

Formation of volatiles in apricot (*Prunus armeniaca* L.) fruit during post-harvest ripening

JAN GOLIÁŠ¹, JIŘÍ LÉTAL², JARMILA KOŽÍŠKOVÁ¹ and LIBOR DOKOUPIL³

¹ Department of Post-Harvest Technology of Horticultural Products
Mendel University Brno
CZ-69144 Lednice, Valtická 337
E-Mail: golias@mendelu.cz

² Advanced Drug Development Services
CZ-602 00 Brno, Jana Úhra 10

³ Department of Crop Science, Breeding of Horticultural Plants
Mendel University Brno
CZ-69144 Lednice, Valtická 337

*A total of 75 volatile compounds are principally responsible for the aroma profiles of apricot fruit. SPME was used to study these volatiles in an attempt to differentiate between fourteen cultivars of apricots (*Prunus armeniaca* L.) with individual compounds being identified by GC-MS. The concentrations of aroma compounds were statistically analyzed using logistic regression analysis and PCA was successful in differentiating between four cultivars of apricots at over-ripe stage of development. Although the numbers of volatile compounds in each sample were similar, the absolute amounts of total volatiles and those of certain individual compounds did vary between the cultivars and also with the stage of ripening. The main groups of volatile compounds identified were C6 alcohols and aldehydes. In particular, (E)-2-hexenol, (E)-2-hexenal and hexenal together accounted for approximately 65 to 73 % of the total alcohols and aldehydes. The important volatiles for differentiating between ripening stages were benzylalcohol, (Z)-3-hexenal and γ -caprolactone. The rate of softening during the post-harvest period gradually decreases. Furthermore, some of the cultivars can be still in the climacteric phase of development with regard to CO₂ production, whereas other cultivars have already moved on to the post-climacteric phase, characterized by a lower rate of respiration. Of the total of fourteen cultivars studied, only four could be clearly distinguished by principal component analysis (PCA) at the over-ripe stage. Practical considerations such as optimal date of harvest should be based on the onset of the climacteric phase of CO₂ production and not ethylene production, which at this time is broadly similar in all cultivars and only ranges from 0.4 to 1.5 $\mu\text{l.kg}^{-1}.\text{h}^{-1}$. When in the over-ripe phase, values for ethylene production range from 30.0 to 51.6 $\mu\text{l.kg}^{-1}.\text{h}^{-1}$ depending on the cultivars.*

Keywords: apricot, volatiles, ethylene production, respiration rate, headspace analysis, PCA

Bildung von flüchtigen Verbindungen in Marillen (*Prunus armeniaca* L.) während der Reifung nach der Ernte. Insgesamt 75 flüchtige Verbindungen sind hauptsächlich verantwortlich für die Aromaprofile von Marillen. Mittels SPME wurden diese flüchtigen Verbindungen untersucht, um vierzehn Marillensorten (*Prunus armeniaca* L.) zu differenzieren; einzelne Verbindungen wurden mittels GC-MS identifiziert. Die Konzentrationen der Aromaverbindungen wurden statistisch mittels Logistischer Regression analysiert, und PCA wurde für die Differenzierung von vier Sorten im Stadium der Überreife erfolgreich angewandt. Obwohl die Anzahl der flüchtigen Verbindungen in jeder Probe ähnlich war, variierten ihre absoluten Gesamtgehalte und die bestimmter einzelner Verbindungen zwischen den Sorten und auch mit dem Reifegrad. Die Hauptgruppen der flüchtigen Verbindungen waren C6-Alkohole und Aldehyde. Insbesondere (E)-2-Hexenol, (E)-2-Hexenal und Hexenal machten zusammen etwa 65 bis 73 % der gesamten Alkohole und Aldehyde aus. Die wichtigen flüchtigen Verbindungen zur Unterscheidung zwischen Reifephasen waren Benzylalkohol, (Z)-3-Hexenal und γ -Caprolacton. Die Rate des Weichwerdens nimmt während der Zeit nach der Ernte graduell ab. Darüber hinaus können einige der Sorten noch in der Hochphase ihrer Entwicklung

im Hinblick auf die CO_2 -Produktion sein, während andere Sorten bereits über diese Phase hinaus sind, was durch eine geringere Respirationsrate gekennzeichnet ist. Von den insgesamt vierzehn untersuchten Sorten konnten nur vier klar durch Hauptkomponentenanalyse (PCA) im Stadium der Überreife unterschieden werden. Praxisorientierte Erwägungen wie der optimale Zeitpunkt der Ernte sollten auf dem Beginn der Hochphase der CO_2 -Produktion und nicht der Ethylenproduktion basieren, welche zu diesem Zeitpunkt im Großen und Ganzen in allen Sorten ähnlich ist und sich nur in einem Bereich von 0,4 bis 1,5 $\mu\text{l}\cdot\text{kg}^{-1}\cdot\text{h}^{-1}$ bewegt. In der Phase der Überreife bewegen sich die Werte für die Ethylenproduktion zwischen 30,0 und 51,6 $\mu\text{l}\cdot\text{kg}^{-1}\cdot\text{h}^{-1}$ abhängig von der Sorte.

Keywords: Marille, flüchtige Verbindungen, Ethylenproduktion, Respirationsrate, Kopfraumanalyse, PCA

La formation de composés volatils dans des abricots (*Prunus armeniaca* L.) au cours de la maturation après la récolte. Ce sont surtout 75 composés volatils au total qui sont responsables des profils aromatiques des abricots. Ces composés volatils ont été examinés à l'aide de la méthode SPME afin de différencier quatorze variétés d'abricots (*Prunus armeniaca* L.) ; différents composés ont été identifiés à l'aide de GC-MS. Les concentrations des composés aromatiques ont été analysées statistiquement au moyen de la régression logistique, et PCA a été employé avec succès pour la différenciation de quatre variétés au stade de la surmaturité. Alors que le nombre des composés volatils était similaire dans chaque échantillon, leurs teneurs totales absolues et celles de certains composés individuels variaient entre les variétés et également en fonction du degré de maturité. Les groupes principaux des composés volatils étaient les alcools C6 et les aldéhydes. Le (E)-2-hexénol, le (E)-2-hexénal et l'hexénal notamment constituent dans leur ensemble près de 65 à 73 % du total des alcools et aldéhydes. Les composés volatils déterminants pour la différenciation entre les phases de la maturation étaient l'alcool benzylrique, le (Z)-3-hexénal et l' γ -caprolactone. Le taux de ramollissement diminue graduellement au cours de la période suivant la récolte. En outre, quelques variétés peuvent se trouver encore dans la phase de pointe de leur développement en ce qui concerne la production de CO_2 , tandis que d'autres variétés ont déjà dépassé cette phase, ce qui est caractérisé par un taux de respiration plus faible. Sur les quatorze variétés examinées, quatre seulement ont pu être clairement identifiées par l'analyse des composantes principales (PCA) dans le stade de la surmaturité. Les réflexions axées sur la pratique, telles que le moment optimal de la récolte, devraient se baser sur le début de la phase de pointe de la production de CO_2 et non pas d'éthylène qui, à ce moment-là, est pratiquement similaire pour toutes les variétés et qui ne varie que dans une plage de 0,4 à 1,5 $\mu\text{l}\cdot\text{kg}^{-1}\cdot\text{h}^{-1}$. Dans la phase de la surmaturité, les valeurs de la production d'éthylène varient entre 30,0 et 51,6 $\mu\text{l}\cdot\text{kg}^{-1}\cdot\text{h}^{-1}$ en fonction de la variété.

Mots clés : abricot, composés volatils, production d'éthylène, taux de respiration, analyse de l'espace de tête, PCA

The stage of maturity when fruit is harvested, the subsequent degree of ripening and the control of temperature during storage have all been identified as the most critical factors in the post-harvest life of apricots, decrease of firmness being the main attribute affecting quality (BIANCO et al., 2010). Apricots must be picked at a stage of ripeness as near as possible to the optimum edible quality in order to have good aroma development, especially for low-aroma cultivars (BOTONDI et al., 2003; GUILLOT et al., 2006). The aromas of apricots vary widely between cultivars with different volatile groups such as terpenols, esters, lactones, and C6 compounds predominating (GÓMEZ and LEDBETTER, 1997), and naturally also depend on the stage of ripeness (GOLIÁŠ et al., 2011; RIU-AUMATELL et al., 2005). Consequently, the profiles of volatile compounds observed in different apricot cultivars also vary significantly, both qualitatively and quantitatively (AUBERT et al., 2010; DEFILIPPI et al., 2009). They are influenced by genotypic background (GONZÁLEZ-

AGÜERO et al., 2009; LEIDA et al., 2011) and a range of other technical parameters (SOLIS-SOLIS et al., 2007; RIU-AUMATELL et al., 2004; SARRY and GÜNATA, 2004). Therefore the availability of rapid and accurate methods to measure the volatile characteristics of fruit at harvest and during subsequent storage is of utmost importance to support product development and quality control. The objectives of this work were to monitor the physical and chemical parameters of ripening in apricot fruit of 14 cultivars when stored for 7 days at 20 °C. Specifically, this meant measuring the production of physiological gases such as ethylene and CO_2 , changes in the concentration of volatile compounds, and the rate and degree of fruit softening.

Material and methods

All the cultivars came from the same area (Velké Bílovice, South Moravia). The trees were aged from 5 to 7

years and were all grown on the same rootstock, MLE-1. Irrigation was used only when a soil moisture deficit was given. A compound NPK fertilizer (1.1 % N, 7.0 % P and 7.0 % K) was applied at 250 kg/ha once a year in early spring, just before budbreak. Cultivars were harvested in a staggered sequence as follows: June, 23th (cvs. 'Silvercot' and 'Pincot'), June, 28th (cvs. 'Orangered' and 'Tomcot'); July, 9th (cvs. 'Betinka', 'C-2927', 'C-3241', 'Kioto' and 'Goldrich'); July, 13th (cvs. 'Velkopavlovicka' and 'Marlen'); July, 19th (cvs. 'Hargrand', 'Bergeron' and 'Bergarouge'). The same criteria for assessing maturity were used for all cultivars and, when picked, half of the freshly picked apricots were analysed immediately and the remainder were stored at 20 °C and analysed when they had ripened for further seven days. Fruit were harvested and removed from the experimental orchard with minimal delay and transported to the Postharvest Laboratory in Lednice within approximately two hours. Fourteen apricot cultivars at the same colour stage were selected for uniformity of colour development and lack of defects. Half of the fruit were used for the initial physico-chemical measurements, and the other half were stored in the dark at 20 °C and 90 to 95 % relative humidity for seven days before analysis.

Firmness and soluble solids measurements

Fruit firmness was measured using a manual penetrometer (Fruit firmness Tester, Turoni, Forli, Italy) with a plunger 7.9 mm in diameter. Measurements were made on the two cheeks of the fruit without removing the skin and the results expressed in MPa. The soluble solids content (SSC) was measured with a manual temperature-compensated refractometer (ATC-1E, Atago, Tokyo, Japan) in a sample of juice from the pulp of each fruit, with results expressed in °Brix. Both evaluations were made using 15 fruit per sample.

Ethylene production and respiration rate

Measurements of the ethylene production rate were carried out twice, once at harvest and again at the end of the ripening period in a chamber at 20 °C. The fruit were stored in sealed flasks at 20 °C for a period of one hour before a sample of 1 ml was taken from the head space, which was then injected into a gas chromatograph (4890D; Agilent Technologies Inc., Wilmington, USA) with an HP-PLOT/Q column and flame ionization detector (FID). The results are expressed in

µl C₂H₄ per kg fruit per hour. Measurements of the respiration rate were conducted with the same fruit as those used for measuring ethylene and were performed using an HP-Al/KCl column and a thermal conductivity detector (TCD). The results are expressed in mg CO₂ per kg fruit per hour. Three replicates with five fruit each were used for each cultivar.

Determination of the volatiles responsible for aroma

A manual solid phase microextraction (SPME) fibre holder coated with a 100 µm layer of poly-dimethylsiloxane (PDMS), purchased from Supelco (Bellefonte, USA), was chosen to absorb the volatile components of fruit samples. Firstly, the extraction head of the SPME was conditioned in the sample valve of the GC-MS at a temperature of 250 °C for 5 min, and then the needle of the SPME device pierced the septum of the vial and the fiber was exposed for 30 min to the headspace of the vial at 50 °C. Subsequently, the needle was removed from the sample vial. Finally, the needle was manually inserted into the gas chromatography injector, where the analyses were thermally desorbed and analyzed. The desorption time was 5 min at 250 °C. GC-MS measurements were made using a gas chromatograph (7890A; Agilent Technologies, Inc., Santa Clara, USA) interfaced to a quadrupole mass spectrometer (Agilent GC MSD 597), using the NIST 98 library of mass spectra. Analyses 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 (Agilent technologies Inc., 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 a standard.

Statistical analysis

All statistical analyses were performed using the SAS statistical software package version 9.2. (SAS Institute Inc., Cary, USA). For each apricot cultivar, descriptive statistics (mean ± standard error) at each stage of maturity were calculated for each parameter under investigation. A stepwise log regression model was used to explore the effect of all parameters (volatiles

and non-volatiles) as explanatory variables in a binary response (ripe/over-ripe). A binary value of 0 corresponded in this model to the ripe stage and the value 1 coded for the over-ripe stage of fruit. Principal component analysis (PCA) was used to discriminate the cultivars at each of the two stages of ripeness. The first three principal compounds were chosen as a linear combination of the observed variables, selected in such a way that the resulting compounds accounted for the maximum amount of variation in the set of volatile and non-volatile variables. Before proceeding with the statistical analysis the data matrix was standardized by setting mean values at zero.

Results and discussion

Physico-chemical changes in ripe fruit

Apricot fruit rapidly softens after harvest, and this is the major factor limiting their shelf-life. It seems likely that ethylene levels are already sufficiently high enough at the point of harvest to initiate softening, since fruit typically start to soften before there is any significant further increase in ethylene levels. At the time of picking, ethylene production in the fruit is at the detection limit ranging from 0.4 to 1.5 $\mu\text{l.kg}^{-1}\cdot\text{h}^{-1}$, although in four cultivars ('Marlen', 'Betinka', 'Goldrich' and 'Velkopavlovicka') it was higher namely at 2 to 8 $\mu\text{l.kg}^{-1}\cdot\text{h}^{-1}$. Subsequently, it becomes possible to separate the cultivars into three groups (Fig. 1, Table 1), depending on the rate of ethylene production. 'Kioto', 'Marlen' and 'Tomcot' have a relatively low rate of ethylene production (0.01 to 0.3 $\mu\text{l.kg}^{-1}\cdot\text{day}^{-1}$), 'C-2729', 'Bergeron', 'Bergarouge', 'Orangered', 'Pincot' and 'Silvercot' have a medium rate (0.3 - 1.5 $\mu\text{l.kg}^{-1}\cdot\text{day}^{-1}$) and 'C-3241', 'Betinka', 'Goldrich', 'Hargrant' and 'Velkopavlovicka' have a high rate (1.5 to 5.5 $\mu\text{l.kg}^{-1}\cdot\text{day}^{-1}$). However, a low rate of softening does not necessarily suggest a low rate of ethylene production, since no significant correlation between the two phenomena was observed ($R^2 = 0.0047$) (Table 1). Table 2 shows values for chemical compounds). The softening rate and rate of ethylene production in the cultivars were so variable that only two cultivars ('Kioto' and 'Marlen') met the requirements for slow post-harvest over-ripening, namely, a low rate of production of ethylene and only slight softening (Table 1). Observations on the production of CO_2 were not helpful in differentiating between the culti-

vars (Fig. 2). The reason for this reduced respiration rate in the period following 7 days of storage at 20 °C is the early achievement of the climacteric peak, where CO_2 production is at a maximum, followed by a transition into a post-climacteric, senescent stage of development. The cultivars 'Velkopavlovicka', 'Silvercot' and 'Marlen' had high rates of CO_2 production at picking time, but lower rates, around 40 to 60 $\text{mg.kg}^{-1}\cdot\text{h}^{-1}$ lead to the full development of fruit at the climacteric stage (Fig. 2), in contrast to as demonstrated by cvs. 'Bergeron', 'Bergarouge', 'Goldrich', 'Betinka' and 'C-3241' where over-ripe fruit exhibited a higher rate of CO_2 production. Only insignificant changes were observed in the remaining cultivars, 'Hargrant', 'Kioto', 'Orangered' and 'Pincot'. As expected, the values for firmness decreased in all cultivars with advancing ripening (Fig. 3), but the levels of soluble solids did not change significantly (Fig. 4), which is consistent with the observations by CHAHINE et al. (1999) and VALDÉS et al. (2009), that sugar content, for example, is not influenced by ethylene levels. Log regression coefficients for ripening are high for ethylene production and clustered together, with negative drifting for the parameters of firmness and CO_2 production but minimal negative drifting for soluble solids (Table 3).

If the cultivar 'Bergeron' is taken as a standard for purposes of comparison, then CO_2 production and soluble solids in the cultivars under investigation are all rather similar, and it is not possible to use these two parameters to separate them.

Although the log coefficients for ripening in terms of rates of ethylene production and firmness are statistically significant, they are not very useful for distinguishing cultivars, although the p-values for cultivars do have higher values than for the ripening process.

Changes of volatiles in fruit

A total of 75 volatile aroma compounds were identified in the 14 cultivars, comprising 22 alcohols, 16 aldehydes, 18 esters, 12 terpenes, 5 lactones and 2 ketones. The mean values for each volatile compound in each functional group from each cultivar are presented in Table 2. Alcohols, which are considered to contribute a faint fruity scent, are already present in high concentrations at harvest time due to the deamination of α -amino acids as an oxidative reaction occurring under aerobic conditions (GÓMEZ et al., 1993; GÓMEZ and LEDBETTER, 1997). The predominant alcohols are ethyl alcohol and branched chain alcohols, such as

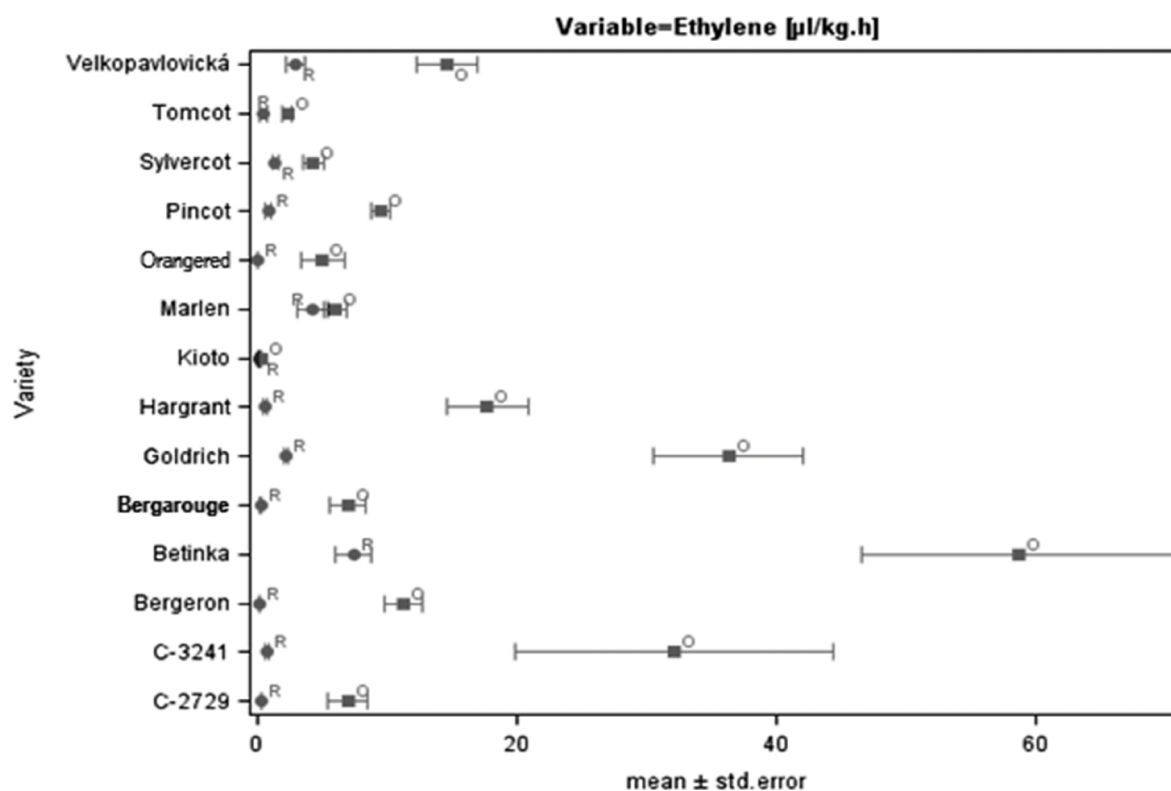


Fig. 1: Production of ethylene ($\mu\text{l}\cdot\text{kg}^{-1}\cdot\text{h}$) during ripening stages ripe (R) and over-ripe (O)

Table 1 :Ethylene production and rates of softening during 7 days of the over-ripening process at 20 °C

Cultivars	Ethylene production	Rate of softening
	$\mu\text{l}\cdot\text{kg}^{-1}$ for 7days	MPa for 7 days
Bergeron	10.95	1.78
Betinka	51.27	2.53
Bergarouge	6.75	1.72
Goldrich	34.60	1.43
argrant	16.48	1.71
Kioto	0.16	1.97
Orangered	5.1	3.17
Pincot	8.65	2.54
Sylvercot	2.94	2.47
Tomcot	1.79	1.96
Velkopavlovicka	11.62	0.88
C-2729	6.64	2.20
C-3241	31.44	1.12

R^2 (correlation coefficient) = 0.0047 for ethylene production and softening

2-methylbutan-1-ol, 2-methylbuten-1-ol, (E)-2-hexenol and benzylalcohol. At post-harvest temperatures of 20 °C the concentrations of these alcohols vary with the cultivar and remain almost unchanged over time, even though they are utilized in the production of esters. Overall, the main volatile compounds identified were C6 alcohols and aldehydes. In particular, (E)-2-hexenol, (E)-2-hexenal and hexenal, taken together, accounted for 65 to 73 % of the total production of alcohols and aldehydes. These have previously been identified as being the characteristic volatile compounds of apricots (GUILLOT et al., 2006; AUBERT and CHANFORAN, 2007; GOKBULUT and KARABULUT, 2012). They are also generated in response to various physiological stresses, such as wounding (GRAY et al., 1999; MYUNG et al., 2006). Esters are another, not insignificant, compositional group with the dominant compounds being ethyl-(E)-3-hexanoate and 2-methylbutyl acetate. On the other

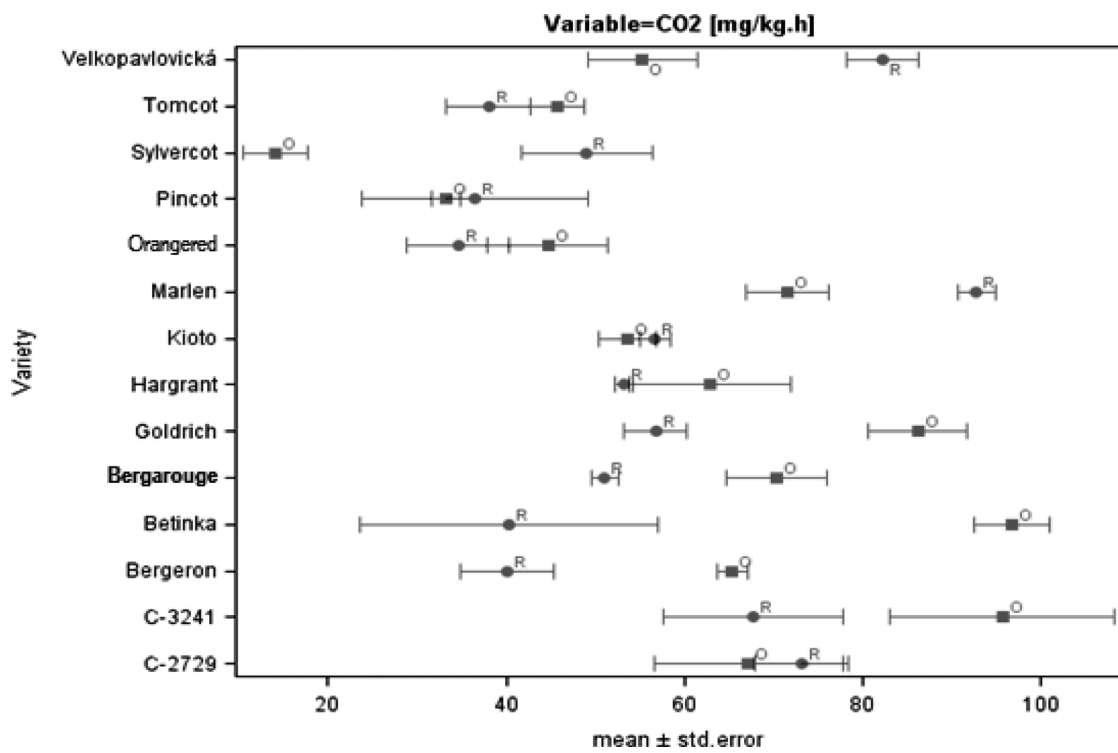


Fig. 2: Production of CO₂ (mg.kg⁻¹.h⁻¹) during ripening stages ripe (R) and over-ripe (O)

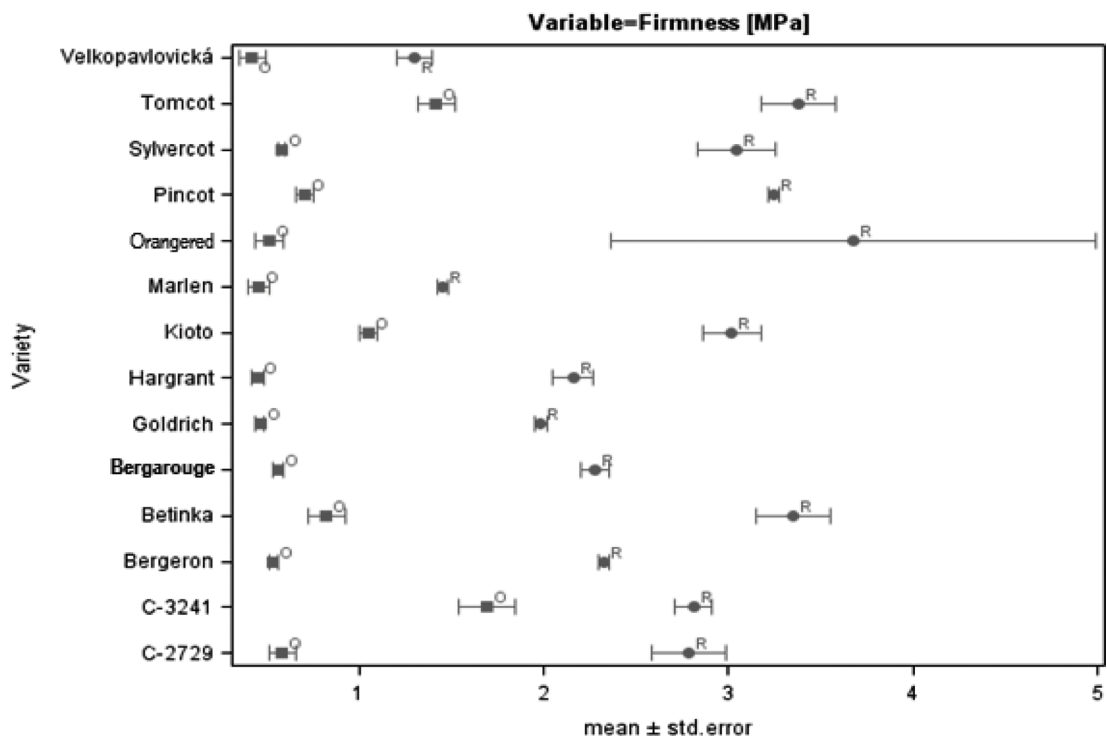


Fig. 3: Changes of firmness (MPa) during ripening stages ripe (R) and over-ripe (O)

Table 2: Volatiles produced by fourteen cultivars of apricot fruit classified as ripe and over-ripe (concentrations expressed as µg per kg fresh weight). Means in the same column followed by different letters are significantly different ($p < 0.01$)

Ripe fruit	Alcohols	Aldehydes	Esters	Terpenes	Lactones	Ketones	Total
Bergeron	10020 cde	4111 ab	508 a	681 ab	68 a	68 b	15456 abcd
Betinka	7065 abcd	10338 cde	2559 f	461 ab	597 bc	4 a	21024 bcdefg
Bergarouge	7536 abcd	4306 ab	589 a	871 abc	122 a	3 a	13427 ab
Goldrich	5490 a	6250 abc	703 abc	253 a	54 a	102 bc	12852 a
Hargrant	16416 f	4180 ab	1693 de	1160 abc	241 ab	124 cd	23814 efg
Kioto	7172 abcd	4473 ab	632 ab	169 a	99 a	90 bc	12635 a
Marlen	5933 ab	18341 f	2703 f	156 a	798 c	5 a	27936 g
Orangered	12410 e	2340 a	2262 ef	1823 cde	46 a	142 cd	19023 abcdef
Pincot	10531 de	1791 a	1550 de	2225 de	242 ab	134 cd	16473 abcde
Silvercot	8748 abcde	2143 a	1402 cd	2416 e	170 a	121 bcd	15000 abc
Tomcot	9544 bcde	6514 abcd	1712 de	1730 cde	229 a	4 a	19733 abcdef
Velkopavlovicka	6702 abc	14751 ef	1349 bcd	594 ab	907 c	3 a	24306 fg
C-2729	8776a bcde	11365 de	1226 abcd	1397 bcd	319 ab	2 a	23085 defg
C-3241	10643 de	8719 bcd	1387 cd	959 abc	404 ab	156 d	22268 cdefg
Total	126986	99622	20275	14895	4296	958	
Quantity	22	16	18	12	5	2	75
Over-ripe fruit							
Bergeron	9241 ab	6401 a	810 a	370 ab	2349 ab	202 e	19373 abc
Betinka	5994 a	4640 a	2299 abc	468 abc	7065 de	112 bcd	20578 abc
Bergarouge	8888 ab	4550 a	973 a	959 d	1783 ab	159 bcde	17312 abc
Goldrich	6483 a	2435 a	9167 d	485 abc	3128 bc	85 ab	21783 abc
Hargrant	18577 c	22670 a	4696 bc	887 cd	2034 ab	123 bcde	48987 c
Kioto	5370 a	2811 a	357 a	289 ab	154 a	108 bc	9089 a
Marlen	8391 a	88649 b	12184 d	747 bcd	8272 e	132 bcde	118375 d
Orangered	6839 a	3715 a	1396 a	921 cd	2320 ab	137 bcde	15328 ab
Pincot	5709 a	1853 a	971 a	921 cd	2891 b	1 a	12346 ab
Silvercot	6296 a	1347 a	1559 ab	912 cd	3421 bc	110 bc	13645 ab
Tomcot	12641 b	19920 a	2204 abc	679 abcd	2236 ab	197 de	37877 abc
Velkopavlovicka	9402 ab	3555 a	4916 c	403 ab	8397 e	144 bcde	26817 abc
C-2729	6485 a	30695 a	1834 abc	243 a	3938 bc	90 b	43285 bc
C-3241	6750 a	2900 a	2242 abc	708 bcd	5470 cd	188 cde	18258 abc
Total	117066	196143	45608	8992	53458	1788	
Quantity	22	16	18	12	5	2	75

Table 3: Significance of log regression coefficients for standard parameters (firmness, soluble solids, ethylene production and CO₂ production) used to differentiate ripening stages and cultivars

Parameter	Ripening ¹		Cultivars ²	
	Coeff.	p-value	Coeff.	p-value
Firmness	-13.3949	0.1082	0.1257	0.5813
Soluble solids	-0.2212	0.8269	0.1834	0.3990
Ethylene production	8.5584	0.1525	0.0496	0.8574
CO ₂ production	-4.1395	0.0657	0.2732	0.2658

¹ probability modeled is ripening stage "over-ripe"² reference cultivar is Bergeron

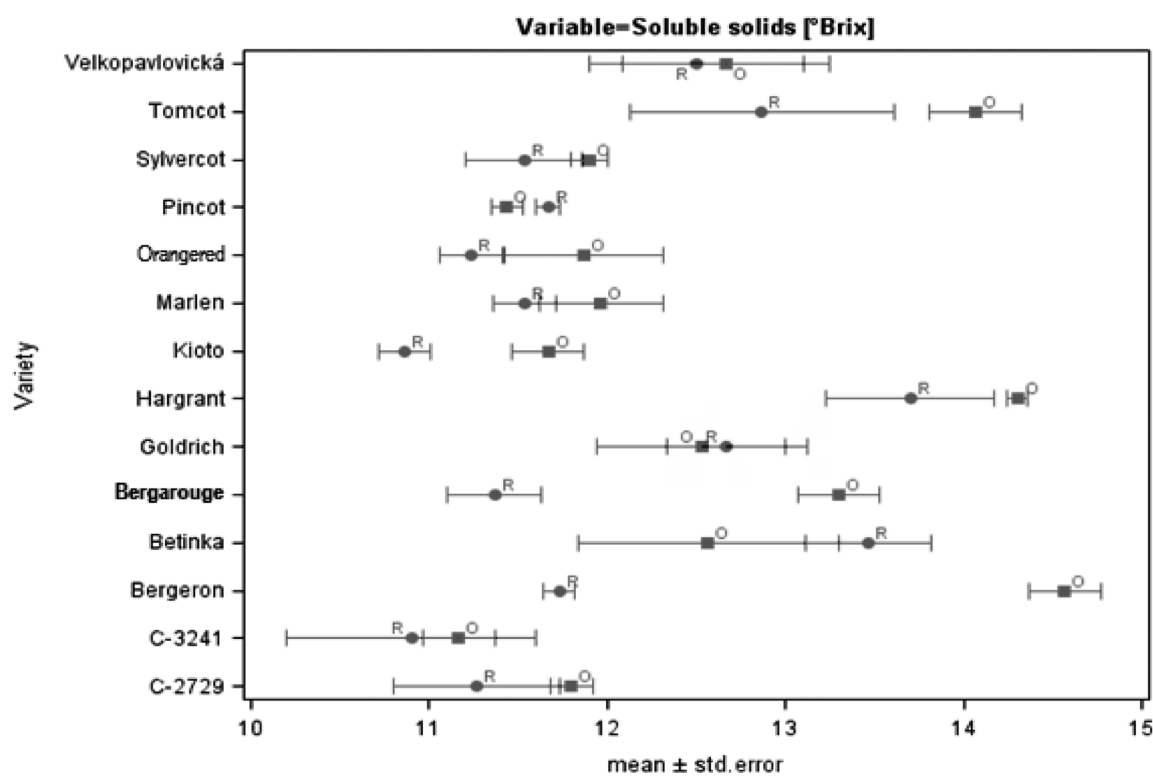


Fig. 4: Changes of soluble solids (°Brix) during ripening stages ripe (R) and over-ripe (O)

hand, in contrast to the findings of AUBERT and CHANFORAN (2007), butyl acetate was almost completely absent from all the cultivars during ripening. Limonene is the dominant terpenic compound, which gives a fruity, especially a citrusy note to the apricot aroma (GUILLOT et al., 2006), and 6-methyl-5-hepten-2-one is one of the two active ketones important for apricot aroma. In this study, the observed values for this ketone in the final stage of ripening of the following three cultivars were: 'Tomcot' $193.1 \pm 23.6 \mu\text{g/l}$, 'Bergeron' $199.0 \pm 19.3 \mu\text{g/l}$ and 'Bergarouge' $155.9 \pm 27.6 \mu\text{g/l}$. However, at the time of picking these concentrations ranged from very low levels, close to the detection limit, to values approximately half of those recorded in the final stage of ripening. As can be seen in Table 4, this compound significantly contributes to the resolution of cultivars. Important volatiles for differentiating between the ripening stages are benzylalcohol, (Z)-3-hexenal and γ -caprolactone, and for differentiating cultivars the important volatiles are 2-hep-

tanol, benzylalcohol, (E)-2-hexenal, ethyl undecanoate, 6-methyl-5-heptene-2-one, nerol, and α -linalool (Table 4). These compounds have previously been reported to contribute to apricot aroma by a number of authors (GÓMEZ and LEDBETTER, 1997; GREGER and SCHIEBERLE, 2007; DEFILIPPI et al., 2009; AUBERT et al., 2010). According to GREGER and SCHIEBERLE (2007), lactones are thought to be responsible for the sweet and fruity sensory properties of fresh apricots. The levels of γ -caprolactone determined in our study were found at the over-ripe stage to range from 149 $\mu\text{g/l}$ in the cv. 'Kioto' to as high as 7505 $\mu\text{g/l}$ in the cv. Velkopavlovicka. However, the other compounds from this chemical group, such as γ -octalactone and γ -Decalactone, were present at levels of tens of $\mu\text{g/l}$ and this applied to all the investigated cultivars. However, significantly higher concentrations were found in the cv. 'Marlen' ($709 \pm 125 \mu\text{g/l}$) and in the cv. 'Velkopavlovicka' ($689 \pm 121 \mu\text{g/l}$). As reported by ENGEL et al. (1988), lactones cannot be detected in mature green samples.

Principal component analysis (PCA) for the two stages of ripening

The first two principal components, PC1 and PC2, for ripe fruit accounted for 44.6 % of the total variance (30.2 % and 14.4 %, respectively; Fig. 5). The first component (PC1) was characterized by major levels of (Z)-3-Hexenal and α -Linalool in terms of positive values. For the second principal component (PC2), the attribute nerol showed high, positive values. The fact that the four cultivars 'Hargrant', 'Pincot', 'Silvercot' and 'Orangered' were well separated from the other ten cultivars in the data sets suggests that the volatiles used to calculate the scores (eigenvalues) were different (Table 5). The remaining cultivars ('Goldrich', 'Bergeron', 'C-2729', 'C-3241', 'Betinka', 'Bergarouge', 'Kioto', 'Tomcot', 'Velkopavlovicka' and 'Marlen') had the greatest similarity (Fig. 5). When the fruit is in the over-ripe stage, the production of other compounds like heptanol and benzylalcohol (significant in PC1), as well as ethylene and CO₂ (significant in PC2), becomes pronounced (Table 5), and their influence on the ripening process is confirmed by the p-values (Table 2). With the exception of alcohols and terpenes, the concentrations of which during ripening remain almost the same or even decrease, the other chemical groups (aldehydes, esters, lactones and ketones) can be used to differentiate between the cultivars because their concentrations in the fruit more than double, even though the total number of compounds in each group does not change. This applies to both ripe and over-ripe fruit (Table 2).

From the fourteen cultivars tested, only four could be clearly distinguished at the over-ripe stage (Fig. 6). The remaining set of cultivars cluster together at the lower left of Figure 6, and even here one can see the similarity in replicated samples of the same cultivar. The general increase in the total level of volatiles during ripening has also been observed by SOLIS-SOLIS et al. (2007); AUBERT and CHANFORAN (2007), AUBERT et al. (2010) and GOLIÁŠ et al. (2011).

Conclusion

The changes in the post-harvest physico-chemical properties of apricot cultivars picked at their optimal harvestable stage of maturity were investigated. Soluble solids ranged from 10.8 to 13.5 °Brix, and firmness from 1.1 to 3.2 MPa. Both ranges are very wide, and cannot be used to infer the earliness of cultivars. Ethy-

Table 4: Significant log regression coefficients for volatiles, used to differentiate ripening stages and cultivars

Differentiation of ripening ¹	Coeff.	p-value
Benzylalcohol	-9.2026	0.1535
(Z)-3-hexenal	-17.7549	0.0964
γ -caprolactone	24.2515	0.0775
Differentiation of cultivars ²		
2-heptanol	-1.094	0.0106
Benzylalcohol	0.6034	0.0476
(E)-2-hexenal	0.9788	0.0026
Ethyl undecanoate	-0.3914	0.1935
6-methyl-5-heptene-2-one	1.4605	0.0036
Nerol	-0.7306	0.0235
α -linalool	-0.5638	0.0728

¹ probability modeled is maturity "over-ripe"

² reference cultivar is Bergeron

Table 5: Eigenvectors of PCA components calculated for ripe and over-ripe fruit, using selected parameters

Parameter	Ripe fruit		Over-ripe fruit	
	PC1	PC2	PC1	PC2
Firmness (MPa)	0.192	-0.039	0.035	0.000
Soluble solid (°Brix)	-0.105	-0.045	-0.056	0.052
Ethylene ($\mu\text{l.kg}^{-1}.\text{h}^{-1}$)	-0.025	0.015	0.115	0.733
CO ₂ ($\text{mg.kg}^{-1}.\text{h}$)	-0.200	0.209	0.236	0.510
Benzylalcohol	0.189	0.397	0.465	-0.141
(Z)-3-hexenal	0.561	-0.023	-0.011	-0.008
γ -caprolactone	-0.017	0.018	0.311	0.188
2-heptanol	0.022	-0.164	0.465	-0.090
(E)-2-hexenal	-0.296	-0.120	0.124	0.095
Ethyl undecanoate	-0.029	0.230	0.271	-0.064
6-methyl-5-heptene-2-one	0.306	-0.355	0.198	-0.070
Nerol	0.240	0.583	0.229	-0.291
α -linalool	0.534	-0.277	0.008	-0.113

lene production at the time of picking is low and still only at threshold values for detection, which corresponds with the beginning of the climacteric phase. The values are similar in most cultivars. On the other hand, the production of CO₂ varies widely, ranging from 30 to 90 $\text{mg.kg}^{-1}.\text{h}^{-1}$. The cultivars could be distinguished from each other in the post-harvest period by differences in their production of ethylene, as well as differences in their rates of softening. Although there was no correlation found between these two parameters, it was observed that at least two cultivars ('Kioto' and 'Marlen') had low rates of ethylene production and also did not soften very well. The rate of CO₂ production, which is a classic parameter traditionally used to define the beginning of the climacteric phase of development, does not provide enough infor-

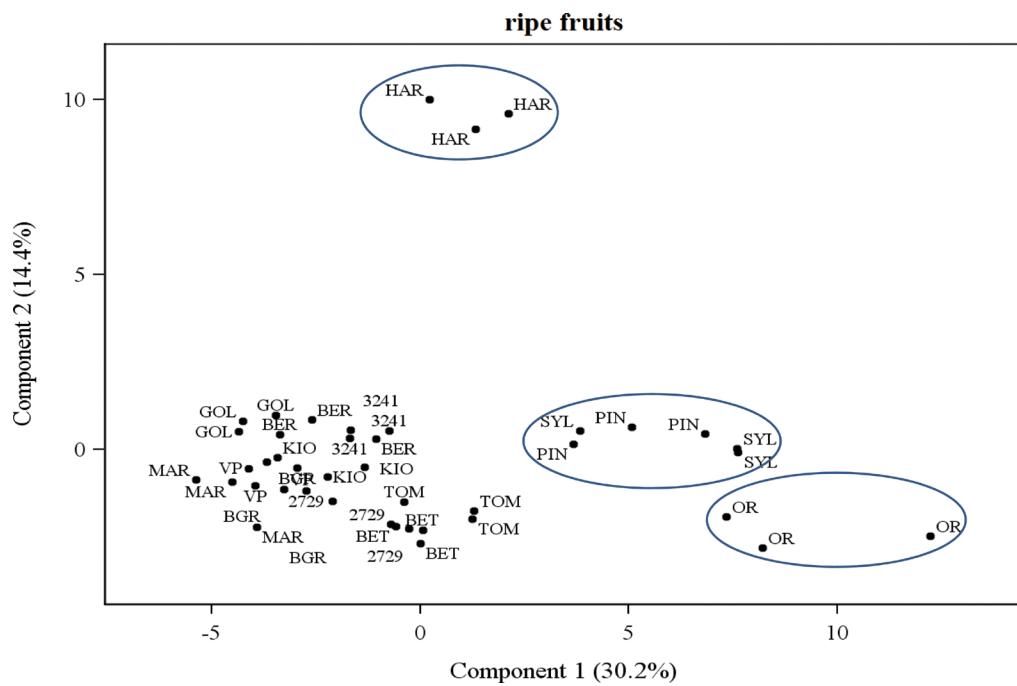


Fig. 5: Patterns of the first two PCA component scores - ripe fruit: BER – 'Bergeron', BET – 'Betinka', GO – 'Goldrich', OR – 'Orangered', PIN – 'Pincot', SIL – 'Silvercor', VP – 'Velkopavlovická', BER – 'Bergeron', BGR – 'Bergarouge', KIO – 'Kioto', HAR – 'Hargrant', 'C-2729' (a new cultivar), 'C-3241' (a new cultivar), TOM – 'Tomcot'

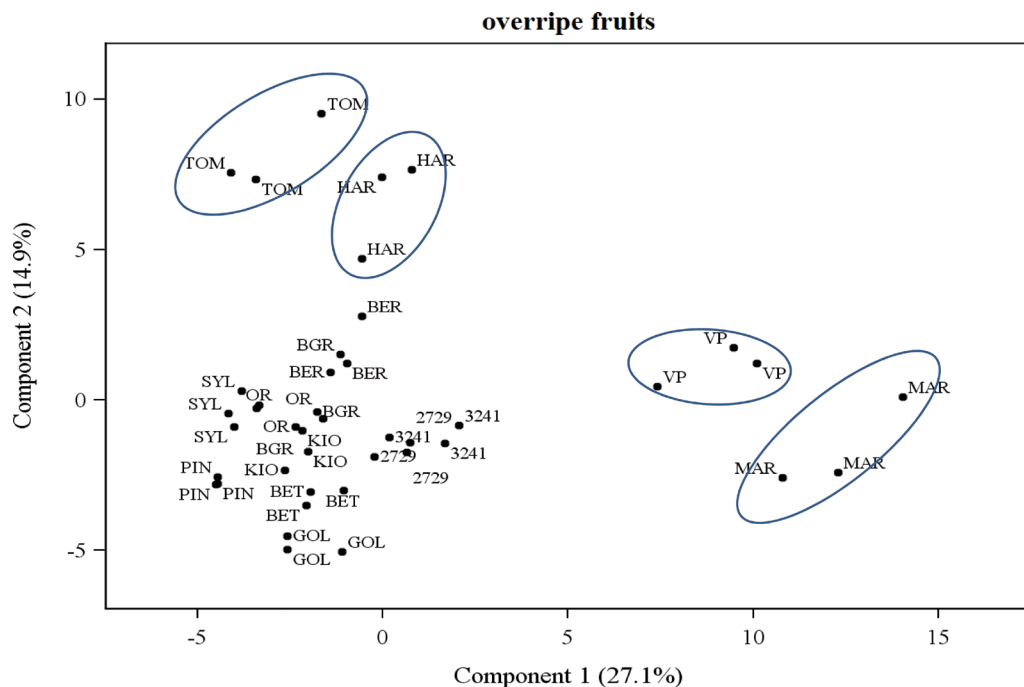


Fig. 6: Position of PC scores for the ten cultivars on the two first PC axes for ripening stage over-ripe (cultivars as in Figure 5)

mation to differentiate these apricot cultivars. The formation of the volatile compounds in apricot fruit is a dynamic process, and generally they are present in only small quantities, or even not at all at the time of harvest, developing only after a period of ripening. In the surveyed chemical classes, the biggest observed increases during the ripening of apricot fruit were in the levels of lactones, which more than doubled, followed by those of esters and aldehydes, whereas the levels of alcohols and terpenes declined during the ripening phase. Just three volatiles were sufficient to identify the over-ripe stage of maturity. When the cv. 'Bergeron' is compared with other cultivars, then a total of seven specific volatiles is required to separate them. Principal component analysis revealed correlations between volatile compounds, and the rate of production of physiologically important gases such as ethylene and CO₂, while fruit softening was not significant.

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