of three plum cultivars were determined during fruit development. In the analyzed samples, depending on cultivar, harvesting time and the position of fruit in the tree crown, the determined total phenolic content varied between 60.31–699.92 mg GAE 100 g^{-1}, while the flavonoids and anthocyanins content ranged between 11.24–254.46 mg QE 100 g^{-1}, and 0.09–1.65 mg CE 100 g^{-1}, respectively. Using ITEX/GC-MS technique, there were 99 volatile compounds detected in the samples of which 93 were tentatively identified. The volatiles present in the plums cultivars included alcohols, aldehydes, ketones, esters, terpenoids, lactones and others. The most abundant class (in all plum cultivars and developmental phases) was that of aldehydes (49.40–87.01%), the main representatives being hexanal, benzaldehyde, nonanal, heptanal and 2-hexenal, with hexanal having the largest relative peak areas. The identification and quantification of volatile compounds and knowing their accumulation dynamic throughout the ripening process may allow better valorising of fruits depending on cultivar and harvesting time.

Keywords: Antioxidant capacity, Phenolic compounds, ITEX/GC-MS Plums, Volatiles.

INTRODUCTION

Plums are part of the Rosaceae family, Prunus genus. The fruits show a wide range of size, flavor, color, and texture (Dugalic *et al.*, 2014). Consumers appreciate plum fruits for their colour, flavour and aromatic characteristics. High intake of fruits and vegetables was associated with reduced incidence of degenerative diseases due to their potential antioxidant capacity (Prior, 2003). Plums are considered to be fruits with a large quantity of bioactives and phytochemicals, such as vitamins (A-9.5 mg 100 g^{-1}; C-72 RE 100 g^{-1}, 717 IU 100 g^{-1}; and E-0.85 mg 100 g^{-1}, 1.3 IU 100 g^{-1}), minerals (265 mg 100 g^{-1}), amino acids (0.18 g 100 g^{-1}), organic acids (0.5 g 100 g^{-1}), phenolics (111 mg 100 g^{-1}) and carotenoids, compounds that positively affect human health and contribute to the antioxidant capacity (Stacewicz-Sapuntzakis *et al.*, 2001).

The composition and distribution of the phenolic compounds depends on the maturity of the fruit, variety peculiarities, geographical origins, cultural practices or storage conditions (Kim *et al.*, 2003a, 2003b). According to Tomás-Barberán *et al.* (2001) the main plum

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pigmentation is due to the presence of anthocyanins, which belongs to secondary plant metabolites class, called flavonoids, being responsible for red, orange or blue colors in many vegetables and fruits (Giusti and Wrolstad, 2003).

On the other hand, the volatile compounds are responsible for the sensory qualities of the fruit flavour (Vendramini and Trugo, 2000). Aroma is one of the most important indicators used to evaluate fruit quality and it is one of the key factors that attract consumers (Chai *et al.*, 2012).

Several studies had as a main focus the volatile aroma compounds and more than 100 flavour compounds were identified in the case of plum cultivars (Nunes *et al.*, 2008).

The most popular protocols used to extract the volatile compounds from vegetable matrices are based on dynamic headspace extraction. 'In-Tube Extraction' technique (ITEX) is a relatively new purge and trap technique that has been successfully applied to determine the volatile profile of different food products (Louw and Theron, 2012; Socaci *et al.*, 2014), no studies being reported for plums.

The aim of this study was to assess the accumulation dynamics of bioactive compounds and volatiles of three plum cultivars ('Stanley', 'Vânăt de Italia', Tuleu Gras') during fruits development, in order to allow better valorising of fruits depending on cultivar and/or harvesting time.

MATERIALS AND METHODS

The studied plum cultivars were 'Stanley', 'Vânăt de Italia' and 'Tuleu Gras' which have been identically harvested in 2013, during fruit development, from a farm in Cluj-Napoca, from three rootstock trees for each variation. Samples were collected at six different harvesting times, starting with the phase when plum fruits had the size of a bean until they reached full maturity (F1 to F6, Figure 1), starting date 27.05.2013 until 9.09.2013 (Figure 1). Samples were harvested from different positions of the tree crown, inside but also from the periphery of the crown; after being collected, the samples were vacuum packed and stored at -18°C until further analysis. Each time 30 samples were collected from inside the tree crown and from its' periphery, for each variety. Each variety has been studied using triplet samples. For a sample extraction, 5 g of plum, in three replications each, was extracted by grinding the sample 1 minute at 20,000 rpm in a blender (Ultra-Turrax Miccra D-9 KT Digitronic, Germany) with 10 ml of acidified methanol (85:15 v/v, MeOH:HCl). The homogenate was centrifuged at 3,500 rpm for 10 minutes. The extract was separated and the residual tissue was re-extracted until the extraction solvents became colorless (the total solvent volume was between 100-250 ml). The solvent was removed on a rotary vacuum evaporator, and then the extract was recovered on 10 ml methanol (Bunea *et al.*, 2011).

Determination of Antioxidant Capacity by DPPH Method, Total Polyphenols by Folin-Ciocalteu Method, Total Anthocyanins, Total Flavonoid

The antioxidant capacity was determined by Free Radical Scavenging effect over 1,1-DiPhenyl-2-PicrylHydrazyl (DPPH) according to the method proposed by Odriozola-Serrano *et al.* (2008). The Total Phenolic Content (TPC) was determined using a modified Folin–Ciocâlteu method (Singleton *et al.*, 1999). Total anthocyanins were determined using the differential pH method (Giusti and Wrolstad, 2001). The total flavonoid content of plum samples extracts was determined by a colorimetric method as described previously (Zhishen *et al.*, 1999; Kim *et al.*, 2003b).

Determination of Volatile Compounds Extraction of Volatile Compounds

The analysis of volatile compounds was carried out on the plum puree, obtained from the whole fruit (flesh and peel) after

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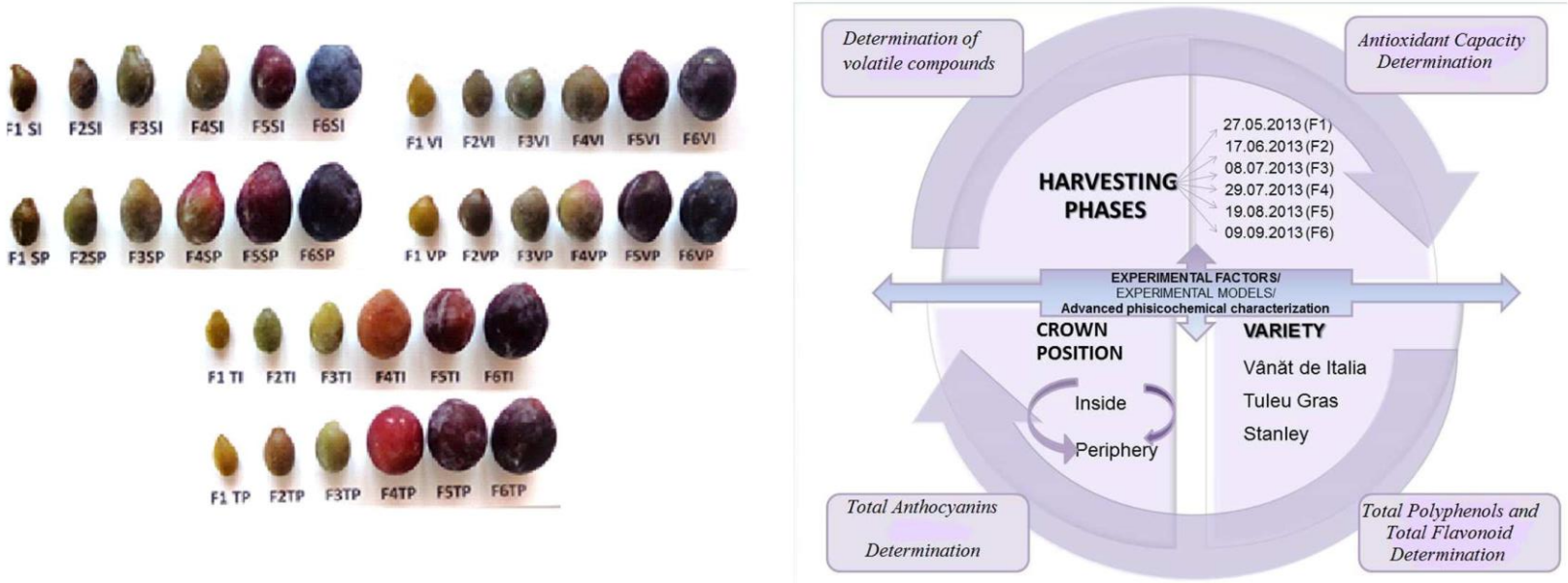

Figure 1. Stanley, Vânăt de Italia and Tuleu Gras plum varieties harvested during fruit growth and overall experimentations used.

destoning and blending using a commercial blender. The extraction of volatile compounds from the plum samples was achieved using (ITEX) technique. The extraction method was adapted after the method described by Louw *et al.* (2012). Thus, 6 g of plum puree together with 1 mL of distilled water and 0.5 g of NaCl were placed into a 20 mL headspace vial. Using a CombiPAL AOC-5000 autosampler (CTC Analytics, Zwingen, Switzerland) the sealed vial was incubated for 15 minutes at 85^{o}C, under continuous agitation. After incubation, the volatile compounds from the gaseous phase of the vial, were repeatedly adsorbed (30 strokes) into a porous polymer fibre microtrap (ITEX-2TRAPTXTA, (G23)-Siliconert 2000, Tenax ta 80/100 mesh, Switzerland). The thermal desorption of volatiles was performed directly into the GC-MS injector at 250^{o}C.

GC–MS Analysis

The separation of the volatile compounds was carried out on a Shimadzu GC-MS QP-2010 (Shimadzu Scientific Instruments, Kyoto, Japan) model gas chromatograph-mass spectrometer equipped with a CombiPAL AOC-5000 autosampler (CTC Analytics, Zwingen, Switzerland). A ZB- 5 ms capillary column of 30 m×0.25 mm id and 0.25 µm film thickness (Phenomenex, USA) was used for the separation. The program for the column oven temperature was: 40˚C (kept for 5 minutes) increased to 120˚C at a rate of 3˚C min^{-1} (hold for 2 minutes) and then raised to 220˚C with 10˚C min^{-1} (hold for 5 minutes). The carrier gas was helium 1 mL min^{-1}; the ion source and interface temperatures were set at 250˚C and the MS detector was used in Electron Impact ionization (EI) mode in a scan range of 35-350 m z^{-1}. The tentative identification of volatile compounds was carried using NIST27 and NIST147 mass spectra libraries and verified by comparison with retention indices drawn from www.pherobase.com and www.flavornet.org (for columns with a similar stationary phase to ZB-5ms) (Louw *et al.*, 2012). All peaks found in at least two of the three Total Ion Chromatograms (TIC) were taken into account when calculating the total area of peaks (100%) and the relative area of the compounds.

Statistical Analysis

In order to show the effect of cultivar, harvesting time and crown position, on the plum bioactive compounds, three-way ANOVA General Linear Model, as well as one-way ANOVA and Tukey's comparison statistical tests (Significance level α= 95%) were performed on Minitab 16.1.0.

RESULTS AND DISCUSSION

Total Phenol Compounds

The TPC measured from the pulp plum samples varied between 60.31 and 699.92 mg GAE 100 g^{-1} (Table 1). TPC has significantly decreased ($P< 0.05$) during fruit growth in the case of 'Stanley' and 'Tuleu Gras' cultivars. Other authors reported also decreased concentrations of phenols during ripening process (Manach *et al.*, 2004). Oscillations were reported by Miletic *et al.* (2012) for 'Vânăt de Italia' species which can be correlated with high anthocyanin content. Overall, similar TPC oscillations have been reported by other authors (Mihalache *et al.*, 2014).

Total Flavonoid Content

Flavonoid concentration decreased once the fruits had reached maturation phases, phenomenon reported by Stohr *et al.* (1975). Tomás-Barberán *et al.* (2001) has observed that for the Wickson variety, the flavonoids diminished together with the fruit maturation. He indicates that these results have presented differences with regard to their taste, because these types of

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Table 1. Variation of bioactive components and antioxidant capacity of three varieties of plum fruit during their development.

Bioactive components/ Antioxidant capacity	Variety	Position in crown	Harvesting time [f] F1	F2	F3	F4	F5	F6
Total phenolic content (mg EAG 100 g^{-1})	S [a]	I [d]	204.58^{AbB}±3.35	198.64^{AaB}±7.08	137.39^{BbB}±4.42	122.57^{BbB}±5.29	88.95^{CbB}±3.66	89.75^{CbB}±3.39
		P [e]	340.16^{AaA}±4.44	219.34^{BaB}±9.88	187.24^{CaB}±9.07	160.79^{CaB}±7.84	127.11^{DaB}±5.87	109.11^{DaB}±4.54
	V [b]	I	201.62^{BCbB}±7.50	233.83^{BbA}±10.60	513.34^{AbA}±16.95	237.24^{BbA}±11.34	190.42^{CbA}±6.93	182.45^{CbA}±8.63
		P	289.36^{CaB}±11.73	543.31^{BaA}±25.37	699.92^{AaA}±24.61	567.14^{BaA}±20.96	532.84^{BaA}±23.36	508.81^{BaA}±17.60
	T [c]	I	318.24^{AaA}±12.43	132.79^{BbC}±4.90	102.79^{BCbB}±5.00	108.69^{CbB}±5.13	98.31^{CaB}±4.17	60.31^{DbC}±2.86
		P	378.35^{AaA}±15.55	204.89^{BaB}±9.38	133.79^{CaB}±6.27	142.09^{CaB}±6.74	108.87^{CDaB}±4.97	75.25^{DaB}±2.84
Flavonoid content (mg QE 100 g^{-1})	S	I	156.81^{AbB}± 6.29	133.48^{BaB}± 3.94	130.17^{BaA}± 3.13	51.82^{CbB}± 2.55	29.90^{DbB}± 1.54	29.15^{DbB}± 1.36
		P	190.27^{AaB}± 8.94	138.65^{BaB}± 4.22	137.45^{BaB}± 4.50	67.51^{CaB}± 2.63	55.93^{CDaB}± 2.68	45.31^{DaB}± 1.48
	V	I	181.84^{AbA}± 6.34	149.35^{BbA}± 4.00	83.48^{CbB}± 3.01	71.54^{CDbA}± 3.25	64.61^{DbA}± 1.92	57.46^{DbA}± 2.69
		P	254.46^{AaA}± 8.34	191.80^{BaA}± 7.69	174.85^{BCaA}± 6.82	169.41^{BCaA}± 5.97	153.80^{CaA}± 6.24	124.93^{DaA}± 5.23
	T	I	94.65^{AbC}± 3.73	80.60^{BaC}± 2.45	67.38^{CaC}± 3.01	42.58^{DaB}± 1.47	19.23^{EaC}± 0.94	11.24^{EaC}± 1.43
		P	133.45^{AaC}± 5.40	87.42^{BaC}± 3.95	55.49^{CbC}± 2.08	47.61^{CaC}± 1.92	20.35^{DaC}± 1.64	16.64^{DaC}± 1.87
Anthocyanin content (mg CE 100 g^{-1})	S	I	-	-	-	0.33^{AbB}± 0.01	0.11^{BbB}± 0.00	0.10^{BaB}± 0.00
		P	-	-	-	0.49^{AaB}± 0.02	0.22^{BaB}± 0.01	0.10^{CaB}± 0.00
	V	I	-	-	-	0.51^{AbA}± 0.01	0.67^{BbA}± 0.01	0.85^{CbA}± 0.03
		P	-	-	-	1.65^{AaA}± 0.01	1.72^{AaA}± 0.01	1.76^{AaA}± 0.06
	T	I	-	-	-	0.27^{AbC}± 0.01	0.11^{BbB}± 0.00	0.10^{BbB}± 0.00
		P	-	-	-	0.40^{AaC}± 0.01	0.22^{BaB}± 0.01	0.09^{CaB}± 0.00
Antioxidant capacity (%)	S	I	49.23^{A}± 0.89	47.71^{AB}± 0.81	45.26^{AB}± 1.27	45.00^{AB}± 1.24	44.18^{AB}± 1.01	44.82^{B}± 1.51
		P	46.78^{A}± 1.29	44.60^{AB}± 1.51	43.84^{ABC}± 1.37	41.45^{BC}± 1.15	40.72^{BC}± 1.22	39.53^{C}± 0.94
	V	I	50.52^{B}± 1.26	53.49^{AB}± 1.61	56.62^{A}± 1.52	53.73^{AB}± 1.46	51.28^{AB}± 1.61	49.20^{B}± 0.49
		P	49.50^{B}± 0.91	51.37^{AB}± 1.48	55.12^{A}± 1.36	50.38^{AB}± 1.22	49.45^{B}± 1.68	47.73^{B}± 1.65
	T	I	51.36^{A}± 1.73	45.61^{AB}± 1.91	41.54^{BC}± 1.30	42.68^{BC}± 1.58	41.61^{BC}± 1.92	38.68^{C}± 1.41
		P	49.45^{A}± 1.15	45.08^{AB}± 1.65	40.40^{B}± 1.61	41.63^{BC}± 2.09	34.58^{CD}± 1.34	33.29^{D}± 1.37

[a] Stanley; [b] Vanat de Italia; [c] Tuleu Gras; [d] Inside the crown; [e] Crown periphery; [f] F1-F6 harvesting times: F1– 26.05.2013, F2– 17.06.2013, F3– 08.07.013, F4– 29.07.2013, F5– 19.08.2013, F6– 09.09.2013; Identical small letters for each variety and each harvest time indicate no statistically significant differences (P> 0.05); Identical italic capital letters indicate for each crown position and each harvest time indicate no statistically significant differences (P> 0.05).

compounds are responsible for plum astringency. Values fell from 254.46 to 11.24 mg QE 100 g^{-1} (Table 1). Similar results were reported by Kim *et al.* (2003b) and Veličković *et al.* (2014).

Total Anthocyanin Content

The anthocyanins concentration in the pulp was determined after the appearance of first color spots on the fruit peel (F4). For 'Stanley' and 'Tuleu Gras' cultivars the concentration of anthocyanins has decreased from 0.49 to 0.09 mg CE 100 g^{-1} for the tree crown periphery and 0.33 to 0.10 mg CE 100 g^{-1} for the interior of the tree crown (Table 1), while for 'Vânăt de Italia' the concentration has increased from 0.51 to 1.76 mg CE 100 g^{-1} for the interior of the tree crown and 1.65 to 1.76 mg CE 100 g^{-1} for the tree crown periphery (Table 1). These differences are closely linked to plum varieties (Prunus salicina Erhr. and hybrids) (Vizzotto *et al.*, 2007), being similar to those previously reported (Cevallos-Casals *et al.*, 2006). Differences scaled from 7 to 10 times bigger regarding the anthocyanin quantity in plum skin in comparison to quantity found in plum pulp have been reported for multiple varieties *Prunus salicina* Erhr (Tomás-Barberán *et al.*, 2001; Cevallos-Casals *et al.*, 2006; Díaz-Mula *et al.*, 2009).

Antioxidant Activity

The antioxidant capacity found in plum fruit pulp has registered statistically significant results ($P< 0.05$) with a descendant route for the Stanley variations (with values set between 44.18 and 49.23% for the fruits collected from the interior of the tree crown, and between 39.53 and 46.78% for those collected from the tree crown periphery) and Tuleu Gras (with values that are set between 38.68 and 51.36% for the skin of the fruits collected from the interior of the crown tree and between 33.29 and 49.45% for the skin of the fruits collected from the tree crown periphery). For the Vânăt de Italia variation the values register an oscillating route (between 49.20 and 56.62% for the pulp of the fruits collected from the interior of the tree crown and between 47.73 and 55.12% for the pulp of the fruits collected from the tree crown periphery) (Table 1). Differences depending on the variety antioxidant capacity registered during maturation (for fruits grown under the same conditions) were reported by Díaz Mula *et al.* (2009) as well, confirming that the variety has a very important role in the biosynthesis of phenolic compounds, which are in correlation with the antioxidant capacity. The same findings were reported by other authors Kim *et al.* (2003a).

ITEX/GC-MS Profile of Volatile Compounds

The volatiles compounds from the studied plum cultivars, isolated by ITEX technique, were separated and identified using gas-chromatography coupled with mass spectrometry. A total of 99 volatiles were found of which 93 were tentatively identified based on their mass spectra and retention indices from spectra databases and published data (Figure 3). Not all the compounds detected are present in all cultivars, and the ones common to all samples have different peak intensities. A typical chromatogram for the volatile profile of 'Vânăt de Italia' fruits in phase F5 of development is presented in Figure 2.

The volatile constituents present in the plum samples include alcohols, aldehydes, ketones, esters, terpenoids, lactones as well as other classes of compounds. The most abundant group (in all plum cultivars and harvesting times) was that of aldehydes (49.40–87.01%). The aldehydes group was also found to be the major group of plum volatiles by Chai *et al.* (2012) accounting over 50% of the total volatile content. The major aldehydes identified in all three

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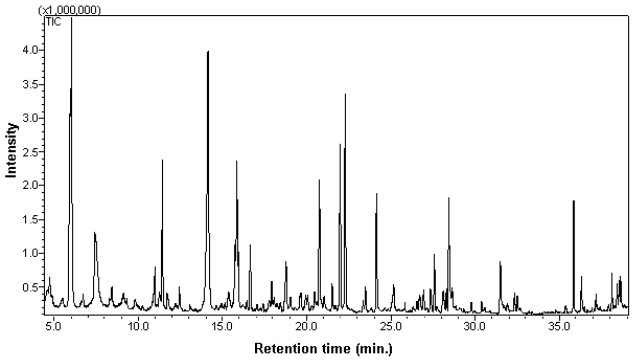

Figure 2. Chromatogram for the volatile profile of 'Vânăt de Italia' plums in phase F5 (fruits harvested on 19.08.2013) of development.

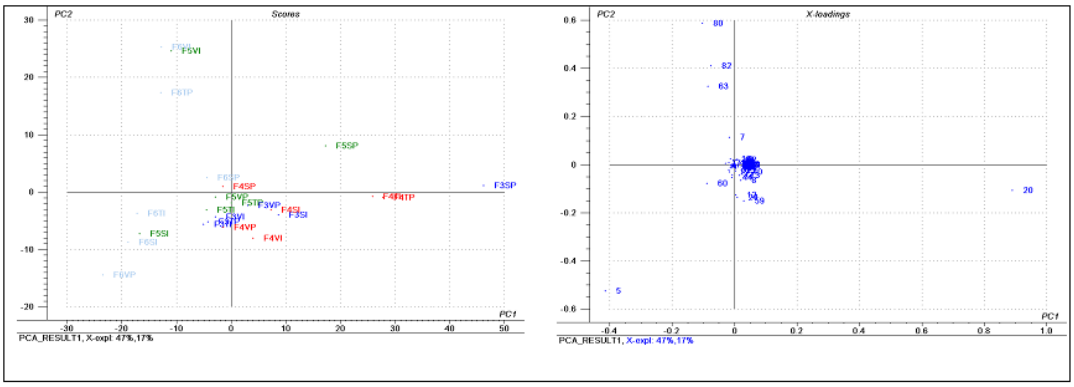

Figure 3. PCA analysis type aroma compounds as a landmark considering harvesting time.

cultivars and in all developmental phases were: Hexanal, benzaldehyde, nonanal, heptanal and 2-hexenal, with hexanal having the largest relative peak areas. Hexanal has been described having a plum-like aroma, while nonanal is a characteristic constituent of skin waxes of plums imparting a fragrant, woody-like aroma (Pino and Quijano, 2011).

Another important group of volatiles was that of terpenoids, their amount ranging from 2.06 to 38.40%, depending on the cultivar as well as on the harvesting time and the position of the fruit in the tree crown (inside or periphery). The main terpenoid was β-linalool. Its highest level was determined for the F3 of harvesting, followed by a sharp decrease starting with F4, especially for the 'Tuleu Gras' and 'Vânăt de Italia' cultivars. There were other two terpenoids identified in all the samples, namely *β*-damascenone and *β*-ionone. Beta-damascenone showed a similar pattern in all three cultivars: its level increased from F3 to F5 and then in F6 decreased to levels close to those found in F3. The same pattern for *β*-damascenone was noticed also by Louw *et al.* (2012) for the analysed Japanese plum cultivars.

Some studies found lactones to be one of the dominant classes of compounds in plums and considered an indicative of ripeness, because in some fruits like apricots and hybrids of apricots and plums their level increases during the ripening process (Gómez and Ledbetter, 1997; Pino and Quijano, 2011). In the present study these compounds were not found among the major volatile compounds in plums.

'Stanley' Cultivar Volatile Profile

The 'Stanley' cultivar is the cultivar with the highest amount of aldehydes (63.75–

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87.01%), alcohols (3.11–8.88%) and esters (0.24–18.12%) detected. 1-Octanol, 1-nonanol and 1-dodecanol are the alcoholic compounds found in all the developmental phases, their level being higher in the immature fruits and decreased towards the final ripening phases (F5 and F6). 1-Hexanol was present in relative high amounts in the riper fruit (4.33–6.89%), especially in those harvested from crown periphery, and with a very low level in the initial phases.

Hexanal showed an increasing trend throughout ripening, reaching its maximum level in F6. Its level was almost two times higher in the fruits harvested from inside the crown compared with those from crown periphery. Benzaldehyde was found in large levels in immature fruits (25.26% for inside the crown fruits, respectively 61.35% for fruit from crown periphery) but then decreased in stage F6 to a lower concentration (3.78% for inside the crown fruits, respectively 12.47% for fruit from crown periphery). Another aldehyde, which is believed to make a significant contribution to the aroma of fresh plums (Chai *et al.*, 2012), present in all development phases was nonanal. Its level increased from F3 to F4 and then it remained relatively constant in the riper fruits (F5, F6). 2-hexenal, heptanal, octanal, 2-octenal and decanal were also abundant and were detected in all phases.

'Stanley' cultivar was found to be the richest cultivar. These are considered key constituents for the aroma of fruits, contributing to the fruity and floral notes (Nunes *et al.*, 2008). The main ester detected in 'Stanley' cultivar was n-hexyl-butanoate (5.99–10.04%). It was identified only in the ripped fruits and in a higher level in the fruits collected from crown periphery. Excepting methyl salicylate, all the other esters were present only in the last phase of fruit development (P6). Instead, methyl salicylate was found in the immature fruits (F3 and F4) and wasn't detected in the riper fruits.

The level of terpenoids was higher in the F3–F5 (2.55–9.87%) but registered a significant decrease in F6 for mature fruits (2.06–4.27%). Compared to the 'Tuleu Gras' and 'Vânăt de Italia' cultivars, 'Stanley' had fewer terpenoid detected, with β-linalool, β-damascone and β-ionone being the major ones.

For 'Stanley' cultivar, the lactones group was represented by 2-hydroxy-γ-butyrolactone and γ-decalatone, which were found solely in the ripped fruits (F6). Lactones are important contributors to the aroma and in particular γ-lactones present fruity odour descriptors (Pino and Quijano, 2011).

'Tuleu Gras' Cultivar Volatile Profile

The major classes of volatiles detected in 'Tuleu Gras' cultivar were those of aldehydes (69.03–83.05%) and terpenoids (3.98–17.37%). Among aldehydes, hexanal and benzaldehyde were found in the highest levels (17.48–38.68%, respectively 4.23–43.56%), followed by heptanal and nonanal. In the case of 'Tuleu Gras' cultivar, the hexanal levels were similar for fruits harvested from inside crown and crown periphery. For benzaldehyde the highest level was recorded in F4 (41.18–43.56%), but these levels sharply dropped (4.23–5.80%) as the fruit reached the harvest stage (F6). Nonanal, had a similar pattern with the one described for 'Stanley' cultivar. Namely, its concentration increased from F3 to F5 and remained relatively constant as ripening proceeded. Octanal, benzenacetaldehyde, 2-hexenal, 2-octenal, decanal and 2-decenal were among the aldehydes found in all ripening phases.

In 'Tuleu Gras' cultivar six esters were detected, including butyl-2-propanoate, ethyl hexanoate, *cis*-3-hexenyl butanoate, methyl salicylate, n-hexyl butanoate and ethyl-3-phenyl-2-propenoate (E). Methyl salicylate and butyl-2-propenoate were present only in immature fruits, while the other esters were solely detected in the mature fruits (F6) (Gómez and Ledbetter, 1997).

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The terpenoids were well represented in 'Tuleu Gras' cultivar (15 compounds). The dominant ones were the terpenic alcohols 'Vânăt de Italia' and α-terpineol together with β-damascenone. The maximum levels of β-linalool and α-terpineol were registered in immature green fruits (F3) (7.24–7.34%, respectively 3.08–3.62%), their levels drastically decreasing or even disappearing during ripening (F6). The decrease of terpenic alcohols has been observed also by other authors and in different fruits (Gómez and Ledbetter, 1997). Beta-damascenone and *β*-ionone are reported as constituents of fresh plums and regarded as products of carotenoid metabolism (Pino and Quijano, 2011). Their levels increased from F3 to F5 and then decreased in F6 to levels similar to the initial ones.

Only one lactone was detected in 'Tuleu Gras' cultivar, namely 2-hydroxy-γ-butyrolactone, which was exclusively found in the mature ripped fruits (F6).

'Vânăt de Italia' Cultivar Volatile Profile

The dominant classes of volatiles found in 'Vânăt de Italia' cultivar were those of aldehydes (49.40–80.35%) and terpenoids (3.61–38.40%). As for the other two studied cultivars, 1-hexanal and benzaldehyde were the most abundant aldehydes, followed by octanal, nonanal, 2-hexenal and heptanal.

The terpenoids, especially the monoterpenols, impart a pleasant fruity aroma (Chai *et al.*, 2012). The 'Vânăt de Italia' cultivar had the highest content of total terpenoids and the highest number of terpenoid compounds detected. From the 17 terpenoids found, β-linalool was the major one (0.00–18.08%), its level being much higher in immature fruits (F3-F4) and drastically decreasing in mature ripened fruits (F6). This compound was described to have a plum-like aroma contributing to the characteristic aroma of European plums (Chai *et al.*, 2012; Pino and Quijano, 2011). Beta-damascenone and β-ionone showed a similar trend as in 'Tuleu Gras' cultivar. There are six terpenoids that were only detected in 'Vânăt de Italia' cultivar: β-*trans*-ocimen, menthol, carvomenthenal, trans-geraniol, germacrene D and *δ*-cadinene.

Even though in relative low levels (0–2.34%), 'Vânat de Italia' has the largest amount and number of lactones, compared with the other two cultivars. These compounds were found in F5 and also in F6 but only in the fruits harvested from inside the crown.

Besides the maturation stage and cultivar, the fruits processing process as well as the preservation methods are factors that directly influenced the volatile composition Vendramini and Trugo, 2000). Thus the identification and quatification of volatile compounds and their accumulation dynamics' throughout the ripening process allow a better valorising of fruits depending on cultivar and harvest stage.

For a better understanding of the correlations of these results, the advanced physico-chemical analysis for these studies has been published and may be consulted (Vlaic *et al.* 2014).

CONCLUSIONS

From the starting results it can be concluded that the bioactive components content in the plums analyzed have large variations in relation to the period until plum fruit maturation, the variety or the position in the tree crown. After the GC-MS analysis of the studied samples from three varieties of plums during their growth and development a total of 99 volatile compounds representative of the class of alcohols, aldehydes, ketones, esters, terpenoids and lactones were separated and quantified.

Young (unripen) plum fruits are recommended to be used for the anthocyanin, polyphenols and flavonoids extractions and the mature plum fruits are recommended to be used for the natural dyes extractions, as well as antioxidant extractions. The flavors may be marketed during their whole development, with a specific preponderance during maturation.

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The results are thus helpful for the industry, but for comsumers as well, whom prefer buying plums, with regard to the bio-active compound composition.

Furthermore the present work brings up basic information, which don't exist in the academic literature and it broadens the reasearch area for further studies.

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ترکیبات بیولوژیکی و تغییرات مواد فرار در طی رشد ارقام مختلف میوه آلو

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چکیده

ارزش درمانی آلو به دلیل وجود ترکیبات فعال زیستی است، اما طعم و عطر محصول که در آن ترکیبات فرار نقش دارند، بسیار در انتخاب مصرف کنندگان مهم است. نوع ترکیبات فعال زیستی ، فعالیت آنتی اکسیدانی و همچنین مشخصات مواد فرار سه رقم آلو در طول رشد میوه ها تعیین شد.

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در نمونه های مورد تجزیه و تحلیل، بسته به رقم، زمان برداشت و موقعیت میوه در تاج درخت، مقدار فنول کلی تعیین شده بین ۶۰.۳۱ – ۶۹۹.۹۲ mg GAE / 100 g بود، در صورتیکه محتوای فلاونوئیدها و آنتوسیانین به ترتیب بین ۲۴.۱۴ - ۲۴.۴۴ میلی گرم QE / 100 گرم و ۰.۰۹ - ۱.۶۵ گرم CE / 100 گرم بود. با استفاده از تکنیک ITEX / GC-MS، ۹۹ ماده فرار در ۹۳ نمونه شناسایی شد. فرآورده های موجود در ارقام آلو شامل الکل، آلدئیدها، کتون ها، استرس ها، ترپنوئید ها، لاکتون ها و سایر هستند. بیشترین فراوانی (در تمام ارقام آلو و فازهای رشد) آلدئیدها (۴۹.۴۰ – ۸۷.۰۱٪) بود، نمایندگان اصلی هگزانال، بنزالدهید، غیرانال، هپتانال و ۲ هگزنال بودند و هگزانال دارای بزرگترین مناطق پیک نسبی بود. شناسایی و اندازه گیری ترکیبات فرار و دانستن پویایی انباشت آنها در طول فرآیند رسیدن، ممکن است به ارزیابی بهتر میوه ها بر اساس رقم و زمان برداشت کمک کند.

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