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Analytical Methods

Volatile characteristics of 50 peaches and nectarines evaluated by HP–SPME with GC–MS

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ABSTRACT

Using HS–SPME–GC–MS, characteristics of the volatiles of 50 peaches and nectarines representing different germplasm origins were investigated. Ten of these peaches and nectarines were studied in two successive years. Eighty-four compounds were identified. Volatile composition was relatively consistent, but the amount of total volatiles and certain individual compounds varied between years. Moreover, the composition of volatiles and their contents depended on genotypic background and germplasm origin. Total volatiles in wild peaches and a Chinese local cultivar 'Wutao' were much higher than in the other groups. All the peaches and nectarines could be classified into four groups by principal component analysis of the volatiles (excluding C_6 compounds): 'Ruipan 14' and 'Babygold 7' with high contents of lactones, Chinese wild peaches and 'Wutao' with high contents of terpenoids and esters, seven cultivars with American or European origins with high content of linalool, and others without characteristic composition of volatiles.

1. Introduction

Aroma is one of the essential components of fruit quality. The relative contributions of specific aroma volatile compounds to the flavour of peaches and nectarines have been examined by many investigators and more than 100 compounds have been identified (Aubert, Günata, Ambid, & Baumes, 2003; Aubert & Milhet, 2007; Chapman, Horvat, & Forbus, 1991; Derail, Hofmann, & Schieberle, 1999; Engel, Ramming, Flath, & Teranashi, 1988b; Jia, Okamoto, & Hirano, 2004; Kakiuchi & Ohmiya, 1991; Lavilla, Recasens, & Lopez, 2001; Robertson, Meredith, Horvat, & Senter, 1990a; Takeoka, Flath, Guntert, & Jennings, 1988). The volatiles of peaches and nectarines include C_6 compounds, alcohols, aldehydes, esters, terpenoids, ketones and lactones, among which the lactones, particularly γ- and δ-decalactones, have been reported to be the major contributors to peach aroma with smaller contributions by other volatiles such as C_6 aldehydes, alcohols and terpenoids (Do, Salunkhe, & Olson, 1969; Engel et al. 1988a; Horvat et al. 1990b; Visai & Vanoli, 1997).

Intensive investigations have focused on the evolution of peach and nectarine aromas during ripening (Chapman et al., 1991; Do et al., 1969; Horvat & Chapman, 1990a; Kakiuchi & Ohmiya, 1991; Lavilla et al., 2001; Visai & Vanoli, 1997) and during cold storage (Robertson et al., 1990a; Watada, Anderson, & Aulenbach, 1979). The composition and content of volatile aromas change during the maturation. In immature fruits, C_6 compounds are the major contributors, but their levels decrease drastically whilst those of lactones, benzaldehyde and linalool increase significantly during maturation (Do et al., 1969; Engel et al., 1988b). Several studies have also investigated the effect of culture techniques and management on composition and content of volatiles. Volatiles may be modified by orchard management, such as fertilisation (Jia, Hirano, & Okamoto, 1999) and bagging (Jia, Araki, & Okamoto, 2005), climate or microclimate conditions as sun light (Génard & Bruchou, 1992), and postharvest treatment (Derail et al., 1999; Kakiuchi & Ohmiya, 1991; Meredith, Robertson, & Horvat, 1989; Sumitani, Suekane, Nakatani, & Tatsuka, 1994). Volatile composition is also cultivar dependent. Engel et al. (1988) concluded that nectarines contain significantly higher amounts of δ-decalactone than peaches do and Robertson et al. (1990b) reported that white-fleshed peaches contain more linalool than yellow-fleshed cultivars.

Peaches and nectarines are native to China where peaches have been cultivated for at least 3000 years, and nectarines for over 2000 years. With a long history of cultivation and extensive geographical distribution, germplasm resources of peaches and nectarines are extensive in China and in the world.

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In this study, headspace-solid phase microextraction (HS–SPME) combined with gas chromatography–mass spectrometry (GC–MS) was applied to study the characteristic volatiles of peaches and nectarines at the germplasm level. This study was essentially focused on comparing the aroma composition and content, particularly among those germplasm resources that have not been extensively studied. These include Chinese local cultivars and a number of cultivars from other countries in order to acquire information for future breeding efforts aimed at improvement of fruit quality via effects on aroma. In addition, 10 cultivars were studied in two successive years to investigate the effects of weather on volatile composition and content.

2. Materials and methods

2.1. Plant materials

In this work, a total of 50 peach (*Prunus persica* L. Batsch) taxa were used to study aroma composition and content in 2006. These taxa included four Chinese wild peaches originally from different locations in China (C_w), 11 Chinese local (C_l) and eight pure Chinese bred cultivars (C_b), five China × foreign (CF), seven Japanese (J), and 15 American and European cultivars (AE) (Table 1). Ten of these, 'Yixianhong', 'Zaohuangjin', 'Wanmi', 'Yanhong', 'Ruipan 14', 'Jincheng', 'Hakuho', 'Yamaichi', 'Red Skin' and 'Early Red 2', were also measured in 2007 in order to investigate the stability of aroma formation between years.

All the samples were collected from the Germplasm Repository for peach in the Institute of Forestry and Pomology, Beijing Academy of Agriculture and Forestry Science. The trees, grafted on a wild *P. persica* rootstock, were planted 3 m apart within rows and 5 m apart between rows in the spring of 1996. They were trained to 'Y' training systems and pruned by the long pruning method in winter (Li, Zhang, Meng, & Wang 1994). The same orchard managements, such as fertilisation and irrigation were applied in the whole orchard. The fruits were harvested from three trees for each cultivar when the green colour of the fruit skin has almost disappeared. At the same time, the ground colour of white-fleshed peaches turned milk white, whilst the ground colour of yellow-fleshed peaches turned yellow or orange. All the fruits were picked from the southern or western crown about 1.5–2 m high from the ground of the tree at maturity. The fruit samples were taken to the laboratory immediately after harvest, washed in deionised water and surface-dried with gauze. Then three slices were taken from different orientations of each fruit. Three fruits were used for one composite sample per tree, and considered as one replication resulting in three replications for every cultivar. Samples were ground to a powder in liquid nitrogen and stored at −40 °C until analysis.

2.2. Isolation and concentration of volatiles

For headspace sampling, SPME fibres coated with polydimethylsiloxane–divinylbenzene (65 μm, PDMS/DVB) (Supelco Co., Bellefonte, PA, USA) were used by optimisation of the method carried out in a previous work (Guillot et al. 2006). The fibre was activated according to the manufacturer's instructions. The method of headspace solid phase microextraction was used for the isolation and concentration of volatiles. For each extraction, 2 g of the pulp powder, 0.6 g NaCl and 10 μl 3-octanol (0.814 g ml^{-1}, added as an internal standard) were placed in a 4 ml capped vial. The vial was placed in a 45 °C water bath with a magnetic stirrer to warm to constant temperature, and the SPME fibre was exposed to the headspace of the sample to adsorb the analytes for 30 min. The fibre was then introduced into the heated chromatograph injector port for desorption at 220°C for 2 min in the splitless mode. Linear retention index (LRI) were calculated by using *n*-alkane standards (C_6–C_{30}) using the method of Ceva-Antunes, Bizzo, Silva, Carvalho, and Antunes (2006).

2.3. GC–MS conditions

The volatile constituents were analysed using an Agilent (Palo Alto, CA) 5973 mass selective detector coupled to an Agilent 6890 gas chromatograph, equipped with a 30 m × 0.25 mm × 1.0 μm HP-5 MS (5% phenyl-polymethylsiloxane) capillary column. Helium was used as the carrier gas at a linear velocity of 1.0 ml/min. The injector temperature was kept at 220°C and the detector at 280 °C. The oven temperature was programmed from 40 °C (2 min), increasing at 3 °C/min to 150 °C (2 min), then increasing at 10 °C /min to 220 °C, and then held for 2 min by optimising the method used in previous work (Aubert & Milhet, 2007; Riu-Aumatell, Castellari, López-Tamames, Galassi, & Buxaderas, 2004). Mass spectra was recorded in electron impact (EI) ionisation mode at 70 eV. The quadrupole mass detector, ion source and transfer line temperatures were set, respectively, at 150, 230 and 280 °C. Mass spectra was scanned in the range *m/z* 30–350 amu at 1 s intervals. Identification of volatile compounds was achieved

Table 1
Peach and nectarine taxa used in this study. The number in parenthesis following the cultivar indicates the accession number.

Populations	Characters	Taxa
C_w[a]	White-flesh peach	Huailaimaotao (1), Xinjiangmaotao (2), Jiangsumaotao (3), Guizhoumaotao (4)
C_l	Purple-flesh peach	Wutao (5)
	White-flesh flat peach	Sahuahongpantao (6), Wanshudapantao (7), Changshengpantao (8), Chenpupantao (9)
	White-flesh peach	Yixianbai (10), Wuyuexian (11), Diaozhibai (12), Yixianhong (13), Qiubaozhu (14)
	Yellow-flesh peach	Zaohuangjin (15)
C_b	White-flesh peach	Yunshu 1 (16), Zaobaimi (17), Baihua (18), Hongganlu (19), Luxiang (20), Xiafengmi (21), Wanmi (22), Yanhong (23)
CF	White-flesh flat peach	Ruipan 20 (24), Ruipan 14 (25)
	White-flesh peach	Beijing 31 (26)
	Yellow-flesh peach	Yanhuang (27), Jincheng (28)
J	White-flesh peach	Kairyo Hakuho (29), Matsumori (30), Takei Hakuho (31), Hakuho (32), Yamaichi (33)
	Yellow-flesh peach	Kanto 14 (34), Nishiki (35)
AE	Yellow-flesh peach	Frederic (36), NJC47 (37), Suncling (38), Vesuvio (39), Troubadour (40), Elberta (41), Evert's (42), Babygold 7 (43), Babygold 8 (44), Cahgahckuei (45), Red Skin (46)
	Yellow-flesh nectarine	NJN69 (47), NJN76 (48), Fantasia (49), Early Red 2 (50)

[a] C_w, Chinese wild peaches; C_l, Chinese local cultivars; C_b, pure Chinese original bred cultivars; CF, China × foreign cultivars; J, Japanese cultivars; AE, American and European cultivars.

by comparing the mass spectra with the data system library (NIST 98) and linear retention index.

2.4. Statistical analysis

Data for each cultivar were averages of three replications. The terpenoids contents in 2006 were analyzed using the method of Kruskal-Wallis analysis because the variances of the populations are not equal. A one-way ANOVA analysis was used to determine significant differences of other volatiles between groups in 2006. The degree of freedom of Kruskal-Wallis and one-way ANOVA analysis is 48. Wilcoxon Signed Ranks Test was used to determine the significant differences in aroma contents between 2006 and 2007 by using the data of the 10 cultivars studied in two successive years. Principal component analysis (PCA) was done to detect clustering formation and establish relations between samples and volatile compounds in 2006.

3. Results and discussion

3.1. Identification of volatiles

Eighty-four volatile compounds were identified and relatively quantified of which some were found only in some taxa in this study (Table 2). Those compounds included seven C_6 compounds, 19 esters, 14 aldehydes, eight lactones, 14 terpenoids, four ketones, seven alcohols and 11 other compounds including some carbonyl compounds.

3.2. Total content of volatiles

Total volatile content ranged from 1386 to 1602 μg kg^{-1} FW for the wild peach germplasm and these values were much higher than all other cultivated cultivars except 'Wutao' (5). All Chinese peaches including Chinese local and bred cultivars with pure Chinese original bred cultivars, and China × foreign cultivars had a median of about 600 μg kg^{-1} FW of volatile content, which was higher than those of the cultivars originated from Japan, and America and Europe.

It is very interesting to note that 'Wutao' (5), a Chinese local cultivar with mauve fresh, had the highest volatile content among all the taxa including the Chinese wild peaches. The volatile content in fruit of 'Wutao' was 1984 μg kg^{-1} FW, which was 3–5 times higher than those of the other cultivars (Table 3). Six cultivars had also high total volatile contents (more than 700 μg kg^{-1} FW): 'Wuyuexian' (11), 'Ruipan 14' (25), 'Jincheng' (28), 'Troubadour' (40), 'Babygold 7' (43) and 'Early Red 2' (50). However, 'Yixianbai' (10) and 'NJN76' (48) had the least among Chinese local cultivars and AE, respectively.

3.3. Composition of volatiles

3.3.1. General

Table 3 gives the contents of all volatiles based on the genotype origins. As described above, 'Wutao' is a special cultivar with very high level of volatiles. So the content of volatiles in 'Wutao' is listed alone in Table 3, and the average contents of compositions in C_l did not include the volatile content of 'Wutao'.

The composition of volatiles and their content varied with genotypic background and the contents of main volatiles (greater than 5 μg kg^{-1} FW in general) and some special volatiles for all taxa are given in Table 4.

3.3.2. C_6 compounds

Seven C_6 compounds including hexane (C1), hexanal (C2), 2-hexenal (C3), (*Z*)-3-hexen-1-ol (C4), (*E*)-2-hexenal (C5), (*E*)-2-hexen-1-ol (C6), and 1-hexanol (C7) were found (Table 2). Hexanal (C2) and 2-hexenal (C3) were the major C_6 compounds (Table 4).

As the major components, C_6 compounds of all the taxa from the six origins contributed 57.4–67.9% to total volatile content whilst it contributed to 81.1% in 'Wutao'. The content of C_6 compounds was significantly higher in C_w than in other groups, and it was also significantly higher in CF than in the groups C_b, J and AE. The lowest C_6 content was found in J (Table 3).

Being described as having a 'grassy' flavour (Kakiuchi and Ohmiya, 1991), C_6 compounds are the major compounds in immature peaches and nectarines; however, as the fruit matures, their levels decrease (Do et al., 1969; Engel et al., 1988a; Horvat et al., 1990a). But in this work, we found that C_6 compounds were also the major compounds in all groups when the fruits matured (Table 3). C_6 compounds are known products of enzyme-catalyzed breakdown of unsaturated fatty acids. The reason for the high contents of C_6 compounds here was probably due to fatty acid breakdown.

3.3.3. Esters

Esters are considered to be main contributors to fruity and floral notes, high content in esters should give a pleasant flavour in peaches and nectarines (Sumitani et al., 1994). Esters were the second most abundant components, contributing to 7.9–17.8% of the total volatiles (Table 3). Among the six groups, the sum of the esters was highest in C_w, and lowest in J group. Moreover, significantly higher content of total esters was found in C_w than in C_l, C_b and J (Table 3).

Although 19 esters in total were found in peaches and nectarines in this study (Table 2), ethyl acetate (E1), (*Z*)-3-hexenyl acetate (E5), hexyl acetate (E6) and 2-hexenyl acetate (E7) accounting for more than 90% of total esters (Table 4). 'Guizhoumaotao' (4) had the highest esters content with 178.5 μg kg^{-1} FW, whilst NJN76 (48) was lowest with only 33.9 μg kg^{-1} FW. As regards individual ester content, the most abundant content in ethyl acetate (E1) was found in 'Luxiang' (20), a Chinese local cultivar with 89.1 μg kg^{-1} FW, followed by an AE cultivar 'Vesuvio' (39). Several taxa, 'Guizhoumaotao' (4), 'Jincheng' (28), 'Babygold 8' (44), 'Red Skin' (46) and 'Early Red 2' (50), had high levels of (*Z*)-3-hexenyl acetate, ranging from 62.8 to 84.0 μg kg^{-1} FW. The most abundant content in hexyl acetate (E6) was found in 'Yixianhong' (13), a Chinese local cultivar with 91.9 μg kg^{-1} FW, followed by 'Guizhoumaotao' (4) and 'Wutao' (5). High 2-hexenyl acetate (E7) levels were observed in one CF ['Jincheng' (28)] and two AE cultivars ['Babygold 8' (44) and 'Cahgahckuei' (45)] with contents of about 28 μg kg^{-1} FW (Table 4). For the other 15 esters, the levels were generally lower than 5 μg kg^{-1} FW, except in 'Yixianhong' (13) where dibutyl phthalate (E17) and isopropyl palmitate (E19) were abundant with 17.4 and 19.6 μg kg^{-1} FW, respectively.

3.3.4. Aldehydes

The total aldehyde content depended on genetic background (Table 3). The sum of the aldehydes in C_w was significantly higher than in other groups, and CF cultivars had significantly higher aldehydes content than AE.

Fourteen aldehydes were detected and benzaldehyde (A5) was dominant with contents ranging from 1.2 to 91.6 μg kg^{-1} FW (Table 4). 'Ruipan 14' (25) had the highest benzaldehyde content (91.6 μg kg^{-1} FW) among all the taxa. Three wild peaches, 'Huailaimaotao' (1), 'Xinjiangmaotao' (2) and 'Guizhoumaotao' (4), two Chinese original cultivars, 'Qiubaozhu' (14), 'Yanhong' (23) and a Japanese cultivar 'Yamaichi' (33) were the cultivars with high benzaldehyde content. The second most abundant aldehyde was nonanal (A10), with 'Jincheng' (28) having the highest (31.1 μg kg^{-1} FW) content among the taxa, and with 'Jiangsumaotao' (3), 'Yixianhong' (13), 'Nishiki' (35), 'Vesuvio' (39) and 'Troubadour'

Table 2
Volatiles detected in fruits of all 50 peaches and nectarines.

	Compounds[a]	Codes	LRI[b]
C_6 compounds	Hexane	C1	600
	Hexanal	C2	802
	2-Hexenal	C3	847
	(*Z*)-3-Hexen-1-ol	C4	851
	(*E*)-2-Hexenal	C5	853
	(*E*)-2-Hexen-1-ol	C6	862
	1-Hexanol	C7	870
Esters	Ethyl acetate	E1	615
	Butyl acetate	E2	819
	3-Methyl-1-butanol acetate	E3	878
	Ethyl hexanoate	E4	1003
	(*Z*)-3-Hexenyl acetate	E5	1005
	Hexyl acetate	E6	1015
	2-Hexenyl acetate	E7	1017
	Ethyl benzoate	E8	1170
	Ethyl octanoate	E9	1199
	(*E*)-2-Hexenyl butanoate	E10	1203
	Nonyl acetate	E11	1317
	Ethyl 4-decenoate	E12	1372
	Methyl 4-decenoate	E13	1389
	Ethyl-4-ethoxy-benzoate	E14	1525
	Dibutyl pentanedioate	E15	1580
	Isopropyl myristate	E16	1829
	Dibutyl phthalate	E17	1969
	Ethyl hexadecanoate	E18	1980
	Isopropyl palmitate	E19	2007
Aldehydes	Pentanal	A1	697
	(*E*)-2-Pentenal	A2	752
	Heptanal	A3	904
	(*E*,*E*)-2,4-Hexadienal	A4	912
	Benzaldehyde	A5	958
	(*Z*)-2-Heptenal	A6	964
	Octanal	A7	1002
	Benzeneacetaldehyde	A8	1043
	(*E*)-2-Octenal	A9	1063
	Nonanal	A10	1105
	(*E*,*Z*)-2,6-Nonadienal	A11	1151
	(*E*)-2-Nonenal	A12	1161
	Decanal	A13	1206
	Undecanal	A14	1307
Lactones	γ-Hexalactone	L1	1056
	γ-Heptalactone	L2	1163
	δ-Octalactone	L3	1250
	γ-Octalactone	L4	1262
	γ-Nonalactone	L5	1362
	γ-Decalactone	L6	1467
	δ-Decalactone	L7	1496
	7-Decen-5-olide	L8	1715
Terpenoids	2-Bornylene	T1	907
	D-Limonene	T2	1026
	Eucalyptol	T3	1032
	Ocimene	T4	1042
	Linalool	T5	1099
	Camphor	T6	1146
	α-Terpineol	T7	1176
	β-Cyclocitral	T8	1218
	(*E*)-Theaspirane	T9	1297
	2,4,4-Trimethyl-3-(3-methylbutyl)cyclohex-2-enone	T10	1341
	à,á-Dihydro-á-ionone	T11	1437
	4-(2,6,6-Trimethyl-cyclohex-1-enyl)-butan-2-ol	T12	1444
	Geranyl acetone	T13	1453
	á-Ionone	T14	1485
Ketones	1-Penten-3-one	K1	690
	1-Octen-3-one	K2	979
	2-Methyl-3-octanone	K3	986
	6-Methyl-5-hepten-2-one	K4	989
Alcohols	1-Penten-3-ol	B1	684
	(*Z*)-2-Penten-1-ol	B2	756
	1-Pentanol	B3	768
	1-Octen-3-ol	B4	982
	2-Ethyl-1-hexanol	B5	1034
	1-Octanol	B6	1037
	Nonanol	B7	1175

Table 2 (*continued*)

	Compounds[a]	Codes	LRI[b]
Other compounds	2-Pentyl-furan	O1	992
	Dodecane	O2	1200
	Tridecane	O3	1300
	Tetradecane	O4	1400
	Pentadecane	O5	1500
	Butylated hydroxytoluene	O6	1518
	Heptadecane	O7	1700
	3,5-Di-tert-butyl-4-hydroxybenzaldehyde	O8	1767
	9-Methylene-9H-fluorene	O9	1773
	Nonadecane	O10	1900
	Heneicosane	O11	2100

[a] Identities confirmed by comparing mass spectra and retention time with those of authentic standards.
[b] Linear retention index calculated using a series of *n*-alkane.

Table 3
Average contents of the groups of volatiles (μg kg^{-1} FW equivalent of 3-octanol) in different origins of peach and nectarine taxa in 2006.

	P-value	Cw[a]	Cl	Cb	CF	J	AE	Wu
C6s	0.000	994.3 ± 115.6a	385.2 ± 90.8bc	356.6 ± 86.4bcd	443.5 ± 24.8b	242.2 ± 60.6d	289.8 ± 134.5 cd	1608.1
C6s% of TV		67.9%	67.5%	66.4%	60.8%	60.6%	57.4%	81.1%
Esters	0.075	115.9 ± 44.1a	75.9 ± 39.1b	70.3 ± 35.6b	79.0 ± 36.3ab	54.0 ± 22.8b	89.7 ± 29.3ab	106.2
Esters% of TV		7.9%	13.2%	13.1%	10.8%	13.5%	17.8%	5.4%
Aldehydes	0.001	64.4 ± 19.6a	37.6 ± 11.0bc	36.6 ± 19.8bc	46.9 ± 31.2b	37.0 ± 12.0bc	25.8 ± 6.4c	33.8
Aldehydes% of TV		4.4%	7.3%	6.8%	6.4%	9.3%	5.1%	1.7%
Lactones	0.247	73.2 ± 29.7	39.8 ± 21.4	40.5 ± 18.0	76.2 ± 90.0	35.7 ± 13.4	43.5 ± 30.3	33.5
Lactones% of TV		5.0%	7.1%	7.5%	10.4%	8.9%	8.6%	1.7%
Terpenoids	0.007	188.5 ± 29.5a	12.4 ± 10.1c	19.3 ± 10.5c	74. 9 ± 51.1b	19.4 ± 16.7c	44.5 ± 44.5bc	187.4
Terpenoids% of TV		13.4%	2.3%	3.6%	10.3%	4.8%	8.8%	9.4%
Ketones	0.001	6.4 ± 0.7a	2.1 ± 2.0b	1.9 ± 1.3b	1.6 ± 0.9b	2.3 ± 2.1b	2.3 ± 1.6b	5.6
Ketones% of TV		0.5%	0.8%	0.8%	0.5%	1.1%	0.7%	0.3%
Alcohols	0.066	6.9 ± 1.3a	4.4 ± 2.1b	4.4 ± 1.7b	3.9 ± 1.3b	4.3 ± 1.9b	3.5 ± 2.2b	5.2
Alcohols% of TV		0.4%	0.3%	0.3%	0.2%	0.6%	0.5%	0.3%
Others	0.076	8.3 ± 3.5a	6.8 ± 3. 6abc	7.4 ± 4.1ab	3.6 ± 1.6c	4.4 ± 2.1bc	5.6 ± 2.7abc	3.8
Others% of TV		0.6%	1.4%	1.4%	0.5%	1.1%	1.1%	0.2%
Total	0.000	1457.9 ± 100.3a	564.1 ± 102.7c	537.0 ± 94.1 cd	729.6 ± 171.8b	399.3 ± 83.0d	504.8 ± 179.6 cd	1983.6

The different small letters indicate significant differences between populations ($P < 0.05$).
TV = the content of total volatiles.
[a] C_w, Chinese wild peaches; C_l, Chinese local cultivars; C_b, pure Chinese original bred cultivars; CF, China × foreign cultivars; J, Japanese cultivars; AE, American and European cultivars; Wu, 'Wutao'.

(40) having more than 15 μg kg^{-1} FW. The other aldehydes were less than 5 μg kg^{-1} FW.

3.3.5. Lactones

Eight lactones were found (Table 2), and these accounted for 5.0–10.4% of the total volatiles. No significant differences were found between the six groups of taxa although lactones levels in C_w and CF were almost double of the others (Table 3).

In all groups, γ-decalactone (L6) and δ-decalactone (L7) were major components accounting for more than 80% of total lactonic compounds, and γ-decalactone (L6) was dominant. One CF, 'Ruipan 14' (25) and one American cultivar 'Babygold 7' (43) had very high levels of γ-decalactone with 143.6 μg kg^{-1} FW and 83.0 μg kg^{-1} FW, respectively. Two Chinese wild peaches, 'Huailaimaotao' (1) and 'Jiangsumaotao' (3) had also high levels of γ-decalactone with more than 60 μg kg^{-1} FW. The other taxa with abundant γ-decalactone content were 'Guizhoumaotao' (4), 'Chenpupantao' (9), 'Yanhong' (23), 'Suncling' (38), 'Vesuvio' (39) and 'Troubadour' (40, Table 4). The second abundant lactone was δ-decalactone (L7). Levels of δ-decalactone tended to be positively correlated with γ-decalactone content, being also high in 'Ruipan 14' (25) and 'Babygold 7' (43). The other six lactones were relatively low and less than 10 μg kg^{-1} FW, except in 'Ruipan 14' (25), 'Wanmi' (22), 'Yixianhong' (13) and 'NJN69' (47, Table 4).

Lactones, particularly γ-decalactone and δ-decalactone, have been reported as "character impact" compounds in peach and nectarine aroma. They act in association with other volatiles, such as C_6 aldehydes, C_6 alcohols and terpenoids, to produce the flavours specific to peach, and lactones contribute the "peachy" background whilst others contribute fruity and floral notes (Horvat et al., 1990a,b). Moreover, Engel et al. (1988) concluded that nectarines contain significantly higher amounts of δ-decalactone than peaches. But in this study, flat peaches had significantly higher content of δ-decalactone (L7) than white- and yellow-fleshed peaches and yellow-fleshed nectarines. There was no significant difference between peaches and nectarines. Flat peaches had significantly higher γ-decalactone (L6) content than white-fleshed peaches and nectarines did. There was no significant difference between flat peaches and yellow-fleshed peaches.

3.3.6. Terpenoids

The total content of terpenoids accounted for 2.3–13.4% of total volatiles (Table 3). The sum of terpenoids in C_w was significantly higher than in other groups and it was also significantly higher in CF than in C_l, C_b and J (Table 3).

Of 14 terpenoids found, linalool (T5) was the major compound. Linalool content, however, ranged from 0 to 207.5 μg kg^{-1} FW. There was no linalool detected in 'Zaohuangjin' (15), 'Yanhong'

Table 4
Contents of the major volatiles (μg kg^{-1} FW equivalent of 3-octanol) in the 50 peach and nectarine taxa in 2006.

	E1[b]	E5	E6	E7	E17	E19	A5	A10	L1	L6	L7	T2	T5	T11
1[a]	5.5	44.9	28.6	9.5	0.5	0.5	49.5	7.9	4.3	64.8	17.5	0.7	165.3	5.8
2	7.3	37.1	19.0	12.2	0.3	1.8	40.5	9.3	4.7	21.3	5.6	0.9	152.9	2.7
3	23.4	45.1	29.4	10.0	0.6	0.2	9.2	16.1	7.4	64.7	23.7	1.1	155.7	3.8
4	6.7	84.0	59.2	26.4	0.4	0.2	69.4	12.2	3.2	44.0	18.5	11.0	207.5	2.6
5	2.9	43.8	42.5	13.4	0.2	0.6	15.4	7.2	4.1	21.4	7.3	0.8	167.3	8.3
6	4.6	21.9	10.1	7.5	0.2	0.8	21.9	2.8	2.8	39.0	12.8	0.2	3.3	2.2
7	5.0	16.4	7.8	7.6	1.4	3.1	25.2	2.9	9.8	25.9	12.9	0.5	19.5	2.9
8	5.4	32.2	18.1	10.8	0.2	0.1	24.0	3.1	4.2	37.4	11.0	0.3	18.8	2.9
9	21.9	31.0	24.3	16.8	0.4	0.4	15.9	2.8	4.3	41.8	13.2	0.3	6.2	–[c]
10	6.7	35.1	1.9	1.9	0.5	0.2	32.7	8.2	2.5	1.1	6.5	0.4	0.9	0.2
11	4.7	43.9	7.0	4.8	0.5	1.3	41.6	2.9	3.1	12.8	2.6	0.3	3.1	0.4
12	5.2	25.8	8.8	6.7	0.4	1.0	28.8	2.9	2.0	3.1	0.7	0.3	1.7	0.3
13	5.0	24.1	91.9	5.3	17.4	19.6	24.7	18.6	18.1	12.2	6.5	1.3	4.6	–
14	5.1	29.9	15.3	16.6	0.7	1.1	68.6	2.0	9.3	26.8	10.2	0.8	15.6	2.6
15	5.0	37.4	14.2	13.7	0.5	2.5	15.1	10.2	8.0	30.5	7.8	0.7	–	–
16	12.5	23.8	10.4	8.7	0.4	0.6	20.3	3.3	1.6	25.4	6.0	0.2	10.4	3.9
17	6.9	19.4	11.5	4.6	0.3	0.9	18.9	2.8	0.4	8.3	1.0	0.2	0.5	3.3
18	3.5	27.3	14.9	13.2	0.4	0.9	26.3	2.2	4.5	21.1	7.0	0.3	17.8	4.1
19	5.2	17.9	8.9	8.4	0.4	0.5	3.5	4.7	1.9	12.5	3.6	0.2	0.7	0.9
20	89.1	12.4	16.1	11.2	0.3	0.2	19.7	9.2	4.6	39.0	3.5	0.4	5.4	–
21	9.0	14.6	3.9	3.0	0.3	0.1	13.2	2.2	2.8	39.3	9.4	0.3	29.3	2.8
22	5.0	39.2	14.3	7.8	1.6	5.3	16.3	4.6	15.0	25.0	7.5	–	3.9	1.7
23	5.0	41.3	14.5	10.1	2.5	1.4	46.9	4.6	8.4	42.8	10.3	0.4	–	5.6
24	0.9	30.9	15.7	7.3	0.2	0.1	25.2	2.5	1.8	18.8	8.1	0.5	85.4	2.4
25	5.0	32.2	14.9	7.1	3.7	2.2	91.6	4.3	21.8	143.6	56.2	0.5	115.0	4.1
26	2.1	22.1	25.2	14.7	0.1	0.1	21.5	1.4	2.0	30.5	6.9	0.2	0.3	3.0
27	4.0	22.2	15.4	9.8	0.3	1.0	20.6	2.4	2.6	14.5	4.2	0.4	34.1	–
28	5.0	75.3	23.0	28.7	1.7	5.7	7.0	31.1	4.6	37.1	10.1	1.2	109.4	–
29	9.3	14.6	5.4	6.1	0.2	0.2	30.8	2.9	2.1	16.9	4.8	0.2	1.1	3.1
30	2.7	21.8	6.4	8.6	0.3	0.1	34.2	3.3	4.6	26.0	6.0	3.0	16.2	2.8
31	2.2	16.3	7.2	6.9	0.2	0.5	19.4	2.6	3.3	15.4	4.8	0.4	8.7	–
32	5.0	17.0	8.2	8.9	1.3	2.0	24.7	4.6	6.4	29.8	10.2	0.2	1.4	3.8
33	5.0	23.7	10.8	8.2	4.3	4.3	45.6	5.0	8.0	18.5	9.2	0.2	41.5	1.3
34	6.5	42.5	29.4	22.4	0.4	0.8	11.9	5.5	3.8	38.6	11.3	0.3	29.3	–
35	4.4	35.5	5.0	8.3	0.3	0.4	4.3	23.0	2.1	14.5	2.9	0.3	–	–
36	2.6	49.1	14.0	14.3	0.5	0.5	3.1	13.4	3.6	36.9	7.0	0.3	7.4	–
37	11.9	43.2	23.0	14.2	0.2	0.9	8.4	6.9	2.6	33.4	8.5	0.4	34.5	–
38	4.2	20.8	13.2	13.3	0.1	0.1	7.1	4.0	2.7	26.2	6.1	0.3	7.3	–
39	45.1	26.3	4.2	5.4	0.4	0.5	5.7	15.9	9.1	43.4	8.1	0.3	–	–
40	12.4	52.1	28.7	19.7	0.7	0.4	2.5	17.6	4.9	63.7	12.1	0.7	1.4	–
41	8.4	30.8	11.6	14.8	0.2	0.6	14.0	7.9	3.5	16.0	4.2	0.3	7.5	–
42	9.0	34.2	20.3	17.1	0.3	0.3	4.3	6.0	1.7	3.6	1.3	0.4	76.7	–
43	18.7	50.2	20.6	21.1	0.5	0.2	16.1	10.8	9.9	83.0	20.0	0.7	84.8	–
44	17.6	62.8	24.6	28.4	0.4	0.2	10.5	9.5	3.2	22.3	5.0	0.3	0.7	–
45	2.4	22.2	28.0	28.0	0.2	0.1	4.3	12.1	2.8	10.4	1.9	0.5	66.4	0.2
46	5.0	65.6	26.3	17.3	1.2	5.2	10.4	9.5	4.9	27.1	7.8	0.7	90.5	–
47	25.3	21.0	18.0	24.8	0.2	0.5	8.5	10.9	11.1	34.4	7.4	0.3	15.5	–
48	6.3	9.1	2.7	7.0	0.5	0.2	7.5	7.6	5.5	19.4	2.2	0.3	0.6	–
49	1.7	31.5	11.8	10.7	0.7	0.4	1.2	7.8	2.0	9.4	2.6	1.1	121.0	–
50	1.5	66.0	11.0	14.0	0.4	4.0	6.1	14.3	1.9	15.2	2.4	0.5	98.2	–

[a] Numbers 1-50 represent the cultivars responding to the accession number in Table 1.
[b] The letter plus the number represents compound corresponding to the code in Table 2.
[c] Not detected in sample.

(23), 'Nishiki' (35) and 'Vesuvio' (39). But, linalool contents in Chinese wild cultivars were very high, especially in 'Guizhoumaotao' (4) with 207.5 μg kg^{-1} FW. Linalool was high in some cultivars with American or European origins: 'Ruipan 20' (24), 'Ruipan 14' (25), 'Jincheng' (28), 'Evert's' (42), 'Babygold 7' (43), 'Cahgahckuei' (45), 'Red Skin' (46), 'Fantasia' (49) and 'Early Red 2' (50) contained 85.4, 115, 109.4, 76.7, 84.8, 66.4, 90.5, 121 and 98.2 μg kg^{-1} FW, respectively (Table 4). Other terpenoids were less than 5 μg kg^{-1} FW except D-limonene (T2) which was 11 μg kg^{-1} FW in 'Guizhoumaotao' (4) (Table 4). α,α-Dihydro-α-ionone (T11) was absent from many taxa, including all American cultivars (Table 4).

Terpenoids contribute fruity characteristics to peach (Engel et al., 1988a). Linalool is one of the major compounds in mature peaches and nectarines, increasing significantly during fruit maturation (Chapman et al., 1991; Horvat and Chapman, 1990a; Robertson et al., 1990a). As previously reported, high linalool levels were found in 'Fantasia' (49) and 'Early Red 2' (50) nectarines in this work, but there were very low linalool levels in the other two nectarines NJN69 (47) and NJN76 (48, Table 4). Linalool content of nectarines was significantly higher than in white-fleshed peaches, but unlike previous reports (Engel et al., 1988a; Horvat et al. 1990b; Robertson et al., 1990b), there was no significant difference between white- and yellow-fleshed peaches.

3.3.7. Ketones, alcohols and other compounds

In this work, four ketones, seven alcohols and 11 other carbonyl compounds were found. The sum of ketones, alcohols and other carbonyl compounds accounted, respectively, for 0.5–1.1%, 0.2–0.6% and 0.5–1.4% of the total volatiles (Table 3). They are not discussed here in detail because of their low levels.

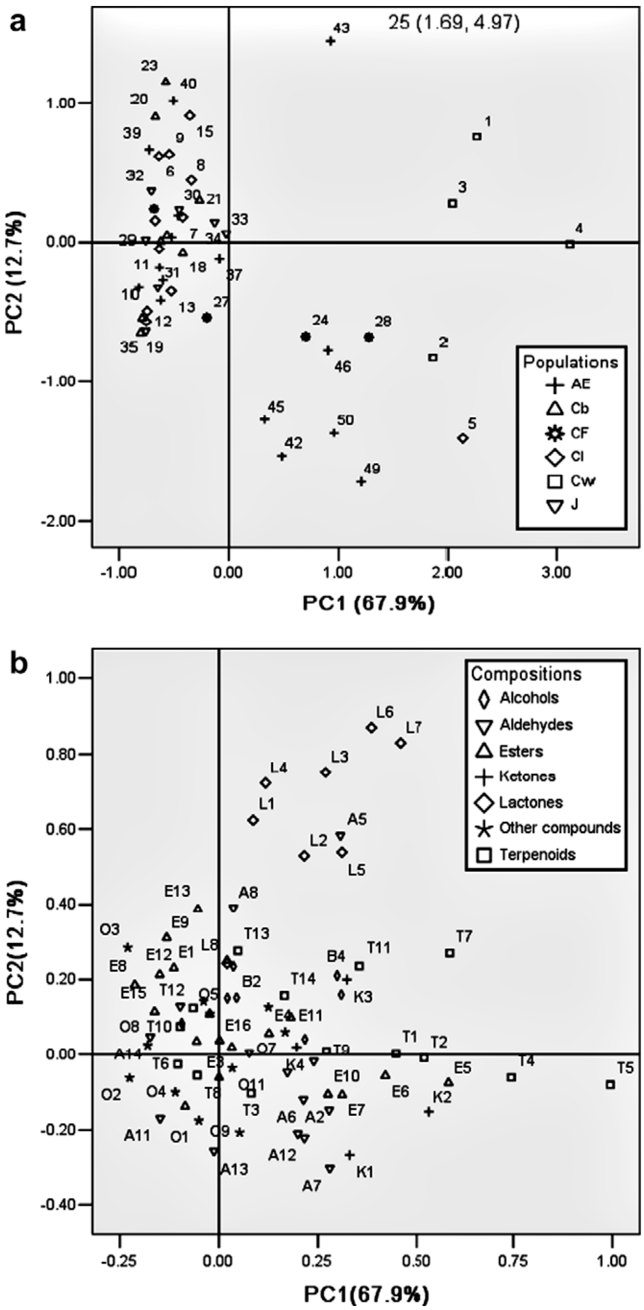

Fig. 1. Positions of PC scores of 50 peaches and nectarines (indicated in numbers) according to PC1 and PC2 obtained by contents of volatile compositions excluding C_6 compounds. (a) Scores scatter plot of PCA, and (b) loadings plot of PCA. Percentages in parenthesis represent the variance of each component. The numbers in Fig. 1a represent the accession number, which corresponds to the same number as in Table 1. The letter plus the number in Fig. 1b is the code of volatiles, which correspond to the same code as in Table 2. C_w, Chinese wild peaches; C_l, Chinese local cultivars; C_b, pure Chinese original bred cultivars; CF, China × foreign cultivars; J, Japanese cultivars; AE, American and European cultivars.

3.4. Principal component analysis

The principal component analysis (PCA) was carried using the compositional data excluding C_6 compounds from the samples identified in 2006. The percent of cumulative contribution of variance of the first two PCs was 80.6%, which was high enough to represent all the variables. PC1 represented 67.9% of the variance and it was correlated to terpenoids, especially linalool (T5) and the esters, whilst PC2 represented 12.7% of variance correlating to the lactones and benzaldehyde (A5, Fig. 1b).

The scores scatter plot of PCA of all peach and nectarines is shown in Fig. 1a and the corresponding loading plot establishing the relative importance of the variables is shown in Fig. 1b. All the peach and nectarine taxa could be divided into four groups (Fig. 1a) based on the position in the scores scatter plot of PCA.

Group I: The position in the upper part of the scatter plot for cultivars ‘Ruipan 14’ (25) and ‘Babygold 7’ (43) (Fig. 1a) was due to high contents of lactones especially γ-decalactone (L6), δ-decalactone (L7) and benzaldehyde (A5, Fig. 1b).

Group II: Four Chinese wild peaches, ‘Huailaimaotao’ (1, originated from Northern Plain of China), ‘Xinjiangmaotao’ (2, originated from North-western China), ‘Jiangsumaotao’ (3, originated from South-eastern China) and ‘Guizhoumaotao’ (4, originated from southern China), and one Chinese local peach ‘Wutao’ (5) were located in the right part of the PC1 axis (Fig. 1a). This group was characterised by high contents of terpenoids [especially linalool (T5), ocimene (T4), α-terpineol (T7) and D-limonene (T2)] and three esters (*Z*)-3-hexenyl acetate (E5), hexyl acetate (E6) and 2-hexenyl acetate (E7, Fig. 1b).

Group III: Four American cultivars, ‘Evert’s’ (42), ‘Red Skin’ (46), ‘Fantasia’ (49) and ‘Early Red 2’ (50), two China × foreign cultivars, ‘Ruipan 20’ (24) and ‘Jincheng’ (28) and one European cultivar ‘Cahgahckuei’ (45) were classified into the same group (Fig. 1a). These seven cultivars all had American or European origins and were characterised by high concentrations of linalool (T5).

Group IV: The remaining peach and nectarine cultivars, including C_l except ‘Wutao’, C_b, the other two CF cultivars, J and the other nine AE cultivars, were classified into the last group (Fig. 1a). It was, however, difficult to find the dominant volatile, i.e. there was no characteristic composition for this group (Fig. 1b).

3.5. Seasonal variation of volatile compositions

Variations of eight groups of volatiles and their contents (greater than 10 μg kg^{-1} FW in general) in the 10 cultivars studied in two successive years are shown in Table 5. The effect of the year varied with the compound. Total volatiles, the sum of C_6 compounds, aldehydes, alcohols and ketones in 2007, were significantly higher than in 2006. On the contrary, the sum of esters was significantly lower in 2007 compared with 2006. However, between the two years there were no significant differences in the sum of lactones and terpenoids.

C_6 compounds were dominant in both years, accounting for 59.9% and 67.2% of total volatiles in 2006 and 2007, respectively. But the second most abundant compounds changed from esters in 2006 to lactones in 2007. Concerning the year effect on the major compounds (contents more than 10 μg kg^{-1} FW), the levels of 2-hexenal (C3) and benzaldehyde (A5) in 2007 were significantly higher than in 2006, whereas the levels of (*E*)-2-hexen-1-ol (C6), 1-hexanol (C7), hexyl acetate (E6) and linalool (T5) were lower. However, other compounds were unaffected with no significant differences between the years.

The results obtained from the 10 cultivars showed that the categories of volatiles were relatively consistent between the years (data not shown). However, as described above, the total volatiles content and the levels of certain individual compounds appeared different one year from the other. Since all the taxa were planted in the same orchard with a similar management between the years, weather would appear to explain the yearly variations.

Table 5
Average contents of the groups of volatiles (μg kg^{-1} FW equivalent of 3-octanol) and major compositions in the 10 cultivars studied in 2006 and 2007.

	P-value	2006		2007	
		Mean ± SD	Percentage (%)	Mean ± SD	Percentage (%)
C2[a]	0.478	208.7 ± 11.4	32.10	224.9 ± 16.8	27.10
C3	0.000	139.4 ± 36.9b[b]	18.30	285.0 ± 20.4a	34.30
C6	0.000	16.6 ± 2.5a	2.50	10.0 ± 1.1b	1.20
C7	0.001	31.1 ± 3.4a	4.60	17.1 ± 2.3b	2.10
E5	0.056	42.8 ± 7.4	6.30	33.9 ± 3.0	4.10
E6	0.005	24.2 ± 4.6a	3.30	9.5 ± 1.5b	1.20
E7	0.210	12.6 ± 2.0	1.80	10.1 ± 1.2	1.20
A5	0.001	28.8 ± 2.1b	4.50	52.3 ± 3.7a	6.30
L6	0.804	38.1 ± 3.9	5.90	47.4 ± 4.3	5.50
L7	0.218	13.7 ± 0.9	1.80	15.6 ± 1.5	1.90
T5	0.024	58.0 ± 7.9a	7.10	42.4 ± 2.1b	4.10
C_6 compounds	0.002	391.4 ± 47.0b	59.90	557.3 ± 29.7a	67.20
Esters	0.024	85.8 ± 11.3a	13.10	63.1 ± 5.5b	7.60
Aldehydes	0.005	48.0 ± 1.2b	7.40	71.7 ± 3.7a	8.70
Lactones	0.491	63.8 ± 4.7	9.80	78.9 ± 7.4	9.50
Terpenoids	0.035	54.6 ± 8.6	8.40	42.1 ± 1.9	5.10
Alcohols	0.000	4.4 ± 0.7b	0.70	8.8 ± 0.4a	1.10
Ketones	0.000	1.3 ± 0.1b	0.20	3.8 ± 0.7a	0.40
Other compounds	0.000	9.3 ± 0.2b	0.60	16.0 ± 0.3a	0.50
Total volatiles	0.002	652.9 ± 66.3b		829.0 ± 23.4a	

[a] The letter plus the number represents compound corresponding to the code in Table 2.
[b] The different letters indicate significant differences between two years ($P < 0.05$).

4. Conclusions

Volatiles composition and content depended largely upon genetic background. Almost all the characteristic volatiles in C_w and 'Wutao' were significantly higher than in the other groups. All the peach and nectarine taxa could be classified into four groups: 'Ruipan 14' and 'Babygold 7' characterised by high contents of lactones (especially γ-decalactone and δ-decalactone) and benzaldehyde, Chinese wild peach taxa and 'Wutao' with high contents of terpenoids and esters, seven cultivars mainly with American or European origins characterised by high concentrations of linalool, and others without any characteristic volatile composition.

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