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Distribution of the volatile compounds in the different parts of a white-fleshed peach (*Prunus persica* L. Batsch)

Christophe Aubert *, Céline Milhet

Centre Technique Interprofessionnel des Fruits et Légumes, route de Mollégès, 13210 Saint-Rémy-de-Provence, France

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Abstract

The quantitative distribution of volatile compounds in the skin, top mesocarp, middle mesocarp, bottom mesocarp, inner mesocarp, and outer mesocarp of a white-fleshed peach (cv. Maura) was investigated. Volatile compounds were extracted by liquid–liquid microextraction (LLME) and analyzed by GC–FID and GC–MS. The results showed that the levels of volatiles in skin were significantly higher than those observed in the other parts of the fruit, whereas top and bottom mesocarp were mainly discriminated by opposite concentrations in unsaturated lactones and C_6-compounds. Distribution of lactones was also found to be different in skin and pulp according to their carbon chain length. Finally, the highest concentrations of benzaldehyde were found to be mainly located close to the stone suggesting that in peach this compound could be derived from enzymatic hydrolysis of amygdalin.

Keywords: *Prunus persica*; Peach; Aroma; Volatile compounds; Mesocarp; Pulp; Skin; Liquid–liquid microextraction

1. Introduction

It is generally agreed that, like apricot, peach (*Prunus persica* L. Batsch) originates from China. Peach tree was introduced in Europe at the beginning of the Roman era, whereas in the United States it appeared later, during the 19th century (Crouzet, Etievant, & Bayonove, 1990). In 1999–2001, the world production was ~13.5 Mt per year, 40% was produced in Asia, 30% in Europe, and 10% in North America. With ~30% of the world production, China was the main producer. In Europe, the production remains concentrated in Mediterranean-like areas, and the main producers are Italy, Spain, Greece and France.

Peaches are members of the genus *Prunus* that includes apricots, plums, cherries, almonds, and nectarines. Peaches and nectarines differ primarily in that nectarines have a smooth skin whereas peaches possess a downy skin, but both may be freestone – the pit is relatively free of the flesh – or clingstone – the pit adheres to the flesh. In this latter case, peaches and nectarines are, respectively, named pavies and brugnons. Botanically, peaches and nectarines are drupes or "stone fruits" – like apricots, plums, cherries, and mangoes – in which an outer fleshy part (exocarp and mesocarp) surrounds an hard stone (endocarp) with a seed inside Fig. 1. Peach and nectarine volatiles have been intensively investigated, and more than 100 compounds have been identified (Aubert, Günata, Ambid, & Baumes, 2003b; Bayonove, 1973, 1974; Berger, 1991; Chapman, Horvat, & Forbus, 1991; Crouzet et al., 1990; Derail, Hofmann, & Schieberle, 1999; Do, Salunkhe, & Olson, 1969; Engel et al., 1988; Engel, Ramming, Flath, & Teranashi, 1988; Horvat & Chapman, 1990; Horvat et al., 1990; Jennings & Sevenants, 1964; Lavilla, Recasens, & Lopez, 2001; Lim & Romani, 1964; Robertson, Meredith, Horvat, & Senter, 1990; Souty & Reich, 1978; Spencer, Pangborn, & Jennings, 1978; Sumitani, Suekane, Nakatani, & Tatsuka, 1994; Takeoka et al., 1992; Takeoka, Flath, Guntert, & Jennings, 1988; Visai & Vanoli, 1997). Nevertheless, if the variability in aroma volatiles has been reported to depend on cultivars (Engel

* Corresponding author. Tel.: +33 490 92 05 82; fax: +33 490 92 48 87.
E-mail address: aubert@ctifl.fr (C. Aubert).

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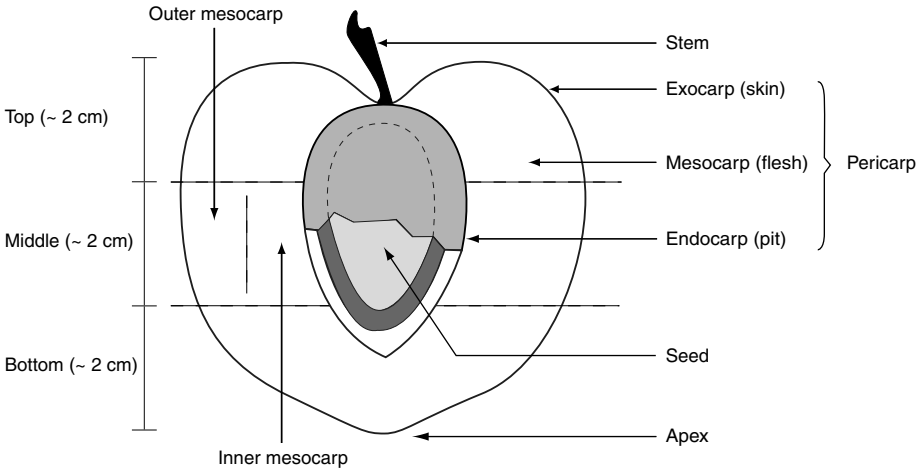

Fig. 1. The pericarp layers and the different parts of peach used for sampling.

et al., 1988; Horvat et al., 1990; Spencer et al., 1978), processing (Derail et al., 1999; Souty & Reich, 1978; Sumitani et al., 1994), storage conditions (Robertson et al., 1990) and stage maturity and/or ripening conditions (Aubert et al., 2003b; Bayonove, 1973, 1974; Chapman et al., 1991; Do et al., 1969; Engel et al., 1988; Horvat et al., 1990; Lavilla et al., 2001; Lim & Romani, 1964; Visai & Vanoli, 1997), to our best knowledge, no study on the distribution of the volatiles within the peach has appeared in the literature. The aim of this work was to investigate the distribution of the volatile compounds in the skin, top mesocarp, middle mesocarp, bottom mesocarp, inner mesocarp, and outer mesocarp of a white-fleshed peach (cv. Maura).

2. Materials and methods

2.1. Solvent and chemicals

Analytical grade chloroform (Chromasolv Plus, 99.9%) and *n*-propyl gallate (⩾98%) were, respectively, from Sigma and Fluka. Ammonium sulfate $(NH_4)_2SO_4$ (puriss p.a., ⩾99%), and *n*-alkane standards (C_8–C_{40}) were from Riedel-de Haën.

2.2. Samples

Fully ripe white-fleshed peaches (*Prunus persica* L.) cv. Maura were obtained from the experimental orchard of the Ctifl of Balandran (Gard, France). The fruits (~5 kg) were washed, dried, halved and freed from the stone. Fruits were then delicately peeled, and the skin was immediately frozen with liquid nitrogen. Halves of peaches were then fractionated in three: top mesocarp (the pulp around the stem), bottom mesocarp (the pulp around the apex) and middle mesocarp (the pulp between the top and the bottom mesocarp) Fig. 1. Top and bottom mesocarp (each of ~1500 g) were immediately frozen with liquid nitrogen, whereas middle mesocarp was divided into two batches (each of ~750 g). Batch one was immediately frozen with liquid nitrogen, whereas middle mesocarp of the second batch were separated into outer mesocarp (the pulp just under the skin, ca. 1 cm thickness), and the inner mesocarp (the pulp close to the stone, ca. 1 cm thickness) Fig. 1. These were also rapidly frozen with liquid nitrogen. In order to estimate the volatile compounds in the pulp of the whole fruit, another batch, named pulp, was made up with equal amounts of frozen tissues (each of ~350 g) randomly taken from the batches previously prepared (top, middle, and bottom) (see above). All the different parts were then stored at −25 °C until analysis.

2.3. Isolation of volatiles

Samples were analyzed according to the liquid–liquid microextraction (LLME) method previously described (Aubert, Baumann, & Arguel, 2005) with some modifications. Amounts of 100 g of samples (25 g for skin), 100 mL of *n*-propyl gallate (10 mM), and 10 μL of 2-octanol (3.32 μg/mL) (internal standard) were homogenized in a Waring blender for 2 min. The mixture was centrifuged (13,000*g*, 5 min, 4 °C) and the supernatant was filtered on a stainless steel sieve (16 mesh). Juice (40 mL) added with 12.8 g of $(NH_4)_2SO_4$ (32%; w/v) was agitated until complete salt dissolution and ultracentrifuged (21,000*g*, 5 min, 4 °C). The supernatant was then filtered through a Whatman paper filter (grade 113v) into a 50-mL screw-capped conical centrifuge tube (34 × 98 mm glass borosilicate) containing a magnetic stir bar (15 × 6mm). 150 μL of chloroform was added, and the mixture was extracted for 60 min under magnetic stirring at room temperature. After removal magnetic stir bar, the tube was sonicated 1 min in a Branson Ultrasonic Cleaner 5510, and centrifuged (1000*g*, 5 min, 4 °C). Chloroform extract was then recovered with a 50 μL syringe, transferred to a 100 μL vial and immediately injected in GC–MS and GC–FID.

2.4. GC–FID Conditions

A Varian 3800 gas chromatograph equipped with a DB-Wax Etr (J&W Scientific) capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness) was used. The flow of hydrogen 5.7 carrier gas was 1 mL/min. The oven temperature was kept at 40 °C for 3 min, then programmed to 250 °C at 5 °C/min, and kept at 250 °C for 15 min. Injections (1 μL) were performed at 220 °C in splitless mode (1.5 min) using a CombiPAL autosampler equipped with a Peltier cooling rack at 4 °C (CTC Analytics). The FID detector was kept at 250 °C. The levels of the volatile compounds were expressed as 2-octanol equivalent (assuming all of the response factors were 1). The concentrations are to be considered as relative data because recovery after extraction and calibration factors related to the standard were not determined.

2.5. GC–MS conditions

A Varian 3800 gas chromatograph was used with the same DB-Wax Etr capillary column as above. Injections (1 μL) were performed at 220 °C in splitless mode (1.5 min) using a CombiPAL autosampler (CTC Analytics). The flow of helium 6.0 carrier gas was 1 mL/min. The oven temperature program was as above. A Saturn Ion-Trap mass spectrometer was used. Mass spectra were recorded in electronic impact (EI) ionization mode. The ion trap, the manifold, and the transfer line temperatures were set, respectively, at 150 °C, 45 °C, and 250 °C. Mass spectra were scanned in the range m/z 30–350 a.m.u. at 1 s intervals. Identifications were carried out by comparison of linear retention indices and EI mass spectra with data from authentic compounds.

2.6. Statistical analysis

Analyses of variance and principal component analysis (PCA) were performed, respectively, using Statbox 6.30 (Grimmersoft) and Statlab 3.0 (SLP Infoware). Significant differences were determined at $p < 0.05$.

3. Results and discussion

Previously described for the analysis of volatile compounds in fruit juices (Aubert et al., 2005), the liquid–liquid microextraction (LLME) is a single-step extraction with a very high liquid sample/solvent ratio and a saturation of the aqueous phase with inorganic salts. LLME avoids the concentration process and minimizes the risk of a thermal degradation of the volatiles, reduces the solvent consumption and the time of analysis. Lastly, this method has been proved to be generally as sensitive and precise as conventional liquid–liquid extraction.

Table 1 shows the volatile compounds extracted from the skin, pulp, top, middle, bottom, outer, and inner mesocarp by LLME using chloroform. Fifty-seven compounds were separated, identified, and quantified by GC–MS and GC–FID. Seven were C_6-compounds, five alcohols, four esters, five carbonyls compounds, nine terpenols, ten lactones, eight C_{13}-norisoprenoids, and nine straight chain hydrocarbons. The relative abundances (%) of the main volatile classes in the different parts of peach are shown in Fig. 2. Three one-way analyses of variance were performed to determine significant differences, respectively, between (1) skin and pulp, (2) top, middle and bottom mesocarp, and (3) inner and outer mesocarp Table 1 and Fig. 2. A principal component analysis (PCA) using 21 samples (7 samples × 3 replications) and 57 variables, was performed to summarize graphically the distribution of the volatile compounds within the different parts of the peach Table 2 and Fig. 3.

As shown in Table 2 and Fig. 3A, 88% of the total variance was explained by the first two axes. The first axis (80.5% of the variance explained) mainly discriminates the skin samples from the others, whereas the second axis (7.2% of the variance explained) mainly discriminates the outer and the inner mesocarp samples. The distribution of the variables is shown in Fig. 3B. Except 3 variables from the 57, 3-hydroxy-5,6-epoxy-7,8-dihydro-β-ionone (N3), vomifoliol (N8), and terpinen-4-ol (T2), most of the volatile compounds are well correlated with the first two axes, and more particularly with the first axis (80% of the variables showing a squared factor loading on the first axis >0.70) Table 2. Skin samples, positively correlated on the first axis, are particularly characterized by high contents in most of volatile compounds, whereas inner mesocarp, positively located on the second axis, are mainly discriminated from outer mesocarp by high levels in benzaldehyde (O4), 3-hydroxy-7,8-dihydro-β-ionol (N4), and dehydrovomifoliol (N7).

3.1. Volatiles in skin and pulp

As shown in Table 1, previous differences observed in the PCA between skin and pulp were confirmed by the analysis of variance. Except for 3-pentanol (A1), terpinen-4-ol (T2), 3-hydroxy-5,6-epoxy-7,8-dihydro-β-ionone (N3), 3-hydroxy-7,8-dihydro-β-ionol (N4), dehydrovomifoliol (N7), and vomifoliol (N8), all the levels of the volatiles were significantly higher in the skin than in pulp ($p < 0.05$). Nevertheless, as shown in Fig. 2, their distribution within the skin and the pulp was different. If the C_6-compounds made up >33% of the total of volatile compounds in the skin, followed by lactones and alkanes (30% and 25%, respectively), the pattern was different in the pulp. The lactones made up near 50% of the total volatiles, followed by C_6-compounds and C_{13}-norisoprenoids (26% and 17%, respectively).

As indicated in Fig. 2, C_6-compounds, aldehydes and alcohols, products of the enzymatic breakdown of unsaturated fatty acids (Schreier, 1984; Tressl, Bahri, & Engel, 1981), are the main volatile components isolated in skin. C_6-aldehydes were predominant in both samples, 84%

Table 1
Concentrations[a] of volatiles within the different parts of peach

Compounds	Code	LRI[b]	Assignment[c]	ANOVA 1		ANOVA 2			ANOVA 3	
				Skin	Pulp	Top	Middle	Bottom	Inner	Outer
Hexanal	C1	1075	A	775.7z	191.1y	112.1x	134.2y	354z	161.4z	86.9y
(*Z*)-3-hexenal	C2	1139	A	2.7z	1.0y	0.7y	0.9y	1.7z	1.1z	0.5y
(*Z*)-2-hexenal	C3	1204	C	11.3z	2.1y	1.1x	1.8y	3.7z	2.7z	1.3y
(*E*)-2-hexenal	C4	1220	A	1642z	429.5y	298.1x	350.9y	721.1z	420z	215.3y
Hexanol	C5	1355	A	170.3z	6.5y	6.6y	5.1x	9.0z	7.7z	3.5y
(*Z*)-3-hexen-1-ol	C6	1386	A	27.4z	3.6y	3.4y	2.9x	5.3z	5.4z	1.5y
(*E*)-2-hexen-1-ol	C7	1409	A	250.3z	11.8y	10.6y	8.9x	15.6z	22.7z	3.7y
Sum of C_6-compounds				2879.7z	645.6y	432.6x	504.6y	1110.3z	621.0z	312.7y
3-Pentanol	A1	1107	A	3.5	4.8	5.1z	5.4z	4.6y	5.7z	4.6y
1-Penten-3-ol	A2	1159	A	3.5z	1.9y	1.7y	2z	1.8y	2.4z	1.5y
3-Methylbutanol	A3	1208	A	3.6z	1.7y	1.8	1.9	1.7	1.6y	2.1z
2-Nonen-1-ol	A4	1395	A	5.3z	1.0y	1.1	0.7	0.9	1.4	1.0
1-Heptanol	A5	1492	A	48.9z	17.4y	14y	18z	19.6z	17.4	19.1
Sum of alcohols				64.8z	26.7y	23.7y	28z	28.6z	28.5	28.3
3-Methylbutyl acetate	E1	1125	A	2.2z	1.3y	1.5z	1.5z	1.1y	1.6	1.6
Hexyl acetate	E2	1275	A	11.1z	3.4y	2.9y	3.6zy	4.2z	2.4y	3.5z
(*Z*)-3-hexenyl acetate	E3	1320	A	11.7z	5.8y	6.2z	6.5z	4.7y	5.5z	4.1y
(*E*)-2-hexenyl acetate	E4	1338	A	13.9z	1.3y	1.7z	1.4z	1.1y	1.1z	0.8y
Sum of esters				38.9z	11.8y	12.3	13.1	11.0	10.6	10.0
2-Octanone	O1	1287	A	15.9z	3.8y	4.1	3.6	3.8	3.8	3.9
Octanal	O2	1291	A	1.8z	0.4y	0.6	0.4	0.4	0.6	0.4
6-Methyl-5-hepten-2-one	O3	1341	A	6.4z	1.2y	1.2y	1.3y	1.4z	2.2	2.1
Benzaldehyde	O4	1526	A	14.7z	8.7y	9.1y	12.2z	9.2y	16.0z	7.0y
Vanillin	O5	2561	A	9.1z	2.8y	3.8z	2.3y	2.3y	5.3	2.5
Sum of carbonyl compounds				47.8z	17y	18.8z	19.7z	17.1y	27.8z	15.9y
Linalool	T1	1526	A	89.9z	46.0y	41.4x	44.7y	55.2z	50z	40.6y
Terpinen-4-ol	T2	1608	A	0.9	0.6	0.4x	0.6y	0.8z	0.6	0.7
Hotrienol	T3	1614	C	60.8z	33.6y	30.7y	36.1zy	39.2z	27.1y	32.1z
α-Terpineol	T4	1691	A	18.9z	5.4y	5.1y	6.2z	6.6z	7.5	7.4
(*E*)-pyran linalool oxide	T5	1740	A	8.2z	5.0y	4.9y	5.1zy	5.6z	6.4z	5.6y
(*Z*)-pyran linalool oxide	T6	1765	A	8.1z	4.4y	4.1y	4.4y	5.4z	5.7	5.2
3,7-Dimethyl-1,5-octadien-3,7-diol	T7	1951	A	43.4z	20.7y	21.9	20.6	26.4	24.0	27.0
(*E*)-8-hydroxylinalool	T8	2274	A	23.7z	4.3y	3.9y	5.4z	5.4z	3.4y	4.8z
(*Z*)-8-hydroxylinalool	T9	2315	A	16.2z	5.4y	5.6	5.5	6.2	4.2y	6.1z
Sum of terpenols				270.1z	125.4y	118.1x	128.7y	150.9z	128.9	129.6
γ-Hexalactone	L1	1703	A	638.4z	516.3y	509.5y	593.1z	582.7z	601.5z	526.6y
γ-Heptalactone	L2	1803	A	24.9z	21.1y	20.2	23.2	20.1	22.7z	20.2y
γ-Octalactone	L3	1916	A	101.3z	70.0y	71.6	78.3	72.2	74.6	69.7
δ-Octalactone	L4	1965	A	31.3z	16.9y	19.3z	20.2z	16.8y	16.9	16.3
γ-Nonalactone	L5	2028	A	18.7z	8.4y	8.0	8.5	7.9	8.0	8.3
γ-Decalactone	L6	2144	A	1029.7z	269.6y	319.1	292.7	254.0	294.1	276
6-Pentyl-α-pyrone	L7	2178	A	259.3z	76.4y	92.1z	84z	55.5y	73.7	79.0
γ-Jasmolactone	L8	2181	A	97.2z	42.4y	53.9z	47.1y	33.2x	58.7	51.6
δ-Decalactone	L9	2192	A	386.2z	142.6y	165.1	152.3	146.1	126.3	140.6
7-Decen-5-olide	L10	2255	B[d]	50.5z	21.7y	33.5z	30.4z	20.9y	34.3	30.5
Sum of lactones				2587.1z	1185.4y	1258.7	1299.4	1188.5	1276.4	1188.4
Unknown C_{13}[e]	N1	2046	C	267.0z	121.5y	96.8	162.4	125.9	106.3	65.0
3-Hydroxy-7,8-dihydro-β-ionone	N2	2559	B[f]	60.9z	14.7y	16.0	13.1	13.5	16.4z	12.4y
3-Hydroxy-5,6-epoxy-7,8-dihydro-β-ionone	N3	2649	C	13.9	11.7	14.0	11.8	12.3	14.1	11.2
3-Hydroxy-7,8-dihydro-β-ionol	N4	2664	B[g]	12.7	9.8	9.9	10.6	9.9	14.4z	4.6y
3-Hydroxy-β-ionone	N5	2679	B[h]	14.1z	5.2y	5.2	4.8	6.5	7.3z	3.3y
3-Hydroxy-5,6-epoxy-β-ionone	N6	2713	B[f]	50.9z	12.3y	12.2	11.4	13.1	12.7z	6.9y
Dehydrovomifoliol	N7	2986	B[i]	237.0	252.3	248.8	233.9	274.7	309.1z	141.8y
Vomifoliol	N8	3048	B[i]	2.8z	4.6y	5.1	4.2	5.1	3.7z	2.0y
Sum of C_{13}-norisoprenoids				659.2	432.0	408.1	452.1	461.0	484.0z	247.3y
Nonadecane	H1	1900	A	17.4z	0.4y	0.5	0.5	0.4	0.4	0.6
Heneicosane	H2	2100	A	63.1z	2.0y	2.7	2.0	2.0	1.6	1.9
Docosane	H3	2200	A	9.6z	1.0y	1.1	1.1	1.1	1.1	0.7
Tricosane	H4	2300	A	544.5z	0.9y	1.0	0.8	0.9	0.9z	0.6y

Table 1 (*continued*)

Compounds	Code	LRI[b]	Assignment[c]	ANOVA 1		ANOVA 2			ANOVA 3	
				Skin	Pulp	Top	Middle	Bottom	Inner	Outer
Tetracosane	H5	2400	A	38.2z	0.3y	0.5	0.3	0.3	0.5	0.4
Pentacosane	H6	2500	A	568.1z	0.2y	0.2	0.2	0.2	0.1	0.1
Hexacosane	H7	2600	A	13.9z	0.1y	0.1	0.1	0.1	0.1	0.1
Heptacosane	H8	2700	A	404.2z	2.8y	2.8	1.8	3.4	2.2	1.7
Octacosane	H9	2800	A	505.5z	32.3y	35.2	28.2	30.5	14.6y	26.4z
Sum of alkanes				2164.6z	39.9y	44.0	35.0	39.0	21.3z	32.4y
Total				8712.2z	2492.0y	2316.3y	2480.5y	3006.3z	2598.6z	1964.7y

[a] Values expressed in μg/kg equivalent of 2-octanol.
[b] Linear retention index calculated using a series of *n*-hydrocarbons.
[c] A, identities confirmed by comparing mass spectra and retention time with those of authentic standards; B, identities tentatively assigned by comparing mass spectra with those obtained from the literature; C, tentatively identified.
[d] Engel et al. (1988).
[e] Major mass spectral fragments [*m*/*e* (%)]: 108 (100), 43 (70), 206 (69), 93 (67), 39 (62), 150 (44), 77 (30), 41 (28), 121 (27), 136 (26).
[f] Krammer et al. (1991).
[g] Winterhalter and Schreier (1988).
[h] Güdner and Winterhalter (1991).
[i] Winterhalter (1990).Values with different letters are significantly different ($p < 0.05$).

and 97% of the total of C_6-compounds, respectively, in skin and pulp. Among them (*E*)-2-hexenal and hexanal were the two main components, and their relative proportions were found similar, respectively, 57–66.5% and 27–30% (skin–pulp%). Results in Table 1 show that the skin had a considerably higher concentration of C_6-aldehydes and a several-fold higher concentration of C_6-alcohols than the pulp. These results were found to be consistent with those previously reported in the skin of tomato and mango (Buttery, Teranishi, Ling, Flath, & Stern, 1988; Lalel, Singh, & Tan, 2003). Due to the isolation method chosen (LOX deactivation with *n*-propyl gallate during homogenization) (Aubert et al., 2005), it seems reasonable to suppose that the concentrations of these so-called green components, given in Table 1, are representative of the endogenous levels of the different parts. Nevertheless, despite the precautions taken during the preparation of the samples, the possibility that this may partly be the result of tissue damage occurring during peeling cannot be excluded. Finally, these results observed in skin would suggest a higher activity of the enzymes involved in the LOX pathway. Hatanaka, Kajiwara, Matsui, and Kitamura (1992) had reported that LOX activity in tomato was mainly localized between the skin and the outer flesh, and/or that may be a higher concentration of fatty acids, especially linoleic and linolenic acids, in these parts of the fruit.

Among peach volatiles previously identified, lactones, in particular γ-C_8, C_{10}, δ-C_{10} and some unsaturated lactones have been reported as important impact compounds (Aubert et al., 2003b; Bayonove, 1973, 1974; Berger, 1991; Chapman et al., 1991; Crouzet et al., 1990; Derail et al., 1999; Do et al., 1969; Engel et al., 1988; Horvat et al., 1990; Jennings & Sevenants, 1964; Lavilla et al., 2001 Lim & Romani, 1964; Robertson et al., 1990; Souty & Reich, 1978; Spencer et al., 1978; Takeoka et al., 1992; Sumitani et al., 1994; Takeoka et al., 1988; Visai & Vanoli, 1997). Ten lactones have been identified in both samples, among them three unsaturated lactones structurally related to γ- and δ-decalactone. As mentioned above, the total amounts of lactones ranged from 30% of the isolated volatiles in skin to near 50% in pulp. As shown in Table 1, the levels of lactones were significantly higher in skin than in pulp, in particular for γ-C_8, γ- and δ-C_{10} (respectively, 1.4, 2.7 and 3.8 times). Lactones with even-numbered carbon chains were quantitatively predominant, whereas γ-heptalactone (L2) and γ-nonalactone (L5) were only minor constituents. Finally, as indicated in Fig. 4, the average distribution of lactones in skin and pulp was found to be different. Lactones with a carbon chain length up to C_9 (L1–L5) are predominant in pulp, in particular γ-hexalactone (L1), whereas those with a ten-carbon chain length (L6–L10) were found to be the major lactones in skin, in particular γ-decalactone (L6).

Among the nine terpenols identified in skin and pulp, three monoterpenols were at the linalool oxidation stage (T1, T2, and T4), and six were at higher oxidation level, one trienol (T3), two linalool oxides (T5, T6), and three monoterpene diols (T7, T8, and T9). Contrary to monoterpenols, compounds previously reported as important aroma compounds in peach (Bayonove, 1973, 1974; Souty & Reich, 1978; Spencer et al., 1978), linalool oxides and monoterpene diols have high sensory thresholds (Bayonove, 1998), but could generate pleasant aroma compounds during the biotechnological transformation of these fruits (Williams, Strauss, & Wilson, 1980). Hotrienol (T3) previously identified in muscat (Bayonove, Richard, & Cordonnier, 1976), in peach (Crouzet et al., 1990; Engel et al., 1988) and in peach after canning (Souty & Reich, 1978) is thought to be derived from 3,7-dimethylocta-1,5-diene-3,7-diol (T7) (Williams et al., 1980). Levels of terpenols were found to be 1.5–2-times higher in skin than in pulp, except for α-terpineol (3.5-fold), (*Z*)- (3-fold) and (*E*)-8-hydroxylinalool (5.5-fold). Their distributions were found to be similar in both parts.

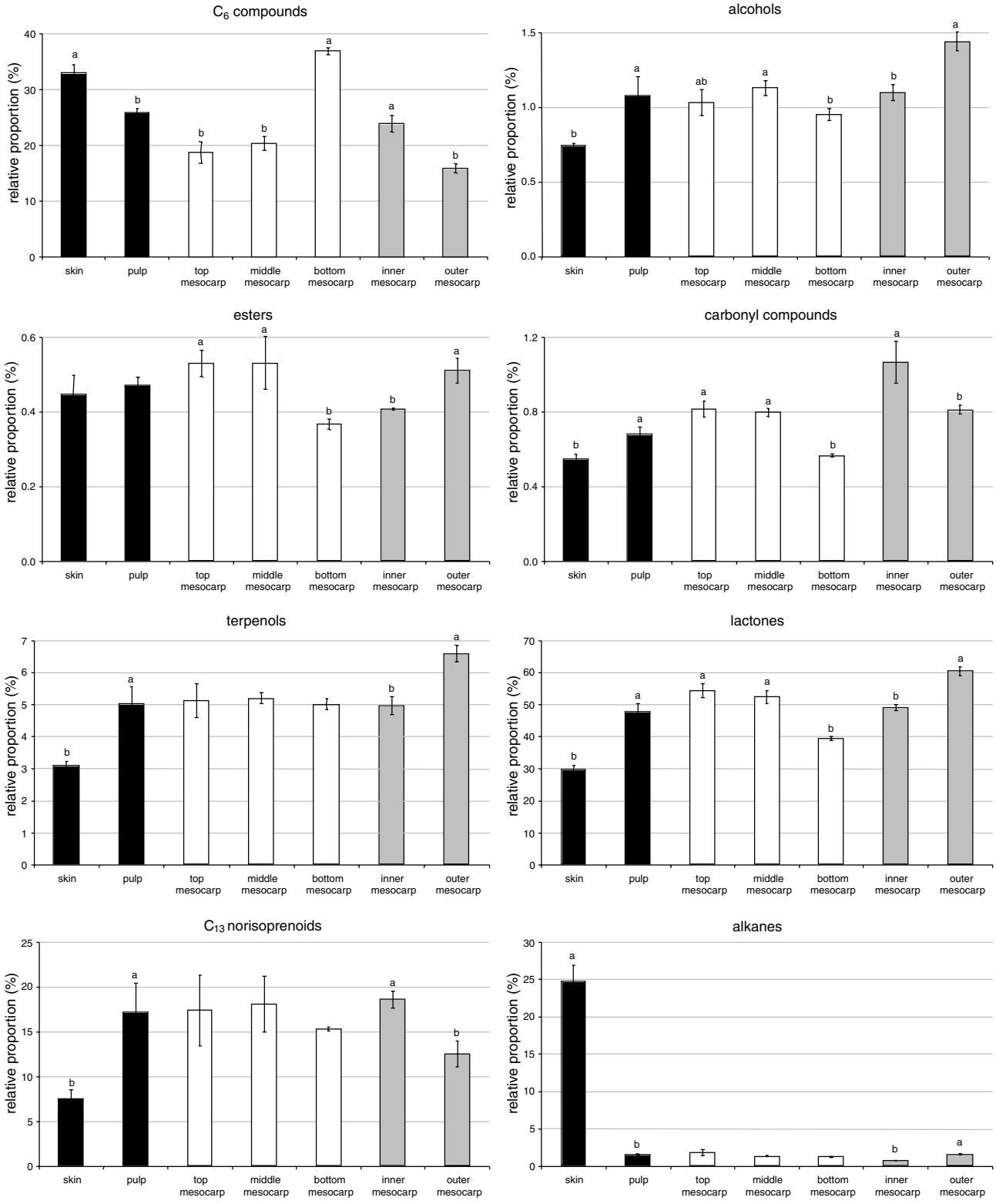

Fig. 2. Relative abundances (%) of the main classes of volatile compounds in the different parts of peach. Similar vertical bars with different letters are significantly different ($p < 0.05$).

Eight C_{13}-norisoprenoids were isolated in skin and pulp. Identification of free and glycosidically bound C_{13}-norisoprenoid compounds has been previously described in peaches and nectarines (Aubert, Ambid, Baumes, & Günata, 2003a; Aubert et al., 2003b; Engel et al., 1988; Ho et al., 1990; Knapp, Weigand, Gloser, & Winterhalter, 1997; Krammer, Winterhalter, Schwab, & Schreier, 1991; Takeoka et al., 1992), and in numerous other natural products

Table 2
Results of PCA

Variable[a]	Principal components				
	1	2	3	4	5
A1	−0.106 (0.508)	0.212 (0.183)	−0.255 (0.144)	0.074 (0.008)	−0.157 (0.026)
A2	0.136 (0.847)	0.131 (0.07)	−0.082 (0.015)	0.022 (0.001)	−0.120 (0.016)
A3	0.139 (0.885)	−0.134 (0.073)	−0.040 (0.004)	−0.011 (0.001)	0.012 (0.001)
A4	0.145 (0.963)	−0.001 (0.001)	−0.024 (0.002)	0.008 (0.001)	0.094 (0.010)
A5	0.146 (0.968)	−0.041 (0.007)	0.048 (0.005)	0.024 (0.001)	−0.019 (0.001)
N1	0.111 (0.565)	0.119 (0.057)	0.087 (0.017)	−0.326 (0.137)	−0.187 (0.037)
N2	0.146 (0.971)	0.003 (0.001)	−0.008 (0.001)	−0.023 (0.001)	0.143 (0.022)
N3	0.060 (0.161)	0.283 (0.325)	−0.097 (0.021)	0.184 (0.044)	0.552 (0.323)
N4	0.064 (0.187)	0.429 (0.748)	−0.040 (0.004)	0.020 (0.001)	0.096 (0.010)
N5	0.136 (0.842)	0.147 (0.088)	0.070 (0.011)	0.089 (0.011)	0.195 (0.041)
N6	0.141 (0.907)	0.050 (0.011)	0.051 (0.006)	−0.035 (0.002)	0.206 (0.045)
N7	0.014 (0.008)	0.462 (0.869)	0.155 (0.053)	−0.021 (0.001)	0.126 (0.017)
N8	−0.048 (0.103)	0.262 (0.278)	0.373 (0.308)	−0.422 (0.231)	−0.021 (0.001)
C1	0.139 (0.885)	0.023 (0.003)	0.215 (0.103)	0.028 (0.001)	−0.004 (0.001)
C2	0.131 (0.784)	0.097 (0.039)	0.243 (0.131)	0.093 (0.012)	−0.024 (0.001)
C3	0.145 (0.961)	0.026 (0.003)	0.111 (0.028)	0.057 (0.005)	−0.024 (0.001)
C4	0.142 (0.914)	0.035 (0.005)	0.180 (0.072)	0.024 (0.001)	−0.010 (0.001)
C5	0.147 (0.989)	−0.036 (0.006)	0.012 (0.001)	−0.020 (0.001)	0.009 (0.001)
C6	0.147 (0.984)	0.014 (0.001)	0.037 (0.004)	0.006 (0.001)	0.008 (0.001)
C7	0.148 (0.992)	−0.018 (0.002)	0.005 (0.001)	−0.009 (0.001)	0.005 (0.001)
O1	0.147 (0.979)	−0.057 (0.013)	−0.003 (0.001)	−0.019 (0.001)	−0.008 (0.001)
O2	0.146 (0.970)	−0.009 (0.001)	−0.045 (0.005)	−0.028 (0.002)	0.059 (0.004)
O3	0.144 (0.946)	−0.046 (0.009)	−0.067 (0.010)	0.124 (0.020)	−0.037 (0.002)
O4	0.081 (0.300)	0.350 (0.498)	−0.237 (0.125)	0.078 (0.008)	−0.198 (0.042)
O5	0.125 (0.706)	0.057 (0.014)	−0.154 (0.052)	−0.059 (0.005)	0.013 (0.001)
E1	0.110 (0.546)	−0.084 (0.029)	−0.347 (0.268)	−0.011 (0.001)	−0.112 (0.014)
E2	0.142 (0.916)	−0.089 (0.032)	0.097 (0.021)	−0.024 (0.001)	−0.094 (0.010)
E3	0.138 (0.870)	0.012 (0.001)	−0.065 (0.010)	−0.220 (0.063)	−0.053 (0.003)
E4	0.146 (0.968)	−0.048 (0.010)	−0.006 (0.001)	−0.063 (0.006)	−0.045 (0.003)
H1	0.144 (0.941)	−0.066 (0.018)	−0.010 (0.001)	−0.040 (0.002)	−0.095 (0.010)
H2	0.147 (0.983)	−0.050 (0.010)	−0.002 (0.001)	−0.043 (0.003)	0.005 (0.001)
H3	0.146 (0.971)	−0.024 (0.003)	0.009 (0.001)	−0.058 (0.005)	0.092 (0.009)
H4	0.147 (0.983)	−0.032 (0.005)	0.003 (0.001)	−0.034 (0.002)	0.084 (0.008)
H5	0.147 (0.982)	−0.031 (0.004)	0.001 (0.001)	−0.034 (0.002)	0.092 (0.009)
H6	0.146 (0.976)	−0.029 (0.004)	0.003 (0.001)	−0.037 (0.002)	0.105 (0.012)
H7	0.147 (0.979)	−0.032 (0.005)	−0.001 (0.001)	−0.043 (0.003)	0.083 (0.008)
H8	0.147 (0.979)	−0.038 (0.006)	0.001 (0.001)	−0.048 (0.003)	0.057 (0.004)
H9	0.145 (0.955)	−0.057 (0.013)	0.006 (0.001)	−0.071 (0.007)	−0.007 (0.001)
L1	0.100 (0.455)	0.261 (0.278)	0.022 (0.002)	0.188 (0.046)	−0.350 (0.130)
L2	0.106 (0.511)	0.214 (0.187)	−0.190 (0.080)	−0.142 (0.026)	−0.249 (0.066)
L3	0.140 (0.895)	0.063 (0.016)	−0.038 (0.004)	−0.117 (0.018)	−0.116 (0.015)
L4	0.140 (0.888)	0.001 (0.001)	−0.042 (0.004)	−0.219 (0.062)	−0.029 (0.001)
L5	0.146 (0.978)	−0.054 (0.012)	−0.003 (0.001)	−0.048 (0.003)	−0.024 (0.001)
L6	0.146 (0.975)	−0.050 (0.011)	−0.037 (0.003)	−0.051 (0.004)	−0.022 (0.001)
L7	0.145 (0.954)	−0.065 (0.017)	−0.075 (0.013)	−0.099 (0.013)	0.024 (0.001)
L8	0.135 (0.833)	−0.029 (0.004)	−0.253 (0.142)	−0.001 (0.001)	0.022 (0.001)
L9	0.145 (0.961)	−0.066 (0.018)	0.014 (0.001)	−0.080 (0.009)	0.027 (0.001)
L10	0.126 (0.727)	−0.003 (0.001)	−0.314 (0.219)	0.004 (0.001)	0.054 (0.004)
T1	0.143 (0.929)	0.046 (0.009)	0.124 (0.034)	0.068 (0.006)	−0.043 (0.002)
T2	0.085 (0.326)	−0.045 (0.008)	0.308 (0.210)	0.460 (0.274)	−0.277 (0.082)
T3	0.135 (0.830)	−0.069 (0.020)	0.185 (0.076)	−0.048 (0.003)	−0.135 (0.020)
T4	0.145 (0.963)	−0.034 (0.005)	−0.026 (0.002)	0.089 (0.011)	−0.086 (0.008)
T5	0.133 (0.804)	0.055 (0.013)	−0.069 (0.011)	0.235 (0.072)	−0.068 (0.005)
T6	0.134 (0.815)	0.030 (0.004)	0.020 (0.001)	0.283 (0.103)	−0.064 (0.005)
T7	0.132 (0.789)	−0.073 (0.022)	0.024 (0.002)	0.238 (0.074)	0.179 (0.034)
T8	0.145 (0.957)	−0.053 (0.012)	0.050 (0.006)	0.005 (0.001)	−0.032 (0.002)
T9	0.142 (0.921)	−0.078 (0.025)	0.069 (0.011)	−0.018 (0.001)	0.114 (0.014)
Eigenvalue	45.858	4.077	2.220	1.293	1.060
Proportion	0.8045	0.0715	0.0389	0.0227	0.0186
Cumulative	0.8045	0.8760	0.9149	0.9376	0.9562

Eigenvectors with the square of the factor loadings in parentheses, and eigenvalues of the correlation matrix for the first five principal components.
[a] For codes see Table 1.

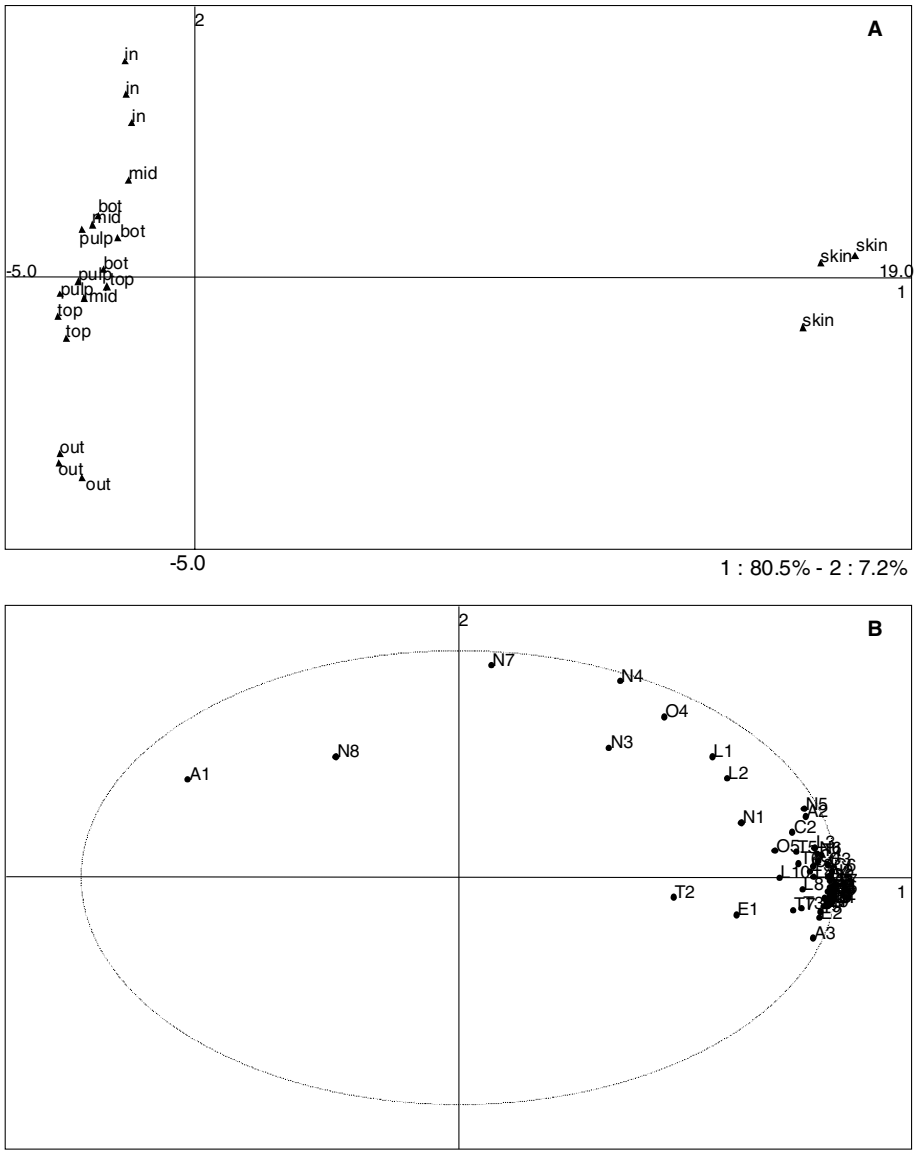

Fig. 3. Results from PCA analysis: (A) projection of the samples (top: top mesocarp; mid: middle mesocarp; bot: bottom mesocarp; in: inner mesocarp; out: outer mesocarp); (B) distribution of variables (for codes see Table 1).

(Winterhalter & Rouseff, 2001). Importance of these carotenoids-derived volatiles for the specific flavor of the white-fleshed nectarine has been clearly demonstrated by Takeoka et al. (1992). Except for dehydrovomifoliol (N7) and vomifoliol (N8), the levels of C_{13}-norisoprenoids were found to be up to 4 times higher in skin than in pulp. These results suggest either (i) a greater degradation of carotenoids in the skin – directly exposed to the air and sunlight, these compounds are more subjected to oxidation and ultraviolet radiation than in the pulp – as previously mentioned in mango by Lalel et al. (2003), or (ii) a higher activity of the carotenoid cleavage enzymes in the skin of the peach as previously mentioned in the quince and star fruit by Fleischmann, Lutz-Röder, Winterhalter, and Watanabe (2001).

Finally, levels of alcohols, esters, carbonyl compounds, and alkanes were found to be higher in skin than in pulp. Because levels of straight chain hydrocarbons were only detected at very low levels in the pulp, the levels of these compounds in skin were found to be up to 3000-fold higher than those observed in pulp.

3.2. Volatiles in top, middle, and bottom mesocarp

As shown in Table 1 and Fig. 2, the lactones made up 40–55% of the total volatiles in the different parts of mesocarp, followed by C_6-compounds and C_{13}-norisoprenoids (respectively, 19–37% and 15–18%). As regards lactones, except for γ-C_6 and δ-C_8 for which the levels were, respectively, significantly lower in top and bottom mesocarp, the main significant differences were observed for the three unsaturated lactones, namely 6-pentyl-α-pyrone (L7), γ-jasmolactone (L8), and (*Z*)-7-decen-5-olide (L10). Their concentration were found to be (i) significantly higher in the top than in the middle mesocarp, and (ii) significantly

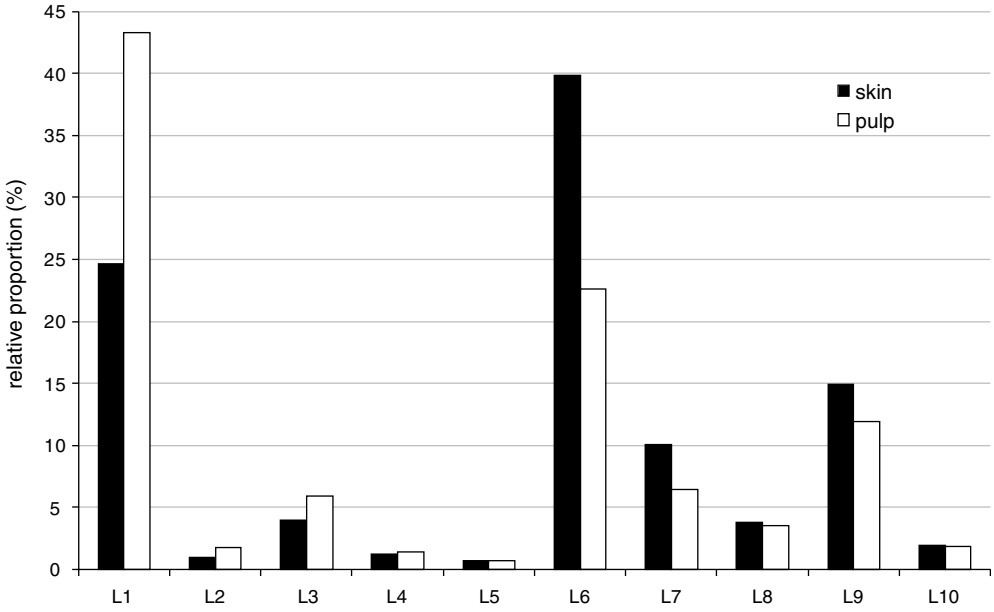

Fig. 4. Average distribution of lactones in pulp and skin (for component listing see Table 1).

higher in the middle than in bottom mesocarp. Results in Table 1 show that the levels of unsaturated lactones were ~1.6 times lower in bottom mesocarp than those observed in the top mesocarp. Thus, it would seem that a concentration gradient for unsaturated lactones exists from stem towards apex. For saturated lactones, and particularly for γ- and δ-C_{10}, although their levels were found to be, respectively, 10–20% lower in bottom than in top mesocarp, the differences were not significant.

About lipid-derived compounds, their levels, and particularly those of hexanal and (*E*)-2-hexenal, were found to be (i) significantly lower in the top than in the middle mesocarp, and (ii) significantly lower in the middle than in bottom mesocarp. As indicated in Table 1, levels of C_6-compounds were 1.5–3 times higher in the bottom mesocarp than those observed in the top mesocarp. So, it would seem that a gradient of concentration exists for the C_6-compounds from the bottom towards the stem, i.e. inverted to what has been previously observed for unsaturated lactones. As regards the other compounds, except for linalool and hotrienol for which the levels observed in bottom mesocarp were significantly higher than those observed in top mesocarp, their levels were found to be very similar and/or no significantly different in the different parts of the fruit.

3.3. Volatiles in inner and outer mesocarp

As indicated in Table 1 and Figs. 2 and 3, inner mesocarp is characterized by higher contents of C_6-compounds, particularly for hexanal (C1) and (*E*)-2-hexenal (C4), C_{13}-norisoprenoids, particularly for 3-hydroxy-7,8-dihydro-β-ionol (N4) and dehydrovomifoliol (N7), benzaldehyde (O4), and γ-C_6 (L1). About C_6-compounds and C_{13}-norisoprenoids, their levels were found to be ~2-times lower in outer than in inner mesocarp, and it would seem that a gradient of concentration exists for these compounds from endocarp towards exocarp. As regards straight chain hydrocarbons, except for octacosane, the levels of alkanes were found to be very similar between inner and outer mesocarp, indicating that the peeling was effective, and that all attached skin was completely removed from the pulp, and vice versa. Otherwise, higher levels of alkanes would have been found in the outer mesocarp, in agreement with the results previously observed in the skin. Finally, the distribution of benzaldehyde in the different parts of the fruit is interesting due its peach stone odor. Previously identified in fresh fruit (Crouzet et al., 1990) as well as in canned fruit (Souty & Reich, 1978), its origin is not yet clearly known but it could originate (i) from enzymatic hydrolysis of amygdalin, a cyanogenic glycoside present in the stone, or (ii) from phenylalanine, or (iii) even from oxidation of benzyl alcohol (*1*). As in this study, the levels of benzaldehyde were significantly higher both in middle and inner mesocarp, it seems reasonable to suppose that the first hypothesis could be the most reliable.

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