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Influence of maturity on volatile production and chemical composition of fruits of six apricot cultivars

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Summary

The fruits of six apricot cultivars were chemically analysed at two distinct stages of maturity, first when ready for picking by conventional commercial criteria, and again after another 6 days of maturation on the tree. Firmness, levels of soluble solids (SS), organic acids (citric and malic acid), sugars (sucrose, fructose and glucose), respiration rates and the production of ethylene and other volatile compounds were measured. Forty-five volatile compounds, including 12 alcohols, 10 aldehydes, 2 ketones, 10 esters, 7 terpenes, 3 lactones and 1 hydrocarbon were sampled by head space SPME and identified by GC-MS. The chemical composition of the non-volatile fraction (soluble solids and organic acids) exhibited only minor differences, insufficient to differentiate between the apricot cultivars or to make any meaningful judgement of the degree of maturity. Some variation between the cultivars in the respiration rate and production of ethylene was observed. However, using a stepwise logistic regression analysis, chemicals were identified among the volatile compounds which allowed the differentiation of fruits at the two different stages of maturity. In addition to the results of physical tests of firmness using standard penetration methods, differences in the degree of fruit maturation were clearly indicated by the levels of volatiles such as trans-2-hexen-1-ol, 2-methylbutylacetate, butyl-2-methylbutyrate, 6-methyl-5-heptene-2-one, acetophenone and γ-octalactone. Principal component analysis (PCA) confirmed the development of significant differences between each of the 6 apricot cultivars over the six day period of extra maturation on the tree, as each cultivar developed its own specific chemical signature. Moreover, this varietal character, which plays such an important part in determining overall attractiveness to the consumer, was only seen in fruits picked at the later stage of maturity.

Introduction

Apricots have climacteric fruits which can only be stored for a short time, as they have a high rate of respiration which typically increases with the commencement of ripening. There is intensive biogenesis of ethylene at this time and the increasing concentration of ethylene itself speeds up the process of ripening. Control of the ripening process therefore depends on either slowing down the build up of ethylene inside the fruits, or inhibiting its production, since ethylene is the trigger for ripening (CHAHINE et al., 1999). However, since apricots do not mature uniformly on the tree, to be of acceptable quality after harvesting and subsequent transportation to market, they have to be picked over a period of several days as they reach the desired stage of maturity. Early harvested fruits will develop volatiles only when kept at room temperature (KADER, 1999). The traditional criteria which have been used for determining the optimum stage for picking include firmness measurements, levels of soluble solids, the sugar/acidity ratio, internal ethylene concentrations and the proportion of green colour on the surface of the fruit. The production of volatile compounds is closely correlated with that of ethylene and indeed appears to be regulated by ethylene in apricots (FAN et al., 2000; GUICHARD and SOUTY, 1988; BOTONDI et al., 2003). These volatiles are important factors determining quality and influencing consumer acceptance (GÓMEZ and LEDBETTER, 1997; GREGER and SCHIEBERLE, 2007) and so deserve greater attention. Solid-phase micro-extraction (SPME) is an appropriate sampling technique for the collection of samples. The target analytes are adsorbed by a fibre exposed to the sample headspace (HS SPME) and coupled to a GC-MS (RIU-AUMATELL et al., 2004; SOLIS-SOLIS et al., 2007) and a gas chromatography-olfactometer (GC-O) (GUILLOT et al., 2006). The volatiles profile of apricot fruit is comprised of many compounds and includes alcohols, aldehydes, ketones, esters, terpenes (AUBERT and CHANFORAN, 2007; AUBERT et al., 2010; GUILLOT et al., 2006) and lactones (TAMURA et al., 2005). GONZÁLEZ-AGÜERO (2009) identified six major volatile compounds which contribute to the aroma of the apricot cultivar 'Modesto', these being hexanal, (E)-2-hexenal, linalool, hexan-1-ol, ethyloctanoate and hexylacetate. However, fruits harvested at more advanced stages of maturity, and subsequently stored and ripened at 20 °C, typically have higher levels of lactones, esters and terpenic compounds than those harvested at an earlier stage (AUBERT et al., 2010), and are therefore more desirable from the consumer's point of view. In this study we identified the volatile components present in six apricot cultivars harvested at two different stages of maturity. The objective was to document the qualitative and quantitative changes in the profile of the volatiles produced by apricot fruits during maturation.

Materials and methods

Plant material and methods

Fruits of six apricot cultivars were harvested at two different stages of maturity. The first harvest date, chosen for being the conventional stage of maturity for commercial harvest, was determined by external appearance and firmness. The ground colour of the skin as the fruit matures gradually changes from green to yellow, and the appropriate yellowish green colour at this stage of maturity depends on the cultivar in question. Guidance was provided by experienced commercial growers. Firmness, as measured by a physical penetration test, was not less than 3.0 MPa. The second stage of maturity at which fruit was harvested came 6 days after the first harvest. Six cultivars were selected for their typical and distinctive aromas, and different maturity dates, from the orchards of the Horticultural Faculty. These were the early-maturing cultivars 'Betinka' and 'Vynoslivyj', the mid-season cultivars 'Goldrich', 'Marlen' and the 'cv. 2927' and the late-maturing 'Bergeron'. Observations were first made on the whole, intact fruits and then pulp samples were prepared by homogenizing the fruits. Samples for aroma analysis were packed in aluminum foil pouches and stored at -24 °C until measurements were made a month later.

Firmness measurement

The technique used was the standard method of pushing a plunger into the intact fruit. Firmness was measured on two opposite sides of each fruit (n = 18), using a fruit firmness tester (Turoni, Italy) with

a plunger of cross-sectional area of 0.5 cm^2, inserted to a depth of 8 mm. The measurements were expressed in units of MPa.

Ethylene and CO_2 Measurement

For ethylene and CO_2 measurements, three samples of 25 fruits each were prepared and each placed in a 1 litre glass jar sealed for one hour. C_2H_4 and CO_2 were monitored by injecting 1 ml of a headspace gas sample into an Agilent 4890D gas chromatograph (Agilent Technologies, Inc.,Wilmington, DE, USA). Both gases were determined simultaneously on dual columns. A HP-Plot/Q column 30 m, I.D.0.53 mm, film 40 µm was used for ethylene and detected on FID, and a HP-AL/KCL column 30 m, I.D. 0.53 mm, film 15 µm was used for CO_2 and detected on TCD. Helium at 1.2 ml/min was used as a carrier gas. Ovens were programmed to rise from 80 to 120 °C at a rate of 10 °C / minute. The concentrations of ethylene are expressed as microliters per kilogram per hour, those for CO_2 are expressed as mg per kilogram per hour.

Soluble solids, sugar and organic acid analyses

The soluble solid content (SSC) was measured using a digital refractometer giving readings as °Brix, with samples taken from the equatorial zone of the fruit. After taking firmness measurements, the samples were frozen to -25 °C. Immediately before the chemical analysis, samples were thawed and levels of individual sugars (glucose, fructose and sucrose) and organic acids (malic, citric) were measured. Samples were diluted by 50% using de-ionized water, filtered (25 mm diameter syringe filter, 0.2 µm nylon with glass Alltech Associates Inc., Belgium) and transferred to a vial. An HPLC system (Watrex Delta Chrom) equipped with a pump (Delta Chrom SDS 030), a refractive index detector (K2301 Knauer) for measuring sugar levels, and a UV/Vis detector (Watrex Delta Chrom UVD 200) monitored at 210 nm, for the measurement of organic acids. The samples were isocratically separated at 0.7 mL/min, using a Watrex 250 x 8 mm column fitted by polymer IEX H form 8 µm, using de-ionized water at 50 °C as the mobile phase for sugars and 0.05 M methansulfonic acid (Sigma-Aldrich Chemie, Steinheim, Germany) for organic acids. Concentrations are expressed as g per kg fresh weight (FW).

Analysis of volatiles

The sampling technique for volatiles produced by the apricot fruits was a solid phase microextraction (SPME). Two grams of apricot pulp were placed in a 4 ml glass vial (Supelco, Sigma-Aldrich Co.) to which was added 10 µl of 2-octanol (as an internal standard), and the vial was then sealed with a Teflon silicone septum. The sample was exposed to the fiber for 30 min in a solid block of ETS-D4 Kika Werke, Germany, maintained at 50 ± 0.5 °C. The fiber, Carboxen/polydimethylsiloxane (CAR/PMDS 85 µm, Sigma-Aldrich Co.) was conditioned in a GC injection port at 250 °C for 1 h prior to use. This fiber was chosen in preference to several other possible coating materials for the analysis of apricot volatile compounds because the results for the analysis of small compounds are more accurate compared to PDMS/DVB, for example, due to the higher number and concentration of volatiles (PEREZ et al., 2002; MARTI et al., 2003). The headspace sampling was performed at the same temperature for 30 min. The desorption of the analytes from the fibre coating took place in the injection port of the GC at 250 °C for 5 min. For each treatment three SPME extractions and desorptions were performed.

Gas chromatography – mass spectrometry

An Agilent Technologies 7890A GC system (Agilent Technologies, Inc., Santa Clara, CA, USA), coupled to a quadrupole mass spectrometer (Agilent Technologies 5975C MSD) fitted with a DB-Wax fused silica capillary column (30 m x 0.25 mm I.D.; J&W Scientific coated with a 0.25 µm layer), was used and operated in a standard manner. Helium at 1.2 mL/min was used as a carrier gas. The transfer line was at 250 °C. Injector and detector temperatures were also both at 250 °C. The oven temperature was programmed to increase from 35 °C (maintained for 4 min) to 250 °C, at a rate of 4 °C/min. Thermal desorption of the compounds took place in the GC injection port, equipped with a 0.75 mm I.D. splitless glass liner, held at 250 °C for 5 min in a splitless mode. Then the split valve was opened (1:50), and the fiber remained in the injection port for the entire GC run to ensure complete desorption of the aroma compounds. The mass spectrometer was operated in the electron impact mode with an electron energy of 70 eV; source temperature 230 °C; quadrupole temperature 150 °C; mass range m/z 50 - 500; scan rate 3.62 s per scan; and EM voltage 1,150V. Compounds were identified based on

Tab. 1: Summary statistics – Acidity parameters

		Variety (mean ± std.error)					
Variable	**Maturity**	**Bergeron**	**Betinka**	**Goldrich**	**Marlen**	**Vynoslivyj**	**cv. 2927**
Citric acid	M	17.9 ± 0.6	22.3 ± 0.7	42.1 ± 2.0	32.9 ± 2.6	8.5 ± 1.5	33.2 ± 2.2
	EM	11.3 ± 0.6	19.1 ± 0.8	25.7 ± 1.2	23.1 ± 3.4	5.9 ± 0.5	23.2 ± 1.2
Malic acid	M	25.9 ± 1.0	21.6 ± 1.0	25.3 ± 0.9	17.0 ± 0.6	23.2 ± 2.6	16.9 ± 0.6
	EM	23.8 ± 1.3	19.7 ± 1.7	21.5 ± 0.5	15.6 ± 0.3	18.7 ± 1.1	14.3 ± 0.4
Sucrose	M	137.5 ± 4.4	126.1 ±16.2	99.6 ± 7.6	117.4 ± 7.9	165.1 ± 9.3	110.5 ± 2.0
	EM	136.1 ± 4.8	133.8 ± 8.3	138.1 ± 5.0	128.0 ± 6.4	179.7 ± 3.8	127.4 ± 2.9
Glucose	M	25.9 ± 2.2	26.6 ± 3.0	21.3 ± 1.1	26.8 ± 2.0	36.7 ± 2.2	25.1 ± 0.4
	EM	23.5 ± 8.7	26.5 ± 0.9	32.8 ± 1.2	31.6 ± 2.4	39.9 ± 1.9	22.6 ± 8.5
Fructose	M	10.9 ± 0.3	6.3 ± 0.2	12.2 ± 0.7	8.3 ± 0.5	15.8 ± 0.7	10.6 ± 0.5
	EM	8.8 ± 3.2	5.5±0.02	14.6 ± 0.6	8.6 ± 0.9	14.2 ± 0.1	9.6 ± 0.8
Soluble solids	M	10.8 ± 0.2	11.3 ± 1.5	9.8 ± 0.3	11.0 ± 0.6	13.0 ± 0.4	9.4 ± 0.3
	EM	13.4 ± 0.8	12.6 ± 0.4	13.5 ± 0.2	12.4 ± 0.8	17.7 ± 0.3	13.1 ± 0.1

M -mature, EM-extra-mature

an NIST mass spectra library search. Most of these compounds were further confirmed by comparing their mass spectra and retention times with those obtained for standards. Estimated concentrations for all compounds were made by GC/MS peak area comparisons of the external components with the area of a known quantity injected in a 4 ml vial with two ml of aqueous solution.

Statistical analysis

All statistical analyses were performed using the SAS package version 9.2. For each apricot variety descriptive characteristics (mean ± standard error) at each stage of maturity were calculated. A logistic regression model (implemented in the procedure LOGISTIC, stepwise approach was used to explain the effects of all volatile and non-volatile parameters as explanatory variables in a binary response (mature / extra-mature). The binary value 0 corresponded in this model to the standard harvest maturity stage; the value 1 coded for the extra-mature stage of fruits. Principal component analysis (PCA), using the procedure PRINCOMP, was used to discriminate between the varieties at each of the two stages of maturity. The first three principal components were chosen as a linear combination of the observed variables, selected in such a way that the resulting components accounted for the maximum amount of variation in the set of volatile and non-volatile variables. Before the analysis the data matrix was standardized by setting mean values at zero.

Results and discussion

Respiration and ethylene production

Fruits judged to be at the optimal degree of maturity for commercial harvest were completely yellow over the whole surface, without any green patches, and presumed to be just starting to produce ethylene. Ethylene production in these fruits varied from 0.19 µl/kg to 0.51 µl/kg per hour. The range of CO_2 production was from 70 mg/kg to 115 mg/kg per hour (Tab. 2), with the exception of cv. 'Betinka', in which the production of both gas compounds was significantly higher in the mature fruits (ethylene 12.15 ± 2.12 µl/kg per hour, CO_2 266.36 ± 25.71 mg/kg per hour). The initial firmness of the fruit pulp in each of the varieties was 3.50 MPa, and decreased during the 6 days of storage in all fruits. Typically, firmness measurements taken from puncture tests performed on the first harvest date varied from 3.43 MPa to 3.16 MPa, although lower values were recorded in the cultivars 'Marlen' and 'Vynoslivyj' - 2.33 and 2.72 MPa, respectively. After a six day period of extra maturation on the tree, the fruits softened further, at a similar rate in all six varieties (ranging from 0.22 MPa/day to 0.17 MPa/day), but still well within the bounds of acceptability. The University of Davis considers that apricots are very acceptable to consumers when firmness is between 0.09 and 0.130 MPa (CRISOSTO and MITCHELL, 2003). The degree of extra-maturation, as measured by the production of ethylene, was lowest in the late-maturing cultivars 'Bergeron' and 'cv. 2927'. This is also seen in apples, where the fruits of early-maturing cultivars frequently produce higher levels of ethylene than late-maturing cultivars, and so typically have a shorter storage life (WATKINS, 2003). The fruits simultaneously exhibit an increasing respiration rate and a similar pattern of ethylene production, with some small differences observed between the cultivars (Tab. 2). However, by discrimination analysis of the physical parameters alone, the mature and extra-mature fruits for these six cultivars can be differentiated only to a limited extent (Fig. 1).

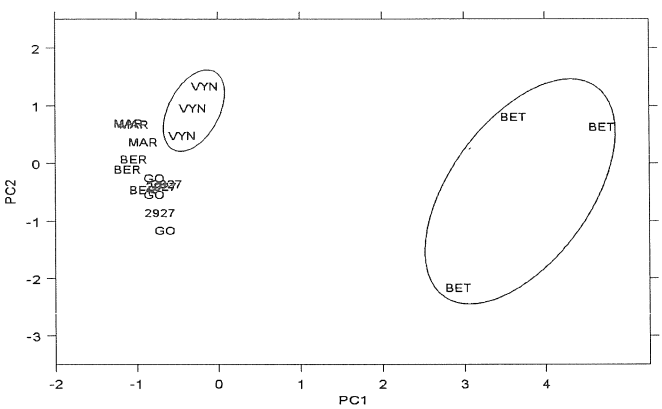

Fig. 1: Patterns of PCA scores for physical parameters – mature fruits

Chemical analysis of the apricot cultivars

Citric acid is usually the principal acid found in fresh fruit, but apricot cultivars have approximately equal amounts of citric and malic acids, even though these acids are closely related to the cultivar. The exact ratios vary with the cultivar, with the cv. 'Betinka' normally having equal levels of both acids, the cvs. '2927', 'Goldrich' and 'Marlen' having higher levels of citric acid and the cvs. 'Bergeron', and 'Vynoslivyj' having higher levels of malic acid. During extra maturation on the tree there is a greater decrease in citric acid levels compared to those of malic acid (Tab. 1). Sucrose was found to be the predominant sugar in all the apricot varieties. Sucrose levels ranged from 126 g/l to 165 g/l and the ratio of glucose to fructose was typically 2.36. The chemical analyses of non-volatile substances showed only small differences, differentiating the cultivars only to a limited extent (Fig. 2). The production of volatile compounds in climacteric fruits maturing on the

Tab. 2: Summary statistics - Ethylen, R-CO_2 and penetration

		Variety (mean ± std.error)					
Variable	**Maturity**	**Bergeron**	**Betinka**	**Goldrich**	**Marlen**	**Vynoslivyj**	**cv. 2927**
Firmness	M	3.2 ± 0.1	3.7 ± 0.6	3.4 ± 0.3	2.3 ± 0.1	2.7 ± 0.2	3.2 ± 0.2
	EM	1.6 ± 0.1	2.4 ± 0.2	1.9 ± 0.2	1.3 ± 0.3	1.3 ± 0.1	1.9 ± 0.1
Respiration	M	70.0 ± 2.8	266.4 ± 25.7	88.0 ± 1.4	78.0 ± 4.5	115.8 ± 7.2	97.6 ± 2.5
	EM	83.4 ± 3.6	132.6 ± 1.3	91.3 ± 1.9	122.6 ± 7.7	123.5 ± 5.3	114.9 ± 10.5
Ethylene production	M	0.3 ± 0.02	12.2 ± 2.1	0.4 ± 0.1	0.5 ± 0.1	0.5 ± 0.5	0.2 ± 0.03
	EM	1.08 ± 0.15	9.8 ± 2.6	6.0 ± 0.5	2.1 ± 0.7	1.5 ± 0.04	1.2 ± 0.1

M-mature, EM-extra-mature

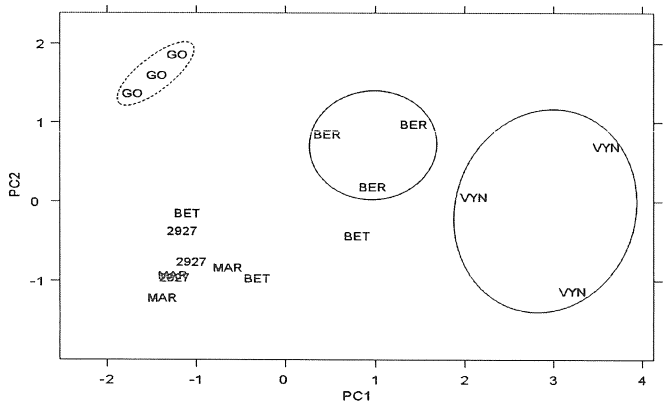

Fig. 2: Patterns of PCA scores for acidity parameters – mature fruits

tree (Tab. 3) is positively correlated with an increase in the ethylene levels in the flesh of the fruit and its subsequent release from the intact fruit. A close correlation of decreasing ethylene production and increasing volatile production has been observed for apricot (FAN et al., 2000) and banana fruits (GOLDING et al., 1998). A list of all the volatile compounds found in each of the analyzed varieties was made: ethanol, 2-methylbutan-1-ol, 3-methyl-2-buten-1-ol, n-pentan-1-ol, 4-methylpentan-1-ol, n-hexan-1-ol, ethylhexan-1-ol, phenol, 2-furfurylalcohol, 3-methylbutanal, n-hexanal, n-nonanal, n-decanal, trans-2-decenal, 2-furfural, 5-methyl-2-furfural, phenethylacetate, benzylacetate, pentylbutyrate, ethyl trans-3-hexenoate, butanedioic-acid diethyl, γ-caprolactone, γ-decalactone, α-terpineol, α-linalool, nerol and β-ionone. The results indicate that in the three to 6 days after reaching the first stage of maturity, the proportion of alcohols (3-methyl-2-buten-1-ol, trans-hexen-1-ol, phenol and 2- furfurylalcohol) and aldehydes decreased, while that of esters

Tab. 3: Summary statistics – Volatiles

			Variety (mean ± std.error)					
Group	**Variable**	**Maturity**	**Bergeron**	**Betinka**	**Goldrich**	**Marlen**	**Vynoslivyj**	**cv. 2927**
Alcohols	Ethanol	M	30.9 ± 4.4	54.2 ± 13.9	25.1 ± 4.8	34.5 ± 3.4	49.7 ± 7.4	33.5 ± 3.7
		EM	30.9 ± 3.3	181.5 ± 55.2	40.2 ± 3.8	100.3 ± 50.7	110.1 ± 8.2	101.7 ± 23.3
	2-Methylbutan-1-ol	M	60.5 ± 7.8	252.5 ±121.3	165.9 ± 12.0	670.9 ±216.1	227.6 ± 38.3	813.1 ±217.4
		EM	145.0 ± 54.6	177.8 ± 98.7	115.1 ± 25.8	118.6 ± 22.9	92.4 ±29.2	133.4 ± 46.4
	3-Methyl-2-buten-1-ol	M	629 ± 18	621 ± 86	628 ± 40	890 ±122	485 ± 67	692 ±119
		EM	432 ± 24	516 ± 86	451 ±151	510 ±169	242 ± 27	578 ± 38
	n-Pentan-1-ol	M	6.3 ± 0.2	4.5 ± 1.0	3.6 ± 0.67	7.2 ± 1.1	10.0 ± 2.0	4.1 ± 0.7
		EM	10.1 ± 1.1	7.8 ± 0.8	6.1 ± 2.1	7.3 ± 1.1	10.7 ± 0.7	10.4 ± 1.4
	3-Methyl-1-pentan-1-ol	M	605 ± 87	1136 ± 272	881 ± 93	2115 ± 248	352 ± 79	304 ± 22
		EM	1540 ± 140	1571 ± 198	1442 ± 247	2259 ± 620	523 ± 98	551 ±105
	4-Methyl-1-pentan-1-ol	M	97.8 ± 3.0	78.6 ± 2.8	137.1 ± 5.6	178.1 ± 44.1	108.9 ± 8.3	128.9 ± 32.1
		EM	99.8 ± 6.6	302.5 ±171.3	212.5 ± 89.3	107.8 ± 28.9	108.6 ± 10.6	90.2 ± 1.3
	n-Hexan-1-ol	M	1.0 ± 0.7	1.7 ± 1.0	14.3 ± 0.8	43.4 ± 5.9	36.1 ± 18.0	27.1 ± 2.5
		EM	34.1 ± 1.2	50.5 ± 14.2	10.5 ± 2.5	32.9 ± 18.8	48.6 ± 4.6	54.3 ± 8.2
	trans-2-Hexen-1-ol	M	484 ±123	712 ±258	618 ±269	700 ±119	404 ± 58	526 ± 72
		EM	250 ± 30	250 ± 43	175 ± 35	300 ± 81	138 ± 19	244 ± 34
	Ethylhexan-1-ol	M	6.0 ± 1.4	6.3 ± 0.3	5.5 ± 0.4	6.1 ± 0.8	5.8 ± 0.4	7.1 ± 1.4
		EM	4.3 ± 0.3	4.4 ± 0.3	4.5 ± 0.5	5.2 ± 0.7	3.9 ± 0.8	4.4 ± 0.6
	Phenol	M	8.7 ± 0.01	7.8 ± 0.6	7.3 ± 0.4	8.2 ± 0.8	14.4 ± 6.9	7.8 ± 0.3
		EM	< 0.01	7.6 ± 1.6	< 0.01	8.1 ± 0.8	5.9 ± 0.01	6.2 ± 0.7
	2-Furfurylalcohol	M	139.2 ± 0.01	157.6 ± 0.01	489.9 ± 73.2	180.2 ± 6.9	< 0.01	238.2 ± 57.7
		EM	< 0.01	91.7 ± 0.0	< 0.01	127.3 ± 0.01	< 0.01	< 0.01
	Benzylalcohol	M	307.7 ± 31.8	323.2 ± 33.8	123.1 ± 26.2	513.3 ±103.9	341.4 ± 38.2	107.5 ± 3.7
		EM	506.4 ± 97.2	331.8 ± 51.5	311.9 ± 60.7	409.1 ±166.5	168.9 ± 16.7	197.6 ± 11.0
Aldehyds	2-Methylbutanal	M	35.2 ± 7.3	15.9 ± 1.2	23.5 ± 4.7	26.8 ± 0.8	42.9 ± 8.9	17.7 ± 0.8
		EM	32.7 ± 3.6	20.1 ± 3.0	60.1 ± 11.9	18.9 ± 1.3	35.0 ± 5.6	39.9 ± 7.5
	3-Methylbutanal	M	62.1 ±19.1	22.3 ± 2.1	32.9 ± 8.4	36.1 ± 3.3	83.3 ±15.9	20.3 ± 2.1
		EM	61.7 ± 6.9	35.0 ± 7.4	115.8 ± 24.1	32.0 ± 2.9	66.5 ±11.8	76.8 ±15.5
	n-Hexanal	M	322 ± 30	837 ± 516	163 ± 37	173 ± 48	158 ± 78	86 ± 16
		EM	321 ± 55	1878 ± 370	673 ± 87	402 ±205	587 ± 97	418 ±112

Group	Variable	Maturity	Variety (mean ± std.error) Bergeron	Betinka	Goldrich	Marlen	Vynoslivyj	cv. 2927
	trans-2-Hexenal	M	207.5 ± 85.7	56.6 ±10.5	235.9 ± 91.3	92.5 ±37.1	71.2 ± 4.5	973 ±319
		EM	144.5 ± 73.2	72.7 ± 4.8	85.3 ± 9.9	99.5 ±33.4	254 ± 64	94.8 ± 9.2
	n-Octanal	M	14.9 ± 2.6	16.0 ± 2.0	29.8 ± 1.6	16.4 ± 1.2	11.4 ± 4.1	22.9 ± 4.2
		EM	12.2 ± 1.7	8.8 ± 0.9	10.4 ± 1.0	10.4 ± 1.6	8.0 ± 2.1	7.1 ± 0.6
	n-Nonanal	M	64.5 ±31.8	273.6 ± 90.4	5.5 ± 3.6	7.4 ± 5.8	431.9 ±119.3	6.1 ± 4.7
		EM	103.4 ± 14.7	322.2 ± 62.9	36.5 ±20.2	222.4 ± 38.0	336.4 ± 76.8	155.6 ± 22.7
	n-Decanal	M	0.63 ± 0.04	0.66 ± 0.03	0.81 ± 0.02	0.69 ± 0.04	0.62 ± 0.11	0.78 ± 0.04
		EM	0.55 ± 0.02	0.64 ± 0.13	0.42 ± 0.05	0.67 ± 0.25	0.46 ± 0.01	0.51 ± 0.08
	trans-2-Decenal	M	0.44 ± 0.04	0.83 ± 0.11	0.44 ± 0.16	0.70 ± 0.09	0.76 ± 0.21	0.19 ± 0.01
		EM	0.53 ± 0.01	0.51 ± 0.01	< 0.01	1.29 ± 0.25	0.60 ± 0.01	1.08 ± 0.01
	2-Furfural	M	14.8 ± 7.1	24.0 ± 2.8	26.0 ± 6.3	23.2 ± 14.5	18.4 ± 5.4	19.6 ± 5.8
		EM	13.8 ± 1.7	28.2 ± 11.4	20.4 ± 3.2	47.8 ± 32.3	12.3 ± 2.2	23.7 ± 9.5
	5-Methyl-2-furfural	M	297 ± 29	179 ± 41	150 ± 44	453 ± 87	498 ± 20	295 ± 67
		EM	143 ± 44	162 ± 32	160 ± 53	211 ± 92	150 ± 36	152 ± 31
Esters	2-Methylbutyl acetate	M	75.0 ± 9.3	84.7 ±11.4	42.4 ± 1.3	146.8 ± 12.4	90.2 ± 5.2	79.3 ±11.1
		EM	148.6 ± 14.9	111.2 ± 5.0	121.3 ± 2.8	137.1 ± 19.8	133.1 ± 9.3	67.8 ± 9.2
	(Z)-2-Hexenyl acetate	M	140.4 ± 21.8	133.9 ± 46.5	66.3 ±43.2	83.6 ±34.3	110.0 ± 28.0	37.6 ± 9.2
		EM	73.8 ±30.0	91.3 ± 8.8	95.2 ± 7.9	108.9 ± 21.8	74.7 ±18.0	69.9 ± 6.5
	Phenethylacetate	M	201 ± 69	184 ± 41	432 ± 69	332 ± 57	1022 ± 116	240 ± 55
		EM	581 ±109	815 ± 24	905 ± 70	990 ±116	364 ± 12	151 ± 12
	Benzylacetate	M	111.4 ± 0.01	< 0.01	64.7 ± 0.01	126.3 ± 28.0	135.1 ± 11.3	123.5 ± 0.01
		EM	< 0.01	< 0.01	< 0.01	122.1 ± 0.01	< 0.01	< 0.01
	Pentylbutyrate	M	< 0.01	229.2 ± 0.01	2010 ± 26	1040 ± 0.01	< 0.01	1424 ± 77
		EM	40.0 ± 16.3	7.7 ± 0.01	131.9 ± 19.2	14.1 ± 7.1	61.9 ± 11.3	144.1 ± 76.2
	Butyl-2-methylbutyrate	M	30.0 ±20.1	38.9 ±16.6	24.3 ± 1.8	111.5 ± 36.1	39.3 ± 7.8	121.4 ± 35.0
		EM	22.8 ± 9.9	27.3 ±15.3	18.2 ± 3.3	26.4 ±10.8	14.4 ± 4.4	22.4 ± 4.3
	n-Hexylbutanoate	M	1.5 ± 0.2	2.5 ± 0.4	1.2 ± 0.2	2.9 ± 0.3	3.1 ± 0.6	1.8 ± 0.2
		EM	2.2 ± 0.2	3.4 ± 0.9	0.9 ± 0.2	2.6 ± 0.8	3.1 ± 0.3	3.6 ± 0.5
	Ethyl trans-3-hexenoate	M	288 ± 5	78 ±15	82 ± 7	41 ± 6	194 ± 70	72 ± 16
		EM	2315 ± 511	205 ± 69	192 ± 30	593 ±222	3064 ± 537	58 ± 26
	Ethylhexanoate	M	97.5 ±43.9	295.3 ± 55.2	47.5 ± 1.2	125.4 ± 48.3	99.1 ±22.9	37.0 ± 9.2
		EM	119.5 ± 40.4	335.9 ± 17.0	287.2 ± 72.3	70.0 ±19.2	106.0 ± 16.6	319.3 ± 40.0
	Butanedioic acid dietethyl	M	90.7 ±60.7	125.0 ± 33.4	709.1 ± 91.4	254.3 ± 15.4	62.5 ± 9.3	381.5 ± 66.9
		EM	40.1 ± 8.2	86.4 ±19.0	32.4 ± 2.8	90.4 ±35.8	31.5 ± 5.0	44.5 ±22.2
Ketons	6-Methyl-5-heptene-2-one	M	< 0.01	152.1 ± 4.1	96.6 ± 6.0	128.8 ± 17.9	< 0.01	< 0.01
		EM	134.8 ± 12.6	150.3 ± 11.1	122.7 ± 16.2	175.1 ± 55.7	< 0.01	103.2 ± 6.9
	Acetophenone	M	3.2 ± 0.6	7.2 ± 1.2	2. ± 0.1	10.8 ± 3.9	3.8 ± 1.0	2.9 ± 0.5
		EM	2.9 ± 0.8	2.5 ± 0.4	2.2 ± 0.1	2.5 ± 0.8	3.0 ± 1.1	2.0 ± 0.4
Lactons	γ-Caprolactone	M	< 0.01	199.2 ± 77.8	< 0.01	28.2 ± 5.7	37.1 ± 13.3	< 0.01
		EM	24.0 ± 14.2	353.6 ± 53.7	< 0.01	161.3 ± 70.3	89.4 ± 24.7	41.7 ± 20.5
	γ-Octalactone	M	0.6 ± 0.01	1.3 ± 0.1	< 0.01	1.3 ± 0.01	0.9 ± 0.01	< 0.01
		EM	1.9 ± 0.1	1.3 ± 0.3	< 0.01	2.1 ± 0.2	1.7 ± 0.2	< 0.01
	γ-Decalactone	M	8.1 ± 1.6	6.5 ± 1.3	< 0.01	13.8 ± 4.0	6.5 ± 0.9	< 0.01
		EM	23.5 ± 3.3	6.7 ± 0.7	6.0 ± 1.4	29.1 ± 7.2	26.1 ± 2.4	2.8 ± 0.2
Terpenols	Citronellol	M	3.4 ± 0.4	4.8 ± 1.0	2.3 ± 0.1	9.5 ± 1.7	2.3 ± 0.3	1.3 ± 0.01
		EM	7.9 ± 1.4	6.5 ± 0.8	6.1 ± 1.1	11.0 ± 2.8	1.9 ± 0.01	2.2 ± 0.5
	α-Terpineol	M	< 0.01	< 0.01	< 0.01	3.6 ± 0.01	< 0.01	< 0.01
		EM	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01

Group	Variable	Maturity	Variety (mean ± std.error) Bergeron	Betinka	Goldrich	Marlen	Vynoslivyj	cv. 2927
	α-Linalool	M	2.2 ± 0.1	3.2 ± 0.5	4.9 ± 1.4	3.1 ± 0.3	3.2 ± 0.9	3.5 ± 0.8
		EM	3.0 ± 0.4	4.0 ± 0.2	3.1 ± 0.3	2.9 ± 0.6	5.5 ± 1.0	3.2 ± 0.3
	cis-Geraniol	M	5.8 ± 1.2	4.4 ± 0.5	2.9 ± 0.01	6.4 ± 1.3	10.9 ± 0.8	6.5 ± 0.01
		EM	< 0.01	< 0.01	< 0.01	5.0 ± 0.01	< 0.01	< 0.01
	Nerol	M	0.42 ± 0.07	0.46 ± 0.01	0.28 ± 0.01	0.62 ± 0.18	1.00 ± 0.16	0.58 ± 0.01
		EM	0.49 ± 0.01	< 0.01	0.36 ± 0.01	0.88 ± 0.01	0.21 ± 0.01	< 0.01
	Limonene	M	204.8 ± 50.8	158.9 ± 22.4	118.7 ± 48.8	336.6 ± 79.8	249.8 ± 96.6	338.3 ± 51.9
		EM	116.5 ± 37.6	62.6 ±10.4	85.6 ±30.3	114.9 ± 23.8	108.6 ± 13.0	78.8 ± 6.9
Miscelaneous	Farnesene	M	56.3 ± 3.5	108.2 ± 13.5	100.5 ± 0.8	69.6 ± 6.9	49.4 ± 9.5	75.7 ± 2.0
		EM	65.1 ± 8.6	105.9 ± 10.4	83.6 ±13.6	57.1 ±27.9	35.7 ± 7.3	81.1 ± 6.8
	β-Ionone	M	32.1 ± 2.8	41.1 ± 5.3	31.7 ± 1.2	43.7 ± 6.3	22.4 ± 2.7	24.2 ± 1.8
		EM	43.9 ± 9.8	40.0 ± 5.5	27.3 ± 5.3	37.2 ± 19.9	12.3 ± 3.1	33.5 ± 3.8

M-mature, EM-extra-mature

and lactones (γ-caprolactone, γ-octalactone and γ-decalactone) increased, especially for γ-caprolactone. Terpenic compounds were present in low concentrations, the main one being limonene. This confirms previously published observations on apricots (SOLIS-SOLIS et al., 2007; AUBERT and CHANFORAN, 2007; AUBERT et al., 2010), that in post-harvest maturation the levels of C_6 compounds decrease dramatically and those of esters, lactones and terpene compounds greatly increase.

Differentiation of apricot cultivars by principal component analysis (PCA)

Tab. 4 presents parameters selected by stepwise logistic regression calculated with seven separate groups, comprising a total of 36 physical and chemical parameters. All variables were standardized with a zero mean. The aim of this procedure was to find those physical and chemical variables which contribute most to the variation seen in mature and extra-mature fruits. This approach helps to reduce the size of the matrix of parameters observed by identifying those key variables whose contribution to the overall variation promise to most effectively differentiate the varieties. Estimations of effects, presented in Tab. 4, show the extent of variation assigned to the process of maturing on the tree. Negative or positive values describe decreasing or increasing effects of the initial variable. Based on 95% confidence intervals the following parameters in Tab. 4 appear to be significant for the process of maturation: firmness, trans-2-hexen-1-ol, 2-methylbutylacetate, butyl-2 methylbutyrate, 6-methyl-5-heptene-2-one, acetophenone, and γ-octalactone. Terpe-

Tab. 4: Logistic Regression – Confidence Intervals for Parameters

Explanation variable: Ripe				
Group	**Parameter**	**Estimate***	**95% Confidence**	**Limits**
Standard parameters	Firmness	**-6,620**	-12,707	-0,533
	Ethylene	1,273	-0,191	2,737
Alcohols	3-Methylpentan-1-ol	1,779	-0,003	3,561
	trans-2-Hexen-1-ol	**-3,273**	-5,390	-1,156
	Benzylalcohol	-0,863	-2,438	0,711
Aldehyds	2-Methylbutanal	1,844	-0,837	4,526
	trans-2-Hexenal	1,596	-1,055	4,248
	n-Octanal	-5,079	-10,394	0,237
Esters	2-Methylbutylacetate	**3,264**	0,671	5,856
	(Z)-2-Hexenylacetate	-1,723	-3,553	0,107
	Butyl-2-methylbutyrate	**-5,205**	-10,066	-0,345
	n-Hexylbutanoate	1,270	-0,222	2,763
Ketons	6-Methyl-5-heptene-2-one	**1,121**	0,193	2,050
	Acetophenone	**-2,255**	-4,039	-0,471
Lactons	γ-Octalactone	**1,134**	0,315	1,952
Terpenols	Citronellol	21,991	-13,396	57,378
	cis-Geraniol	-39,219	-103,900	25,473
	Limonene	-20,963	-53,573	11,648
Miscelaneous	Farnesene	-23,933	-62,566	14,700

* Significant values are in bold

nols do not appear to play a significant role. All standardized variables contributing to the total variation observed in the mature and extra-mature fruit samples were taken as the input matrix to a principal component analysis (PCA), done separately for each stage of maturity. Fig. 3 shows the proportion of the variance in both mature and extra-mature fruits which can be explained by six principal components. Just three principal components explained 65% of the total variation in the case of mature fruit and nearly 78% in the case of extra-mature fruits, taking into account the scores presented in Tab. 5. Fig. 4 and 5 show the first three component scores for each of three samples of six apricot cultivars. It can be seen that all samples are relatively homogenous within each variety, allowing one to differentiate between the selected apricot cultivars. In the case of ripe fruits the best differentiated cultivars are 'Vynoslivyj', 'Bergeron', 'Goldrich', 'Betinka' and 'cv.2927', the exception being 'Marlen'. Since the first principal component consists of benzyl alcohol and acetophenone, then cvs. 'Vynoslivyj', 'Bergeron' and 'Betinka' must have different levels of these volatiles (Fig. 4 – extra-mature fruits). Fruit maturing on the tree can be differentiated similarly, using volatiles such as 3-methylpentan-1-ol, benzylalcohol, 6-methyl-5-heptenone-2-one and citronellol (Tab. 5). The cv. 'Marlen' is more sensitive regarding the stage of maturity but, for mature and extra-mature fruits, scores were not homogenous for the evaluated variables (Fig. 4 and 5).

Differentiation of different stages of maturity in apricot cultivars

Tab. 5 presents the scores of the first three PCA components, formed by the linear combination of their constituent parameters. Among the set of 19 variables, the biggest contribution to the observed variation is derived from acetophenone and benzyl alcohol combined. The composition of eigen values in each component depends on the stage of maturity. The first three components explained the larger proportion of variability in extra-mature fruits compared with mature fruits. The components highlighted measurable differences between

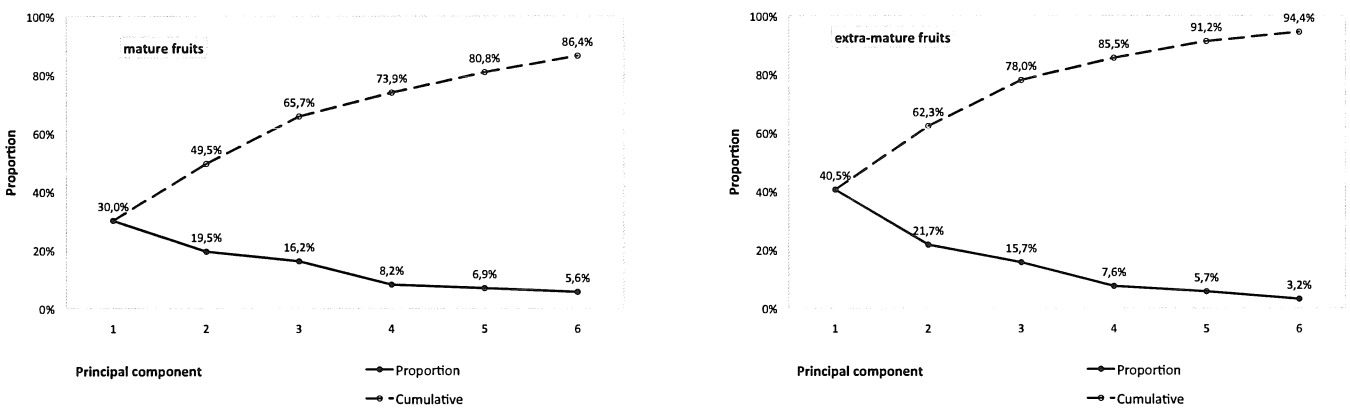

Fig. 3: The proportion of variance explained by PCA

Tab. 5: Eigenvalues of first three components of PCA by maturity stage

Parameter	mature fruits			extra-mature fruits		
	PC1	PC2	PC3	PC1	PC2	PC3
Firmness	-0,141	-0,133	0,073	0,094	0,225	0,068
Ethylene	0,107	-0,238	0,286	0,130	0,190	0,105
3-Methylpentan-1-ol	0,290	0,013	0,256	**0,430**	-0,080	-0,160
trans-2-Hexen-1-ol	-0,005	-0,024	0,170	0,123	0,001	0,063
Benzylalcohol	**0,355**	0,018	-0,039	**0,440**	-0,043	-0,123
2-Methylbutanal	0,047	-0,079	-0,336	-0,145	**0,432**	**-0,380**
trans-2-Hexenal	-0,332	**0,409**	0,126	-0,009	-0,067	0,038
n-Octanal	-0,244	0,009	0,285	0,108	-0,038	-0,095
2-Methylbutylacetate	0,298	0,209	-0,059	0,013	-0,316	-0,315
(Z)-2-Hexenylacetate	0,133	**-0,441**	-0,247	0,124	0,022	-0,014
Butyl-2-methylbutyrate	0,120	**0,533**	0,064	0,090	0,002	0,086
n-Hexylbutanoate	0,219	0,062	-0,100	0,112	-0,075	**0,761**
6-Methyl-5-heptene-2-one	0,171	-0,097	**0,379**	**0,400**	0,163	-0,085
Acetophenone	**0,417**	0,033	0,221	0,065	-0,041	0,044
γ-Octalactone	0,191	-0,057	0,114	0,125	**-0,610**	0,055
Limonene	0,137	**0,440**	-0,077	0,064	-0,065	-0,015
Farnesene	-0,027	-0,135	**0,416**	0,348	**0,435**	0,216
Citronellol	0,331	0,017	0,109	**0,442**	-0,109	-0,199
cis-Geraniol	0,223	0,005	**-0,364**	0,099	-0,019	0,022
Variation explained	30%	20%	16%	41%	22%	16%

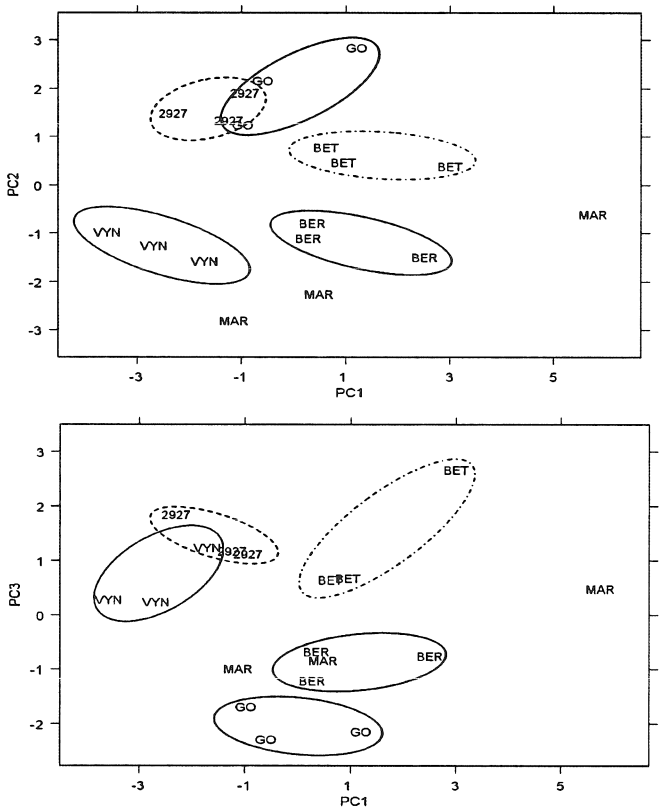

Fig. 4: Patterns of PCA component scores for mature fruits

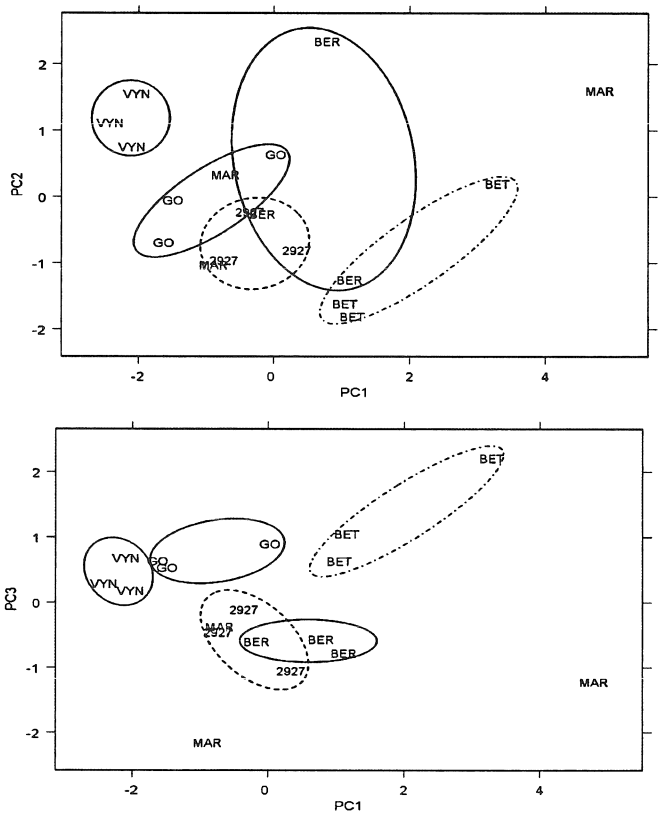

Fig. 5: Patterns of PCA components for over-mature fruits

the cultivars, confirming that each has its own unique chemical signature and consequently a distinctive and characteristic varietal aroma. Benzyl alcohol appears to be a useful indicator of differences in the degree of maturation (Tab. 5). When the fruits are extra-mature, other compounds, like 3-methylpentan-1-ol, 6-methyl-5-heptenone-2-one and citronellol, become more pronounced.

Conclusions

This paper has established the feasibility of using various physico-chemical parameters to study the process of maturation in apricot cultivars. The main compounds, such as individual sugars (sucrose, glucose, fructose) and organic acids (malic and citric acid), have approximately the same proportions during maturation. Only high levels of sucrose in the cv. 'Vynoslivyj' were able to distinguish this variety from the others, at both stages of maturity. Soluble solids, measured as a refractometric value, and measures of firmness, which are traditionally used to assess maturation, are not sufficiently different to provide a useful means of discriminating between the varieties as they mature on the tree. Likewise, neither does the rate of production of certain gases, such as CO_2 and ethylene, although the late-maturing cv. Bergeron can be distinguished from the others by its relatively lower production of both these gases. On the other hand, however, HP SPME methods were successful in satisfactorily analysing the aroma profiles of the six apricot cultivars at the two different stages of maturity. Lactone compounds were shown to increase in concentration during the six days of further maturation on the tree and these contribute to the more pleasant flavour of the more mature fruit. On the other hand terpene compounds, of which the most abundant was limonene, significantly decreased during this time. The detection of a wide profile of aroma compounds was achieved using PCA analysis, and suggests that various groupings of volatile compounds might be useful as potential chemical markers for identifying individual apricot cultivars. Benzyl alcohol in particular is useful for distinguishing the different cultivars at the two stages of maturity examined here. For the first stage, benzyl alcohol and acetophenone taken together suffice, and at the second, later stage of maturity, differentiation is achieved by the combinations of four compounds: benzylalcohol, 3-metylpentan-1-ol, 6-methyl-5-heptene-2-one and citronellol.

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