Physico-chemical changes and volatile constituents observed in 10 apricot cultivars (*Prunus armeniaca* L.) during post-harvest ripening

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Abstract

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Physico-chemical changes included a significant decrease in firmness during post-harvest ripening, whereas the levels of total soluble solids were found to be very similar. Ethylene as a parameter of ripening contributed to the resolution of cultivars in the over-ripe phase. On the other hand, fruit softening was not a useful parameter for distinguishing cultivars. 59 of volatiles were determined by the static headspace SPME gas chromatography with mass spectrometry and included 18 alcohols, 12 aldehydes, 10 esters, 11 terpenes, 5 lactones and 3 miscellaneous. Actually, the production of alcohols at ripe stage had almost been completed, since at the over-ripe stage they increased only slightly. Terpene levels were highest for the medium-late cultivars (Orangered, Velkopavlovická, Pinco, Silvercot and Leskora); they were predominantly limonene, α-terpineol and β-Ionone. The decrease in the concentration of terpenes in over-ripe fruit was statistically significant. There are six compounds (2-methylbutan-1-ol, 2-methylbutanal, *n*-hexylbutanoate, 3-methyl-3-methylbutyric acid, γ-caprolactone and γ-octalactone) which taken together can be used to distinguish the two different stages of maturity, ripe and over-ripe. The most abundant of these are γ-caprolactone and γ-octalactone, followed by 2-methylbutan-1-ol. If the volatiles from the cultivars used in this investigation are compared using cv. Bergeron as a standard, then only 10 are required to separate each variety at the over-ripe phase. Principal component analysis clearly separated the cvs Velkopavlovická and Bergeron from all the others, which probably reflects major differences in the production of volatiles and ethylene.

Keywords: volatile compounds; ethylene; respiration rate; firmness; HP-SPME-GC-MS

Optimum fruit quality depends upon a number of factors, including the fruit developmental stage at the point of harvest and the subsequent changes during the period of post-harvest maturation. Ripening to achieve optimum quality means that there must be good aroma development (Botondi et al.

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2003; Aubert et al. 2010), while other features correlated with maturity, such as changes in firmness and the presence of soluble solids, must stay in line with the quality characteristics demanded by consumers. In practice, this means that the fruit must have good aroma and flavour, be sweet to taste, and yet still remain firm enough to avoid physical damage up to the point of its consumption. The production of volatile compounds is closely correlated with ethylene production, and appears to be regulated by ethylene influencing ester production (Fan et al. 2000; Defilippi et al. 2005). Autocatalytic ethylene apparently softens fruit right from the beginning of maturation (Chahine et al. 1999), whereas during the climacteric phase it controls the production of volatiles (Takeoka et al. 1990; Fan et al. 2000). The degree of ripeness affects the production of volatiles from a diverse range of chemical groups such as alcohols, aldehydes, esters, terpenes and lactones (Guillot et al. 2006; Greger, Schieberle 2007; Gokbulut, Karabulut 2012). Variation in the production of aroma compounds was previously reported to vary with the choice of cultivars (Gurrieri et al. 2001; Solís-Solís et al. 2007; Lo Bianco et al. 2010) and the stage of maturity (Aubert, Chanforan 2007; González-Agüero et al. 2009; Aubert et al. 2010). Important differences were found in the concentrations of lactones and terpenic alcohols (Goméz, Ledbetter 1997; Botondi et al. 2003). Fruit ripening involves several different processes, both metabolic changes and physical softening, which can result, in the commercially important apricot cultivars, in serious post-harvest deterioration. The loss of firmness during ripening is considered to be the key factor limiting this deterioration (Palou, Crisosto 2003; Leida et al. 2011). The aim of the present work was to characterize the aroma of apricot cultivars using SPME coupled with GC–MS and the changes in ethylene production, respiration rates and fruit firmness at two different stages of maturity. Subsequently, the principal component analysis (PCA) was performed by ripening stage taking into account the distribution of all selected variables. Some of the fruits of each variety were then ripened under controlled conditions at 20°C for further 7 days, to produce over-ripe fruit.

MATERIAL AND METHODS

Twenty-five kg each of ten apricot cultivars growing in two experimental orchards were picked. Each cultivar was harvested at just one stage of maturity, either ripe or over-ripe. Healthy fruits were then immediately selected on the basis of skin colour, uniformity and size. Fruits were divided into two batches. The first batch was used to measure ethylene and CO_2 gaseous components released from the intact fruit into its environment (CO_2 and ethylene production) and also for physico-chemical analysis (measurements of fruit firmness and soluble solids). All measurements were performed in triplicate (3 replications of 5 fruits each). The fruits from each replication were immediately homogenized and 100-g samples were frozen and stored at –27°C. The total time taken to analyze the volatiles did not exceed 10 days (for fruit picked at the ripe stage). The second batch was stored at 20°C and in 60–80% relative humidity for 7 days before being analyzed. These fruits were designated "over-ripe", and the analyses were performed in exactly the same way as those carried out immediately after harvest.

Ethylene and respiration rate. Ethylene production and respiration rates were measured for intact fruit using a static system. At each sampling date, five fruits were weighed and placed in 1.0 l jars. The jars were sealed and kept at 20°C for 1 h prior to measurement. The concentrations of carbon dioxide (mg/kg/h) and ethylene (ml/kg/h) in the jar headspace were then measured using a gas chromatograph Agilent 4890D equipped with a flame ionization detector FID, and thermal conductivity detector TCD (all Agilent Technologies, Inc., Wilmington, USA).

Firmness measurement. Fruit firmness was measured as being the load in kilograms needed to break the skin of fruit in the equatorial zone, using a 8-mm diameter plunger (Fruit Firmness Tester, Turoni, Italy).

Soluble solids measurement. Soluble solids were measured with a digital refractometer (model PR-1, Atago, Tokyo, Japan) and expressed as °Brix.

Determination of volatiles by SPME. Fresh fruits of the apricot cultivars were homogenized and stored at –27°C until the analyses were performed. Then 2 g of the homogenate were rapidly transferred to a 4 ml sample bottle and kept for 30 min at 50°C. The SPME device for manual use and the 75 mm Carboxen polydimethylsiloxane (CAR/PDMS) fibres were obtained from Supelco (Bellefonte, USA). The fibre was conditioned at 250°C for 30 min before use. The extraction fibre was then inserted into the headspace of the sample bottle, and extraction was performed while using a magnetic stirrer (Ika

Werke, Staufen, Germany) for 30 min at 50°C. The extraction fibre was removed from the sample bottle and inserted into the input port of a GC-MS with pre-set conditions. After desorption for one minute at 250°C, the extraction fibre was removed and data collection commenced. GC-MS measurements were made using a gas chromatograph Agilent 7890A interfaced to an quadrupole mass spectrometer Agilent GC MSD 597 (both Agilent Technologies, Santa Clara, USA), using the NIST 98 spectra library. Analytes were separated using a DW WAX fused silica capillary column of 30 m × 0.25 mm with a phase thickness of 0.25 µm from J &W Scientific (Santa Clara, USA), which was inserted directly into the ion source of the MS. Compounds were provisionally identified using the NIST mass spectra library search, and the identity of most of these compounds was confirmed by comparing their mass spectra and retention times with those obtained for standards.

RESULT AND DISCUSSION

The use of physical and chemical features to differentiate cultivars

Firmness, total soluble solids (TSS), ethylene production, respiration and the levels of the main volatiles were measured. Physico-chemical changes included a significant decrease of firmness during both storage and post-harvest ripening, but the levels of TSS are not useful in attempting to distinguish cultivars. Ethylene has a significant role in the ripening processes of climacteric fruit, and ethylene production increased roughly 50-fold in the course of the 7 days of the experiment, signalling the onset of the climacteric stage (Table 1). However, the late maturing cvs Leskova and Bergeron demonstrated a low rate of ethylene production. Production of CO_2, on the other hand, does not provide any useful basis

Table 1. Firmness, soluble solids, ethylene production and CO_2 production in ripe (R) and over-ripe (OR) apricot fruits (all values – mean ± standard error)

Cultivar	Maturity	Firmness (MPa)	Soluble solid (°Brix)	CO_2 (mg/kg/h)	Ethylene (µl/kg/h)
Bergeron	R	1.28 ± 0.17	11.00 ± 0.80	61.21 ± 10.47	53.71 ± 12.58
	OR	0.72 ± 0.09	12.30 ± 0.35	67.78 ± 6.18	159.9 ± 31.4
Betinka	R	3.56 ± 0.16	13.10 ± 0.21	95.22 ± 19.68	17.33 ± 4.18
	OR	1.94 ± 0.03	14.93 ± 0.22	116.4 ± 10.2	5,823 ± 516
Exnerova	R	2.26 ± 0.16	11.17 ± 0.28	119.1 ± 2.8	179.2 ± 20.1
	OR	0.61 ± 0.01	12.10 ± 0.10	149.2 ± 13.5	9,156 ± 504
Goldrich	R	1.97 ± 0.11	13.03 ± 0.26	75.07 ± 6.42	74.91 ± 28.29
	OR	0.67 ± 0.02	14.27 ± 0.27	91.11 ± 16.66	4,074 ± 782
Lenova	R	1.35 ± 0.13	14.27 ± 0.41	146.7 ± 14.5	74.50 ± 15.46
	OR	0.38 ± 0.05	12.97 ± 0.09	139.7 ± 2.7	1,143 ± 236
Leskova	R	1.46 ± 0.09	16.53 ± 0.03	120.2 ± 11.3	407.8 ± 24.8
	OR	0.60 ± 0.01	16.50 ± 0.40	113.9 ± 14.0	974.6 ± 152.0
Orangered(R)Bhart	R	1.40 ± 0.08	13.00 ± 0.40	73.04 ± 4.46	22.79 ± 8.16
	OR	0.39 ± 0.06	12.93 ± 0.23	137.4 ± 3.0	1,362 ± 260
Pinkot	R	2.31 ± 0.11	12.87 ± 0.26	87.05 ± 1.45	3.61 ± 0.23
	OR	0.80 ± 0.04	12.60 ± 0.35	79.78 ± 2.84	274.8 ± 110.2
Silvercot	R	1.18 ± 0.14	11.60 ± 0.47	37.69 ± 8.37	18.30 ± 9.40
	OR	0.39 ± 0.03	11.80 ± 0.12	90.10 ± 2.48	477.0 ± 44.6
Velkopavlovická	R	0.95 ± 0.08	12.67 ± 0.49	159.5 ± 21.7	17.94 ± 1.65
	OR	0.47 ± 0.03	13.47 ± 0.07	99.83 ± 9.79	256.7 ± 4.7

Table 2. Concentration (mg/kg f.w.) of volatile compounds in different chemical groups in ten ripe apricot cultivars

Cultivar	Alcohols	Aldehydes	Esters	Terpenes	Lactones	Misc.	Total
Bergeron	3,762[b]	1,751[ab]	1,257[b]	562[ab]	72[ab]	15[a]	7,421[bc]
Betinka	2,444[ab]	1,209[a]	1,034[ab]	859[ab]	73[ab]	17[a]	5,638[ab]
Exnerova	1,179[a]	1,365[ab]	598[ab]	616[ab]	199[bc]	16[a]	3,975[a]
Goldrich	2,179[ab]	2,274[b]	582[ab]	455[a]	53[ab]	13[a]	5,558[ab]
Lenova	2,886[ab]	1,031[a]	359[a]	308[a]	269[cd]	21[a]	4,875[ab]
Leskora	1,986[ab]	2,064[ab]	1,020[ab]	1,563[cd]	727[e]	21[a]	7,382[bc]
Orangered(R)Bhart	2,801[ab]	1,695[ab]	1,091[b]	2,027[d]	103[ab]	14[a]	7,738[bc]
Pinkot	7,231[c]	2,268[b]	1,074[ab]	1,864[d]	48[a]	19[a]	12,507[d]
Silvercot	6,878[c]	1,156[a]	698[ab]	1,113[bc]	357[d]	27[a]	10,230[cd]
Vekopavlovicka	4,113[b]	1,558[ab]	3,612[c]	1,749[d]	164[abc]	36[a]	11,233[d]
Total	35,462	16,375	11,333	11,118	2,069	200	76,559
Quantity	18	12	10	11	5	3	59

non-significant differences in concentrations in each chemical group are indicated by common letters; Misc. – miscellaneous

for distinguishing between cultivars. In the group of cultivars used for this study, cv. Betinka underwent rapid metabolic changes, producing high levels of ethylene, alcohols and lactones, while aldehydes and terpenes actually declined in more advanced ripening stages. Measurements of firmness in the over-ripe fruit were in the range of 0.5 to 0.7 MPa, and the rate of softening in all the cultivars was approximately the same. As reported by Gonzales-Agüero et al. (2009), ethylene production does not begin until the fruit has a definite orange colour, and then production increases more than 20-fold. The over-ripe phase, associated with softening and ethylene production, is demonstrated by low correlation (r = 0.4201, P = 0.2269) between these two parameters, where there is no obvious relationship between CO_2 production and softening. Logistic regression coefficients for ripening are high and together with nega-

Table 3. Concentration (mg/kg f. w.) of volatile compounds in different chemical groups in ten over-ripe apricot cultivars

Cultivar	Alcohols	Aldehydes	Esters	Terpenes	Lactones	Misc.s	Total
Bergeron	3,218[abc]	1,435[abc]	1,437[a]	535[a]	66[a]	2[a]	6,695[a]
Betinka	3,521[abc]	1,390[ab]	660[a]	582[a]	933[bc]	19[cd]	7,105[a]
Exnerova	3,712[bc]	1,145[a]	1,559[a]	472.8[a]	331[a]	5[a]	7,224[a]
Goldrich	2,413[ab]	2,660[c]	1,365[a]	380[a]	188[a]	8[ab]	7,015[a]
Lenova	3,933[c]	1,088[a]	635[a]	657[a]	1,197[c]	22[d]	7,533[ab]
Leskora	3,126[abc]	1,586[abc]	1,186[a]	1,230[abc]	2,812[e]	15[bcd]	9,955[bcd]
Orangered(R)Bhart	2,206[a]	1,427[abc]	1,147[a]	1,901[c]	946[bc]	12[abc]	7,640[abc]
Pinkot	5,620[d]	2,444[bc]	1,066[a]	2,044[c]	448[a]	6[ab]	11,629[d]
Silvercot	6,720[d]	712[a]	589[a]	868[ab]	1,893[d]	21[cd]	10,804[d]
Velkopavlovicka	3,602[abc]	1,221[ab]	3,176[b]	1,642[bc]	505[ab]	24[d]	10,170[cd]
Total	38,073	15,111	12,820	10,314	9,315	134	85,772
Quantity	18	12	10	11	5	3	59

non-significant differences in concentrations in each chemical group are indicated by common letters

Table 4. Significance of logistic regression coefficients for standard parameters (soluble solids, firmness, ethylene production and CO_2 production) used to differentiate stages of ripening and cultivars

Parameter	Ripening[1]		Cultivars[2]	
	coeff.[3]	*P*-value[4]	coeff.[3]	*P*-value[4]
Firmness	–27.1762	0.1026	0.3025	0.2096
Soluble solids	–0.4134	0.9378	–0.1307	0.5626
Ethylene production	28.2464	0.1039	0.3749	0.1512
Production CO_2	–1.6788	0.3646	–0.1606	0.4787

[1]referenced maturity level is 0 = ripe (negative values indicate decrease of over-riped fruits in selected parameter); [2]referenced cultivar is Bergeron; [3]regression coefficient (logit) showing the tendency of parameter with respect to the referenced level; [4]corresponding *P*-value, demonstrating the significance of regression coefficient

tive drifting for firmness, but minimal for soluble solids and production of CO_2 reversely over ripening stage are significantly supported by the ethylene production (Table 4). Should cultivar Bergeron serve as a reference standard, then the CO_2 production and soluble solids are of the same level. Although the logistic coefficients for ripening in terms of ethylene and firmness are significant, they are not very useful for distinguishing cultivars (*P*-values in Table 4).

Differentiation of cultivars using aromatic compounds

Aroma compounds were identified and quantified at two different stages of ripening, the first corresponding to the normal commercial harvest date and the second after 7-day storage at 20°C. A total of 59 volatile compounds were detected, including 18 alcohols, 12 aldehydes, 1 ketone, 10 esters, 11 terpenoids, 5 lactones, 2 organic acids and 1 hydrocarbon (Tables 2 and 3). The commencement of ripening is defined as the stage at which ethylene production commences, according to conventional notions of ripening (Table 1), but the production of alcohols at this point has almost been completed, since levels at the second, over-ripe stage show only a slight increase (Tables 2 and 3). The production of esters has also been successfully completed at this stage and, in the early and medium-early cultivars, such as Betinka, Velkopavlovická, Silvercot and Pinkot, the formation of esters even started to decline. A lack of ethylene due to 1-MCP treatment (1-methylcyclopropen) was shown to result in a decrease in alcohols and esters (Fan et al. 2000; Botondi et al. 2003). A reduction in aldehyde and alcohol production in late-harvested fruit compared to early-harvested fruit was also reported by (Botondi et al. 2003; González-Agüero et al. 2009). Terpene levels are highest for medium late cultivars (Orangered, Velkopavlovická, Pincot, Silvercot and Leskora), where limonene, α-terpineol and β-ionone predominate. The decrease in the concentration of terpenes in over-ripe fruit is statistically significant (Table 5). At the over-ripe fruit stage, lactone concentrations are several times higher, with the exception of the cv. Bergeron (Tables 1 and 2). In the final period of ripening lactone formation was confirmed in apricot fruits (Goméz, Ledbetter 1997; Aubert et al. 2010) and in nectarines

Table 5. Significant log regression coefficients for volatile parameters used to differentiate ripening and cultivars

Parameter	Coeff.[3]	*P*-value[4]
Differentiation of ripening[1]		
2-Methyl butan-1-ol	1.4607	0.0530
2-Methylbutanal	–2.4621	0.0418
n-Hexyl butanoate	–3.2282	0.0360
3-Methyl-3-methylbutyric acid	–6.1039	0.0067
γ-Caprolactone	5.1587	0.0385
γ-Octalactone	5.7872	0.0113
Differentiation of cultivars[2]		
n-Butan-1-ol	–2.2293	< 0.0001
n-Pentan-1-ol	0.8721	0.0099
2-Methyl-1-pentanol	–4.8461	< 0.0001
(*E*)-2-hexenol	–0.5951	0.0309
2-Heptanol	–1.1563	0.0168
(*Z*)-3-octen-1-ol	0.6905	0.0435
Phenethyl alcohol	0.4158	0.1086
Ethyl butyrate	6.3641	< 0.0001
Limonene	–0.4943	0.0952
(*E*)-linalool oxide	–0.4196	0.1369

[1]referenced maturity level is 0 = ripe (negative values indicate decrease of over-riped fruits in selected parameter); [2]referenced cultivar is Bergeron; [3]regression coefficient (logit) showing the tendency of parameter with respect to the referenced level; [4]corresponding *P*-value, demonstrating the significance of regression coefficient

Table 6. Eigenvectors of PCA components calculated on aroma compounds for ripe and over-ripe fruits using selected parameters

Compounds*	Ripe fruits			Over ripe fruits		
	comp1	comp2	comp3	comp1	comp2	comp3
Firmness	–0.180	–0.013	–0.123	0.001	–0.023	–0.130
Ethylene	0.001	0.001	–0.010	0.360	**–0.368**	–0.101
2-Methyl butan-1-ol	0.278	**–0.432**	0.242	0.206	**0.394**	–0.105
2-Methylbutanal	**0.521**	0.057	0.048	0.229	0.138	0.239
n-Hexyl butanoate	–0.311	–0.222	**0.407**	0.070	–0.022	–0.106
3-Methyl-3-methylbutyric acid	0.225	0.357	0.052	–0.149	0.037	0.172
γ-Caprolactone	–0.020	0.039	–0.028	–0.306	–0.281	**0.349**
γ-Octalactone	0.080	0.084	–0.028	0.172	–0.032	**0.567**
n-Butan-1-ol	0.008	–0.002	–0.014	**0.419**	**–0.384**	0.106
n-Pentan-1-ol	–0.154	–0.116	**0.475**	0.113	0.235	–0.287
2-Methyl-1-pentanol	**0.434**	0.215	0.080	0.066	**0.400**	0.279
(*E*)-2-hexenol	–0.202	**0.374**	**0.502**	–0.210	–0.081	0.013
2-Heptanol	0.009	–0.062	0.071	0.315	–0.211	0.183
(*Z*)-3-octen-1-ol	0.237	**–0.467**	0.183	0.133	0.229	–0.133
Phenethyl alcohol	–0.053	0.104	–0.058	–0.137	–0.259	–0.262
Ethyl butyrate	**0.372**	–0.088	0.112	**0.440**	0.176	0.001
Limonene	0.109	0.237	**0.459**	–0.199	0.209	**0.350**
(*E*)-linalool oxide	0.059	**0.359**	0.063	0.143	0.012	0.081

*effects with absolute value > 0.3 are highlighted, which demonstrate a distinctive contribution of selected parameter associated with ripening

(Engel et al. 1988). It was suggested that lactone is responsible for sweet and fruity sensory properties (odour and taste) of fresh apricots and processed products such as jam (Takeoka et al. 1990; Guillot et al. 2006; Greger, Schieberle 2007).

Volatile compounds that can determine the degree of maturity and differentiate varieties

Table 4 shows that in over-ripe fruits there is a high risk of loss in firmness and a marked increase in ethylene production, but that measurements of soluble solids and CO_2 production are not useful parameters of ripening and cannot be used to distinguish cultivars (*P*-values in Table 4). To examine the association between concentrations of volatile parameters in fruits and the level of ripening (ripe versus over-ripe) as a binomial response variable, stepwise logistic regression model was used. The aim was to identify volatiles significantly associated with ripening. Logistic regression was also applied to determine parameters that could differentiate varieties – in this case, the response variable is categorical (varieties 1–14), with cv. Bergeron as a reference cultivars. Before calculation, all input

Table 7. Proportion of variance explained by PCA components

Component*	Ripe fruits		Over ripe fruits	
	eigenvalue	share (%)	eigenvalue	share (%)
1	3.294	23.2	4.875	26.1
2	2.437	17.2	3.227	17.3
3	1.998	14.1	2.558	13.7
4	1.576	11.1	1.994	10.7
5	1.342	9.5	1.451	7.8
6	0.933	6.6	1.197	6.4
Total		81.5		81.9

*first six principal components explained > 80% of total variability between varieties associated with distinctive standard and volatile parameter (see Figs 1 and 2)

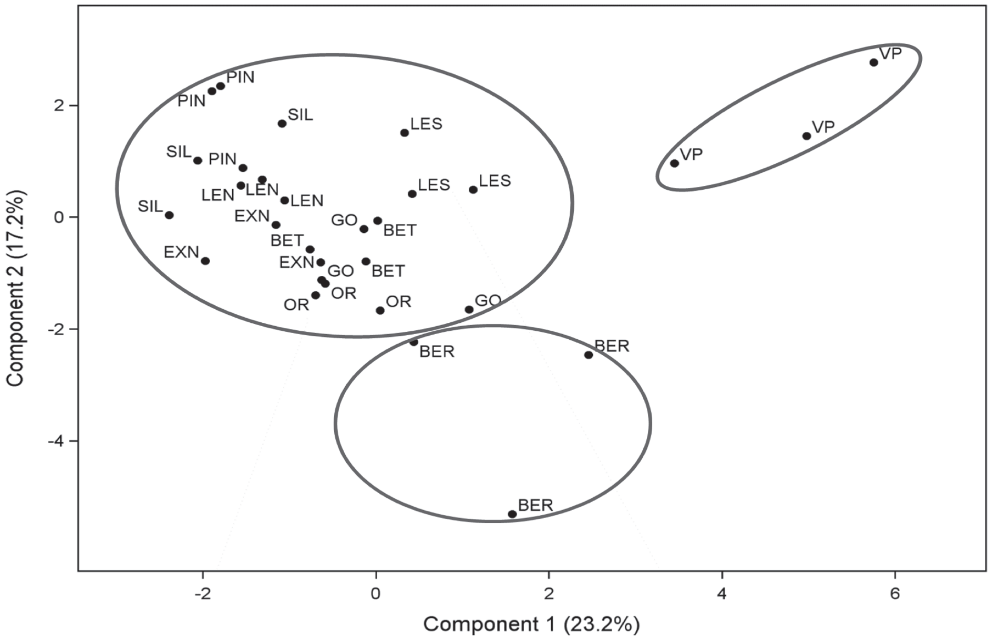

Fig. 1. Patterns of first two PCA component scores – ripe fruits
BER – Bergeron, BET – Betinka, GO – Goldrich, LEN – Lenova, LES – Leskova, OR – Orangered(R)Bhart, PIN – Pinkot, SIL – Silvercot, VP – Velkopavlovická

(independent) variables were standardized to express the variability around mean value. The significance of estimated regression coefficients (logits) is demonstrated by corresponding P-values. If the cv. Bergeron is taken as a standard, then the other cultivars have higher firmness but also produce more ethylene than cv. Bergeron. Furthermore, there are six compounds (2-methyl-butan-1-ol, 2-methylbutanal, n-hexylbutanoate, 3-methyl-3-methylbutyric acid, γ-caprolactone and γ-octalactone) which taken together can be used to distinguish the two different stages of maturity, ripe and over-ripe. The most abundant of these are γ-caprolactone and γ-octalactone, followed by 2-methylbutan-1-ol. Even though the

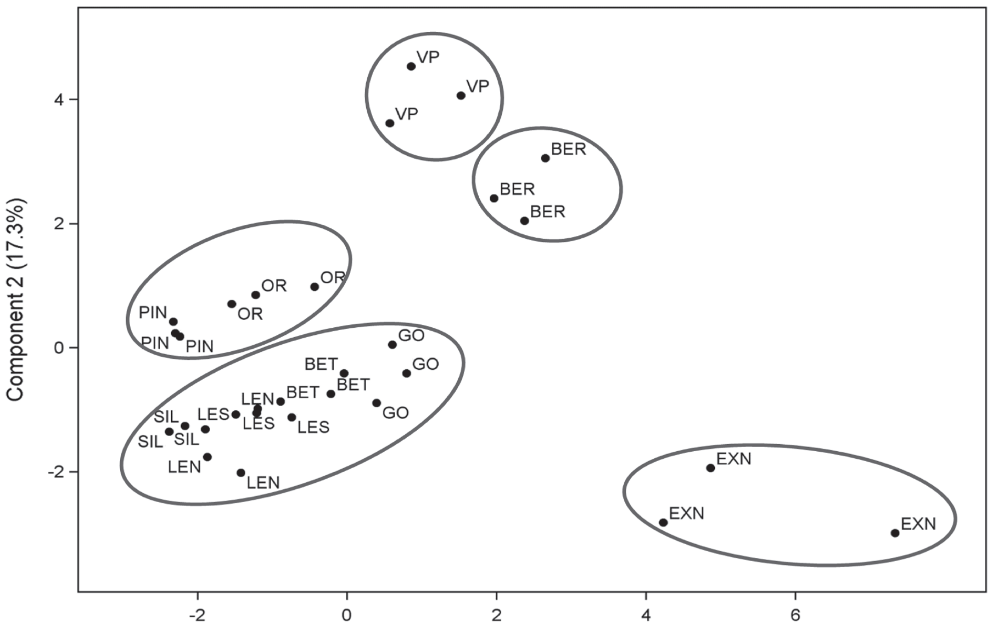

Fig. 2. Position of PC scores for the ten cultivars on the two first PC axes – over-ripe fruits (cultivars as in Fig. 1)

ripening process which continues after harvest generally sees an increase in the production of these compounds, the levels of three compounds (2-methylbutanal, *n*-hexyl butanoate and 3-methyl-3-methylbutyric acid) actually fall (Table 5). Other compounds which are produced in greater amounts in the varieties under investigation, compared to the chosen standard cv. Bergeron, are *n*-pentan-1-ol, (*Z*)-3-octen-1-ol and phenethyl alcohol, with ethyl butyrate also being important. Among the higher alcohols, *n*-butan-1-ol, 2-methyl-1-pentanol and 2-heptanol predominate, and there are also two terpenoids (limonene and (*E*)-linalool oxide) which decrease in concentration at the over-ripe stage. In conclusion, 10 compounds were selected as being sufficient to distinguish the cultivars studied in this investigation (Table 5). This may be compared to Greger and Schieberle (2007), who concluded from their analysis of volatiles in apricot fruits that a set of 18 compounds was enough to identify a cultivar. The importance of these terpenoids for sensory perceptions of quality was already emphasized by Guillot et al. (2006), since limonene and β-cyclocitral contribute fruity, and especially citrus notes, to the aroma of apricots.

Principal Component Analysis (PCA)

Firmness, ethylene and the 16 compounds listed in Table 6 were chosen as the input parameters for PCA analysis. This was used to analyse the relationships between physiological parameters (CO_2 and ethylene production), physico-chemical parameters (soluble solids and firmness) and the composition of the volatiles produced. Eight compounds are sufficient for distinguishing apricot cultivars at the earlier ripe stage (2-methylbutan-1-ol, 2-methylbutanal, 2-methyl-1-pentan-1-ol, (*E*)-2-hexen-1-ol, (*Z*)-3-octen-1-ol, ethyl butyrate, *n*-hexyl butanoate and (*E*)-linalool oxide), but for over-ripe fruit four more compounds are required *(n*-butan-1-ol, 2-methylbutan-1-ol, 2-methylpentan-1-ol and ethyl butyrate). This group promotes the production of ethylene as a statistically significant variable.

For ripe fruit the first principal component (PC1) explained 23.2% of the data variation and showed a high correlation with 2-methylbutanal (0.521), 2-methyl pentan-1-ol (0.434) and ethyl butyrate (0.372). Moreover, two parameters showed no correlation with PC1, namely firmness (–0.180) and ethylene (0.001). The second principal component (PC2), at the identical stage of maturity, explained 17.2% of the data variation and correlated with the volatile compounds 2-metyl butan-1-ol (–0.432), (*Z*)-2-hexan-1- ol (0.374), (*Z*)-3-octen-1-ol (–0.467) and (*E*)-linalool oxide (0.359). The third principal component (PC3) explained 14.1% of the data variation and correlated with *n*-hexyl butanoate (0.407), *n*-pentan-1-ol (0.475), (*Z*)-2-hexen-1-ol (0.502) and limonene (0.459) (Tables 6 and 7). Figure 1 shows the ten cultivars as defined by PC1 and PC2, which together explain 40% of the data variation. As can be seen, PC1 shows a high positive value for the cv. Velkopavlovicka, and something somewhat lower for the cv. Bergeron, and high negative values for all the other cultivars. Therefore PC1 mainly shows a separation between cultivars due to the differences in their volatile matrix composition. PC2, however, showed minimal differences between all cultivars with the exception of the cv. Bergeron. Interestingly, fruit stored at 20°C (over-ripe) showed a clear separation, not only of the two cvs Velkopavlovická and Bergeron from all the others, but cvs Goldgrich, Leskora, Lenova, Silvercote and Betinka were not distinguished. This must probably reflect major differences in the volatiles produced in the fruit harvested at the same stage of ripeness (Tables 6 and 7, Fig. 2), as reflected in the changes in firmness and ethylene production (Table 1).

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