

Investigation of Volatiles in Charentais Cantaloupe Melons (*Cucumis melo* Var. *cantalupensis*). Characterization of Aroma Constituents in Some Cultivars

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Volatile compounds of 15 Charentais melon cultivars, known to exhibit differences in their ripening behaviors and in their storage lives (wild, mid, and long shelf life), were investigated. Twenty-eight volatiles (11 esters, 8 sulfur compounds, 6 alcohols, and 3 carbonyl compounds) were isolated by direct dichloromethane extraction and analyzed by means of GC-MS and GC-FID. A considerable reduction in the aroma profile was observed for the long shelf life cultivars, in which total volatiles were 49–87% lower than in the wild or mid shelf life melons. Most of the esters such as ethyl 2-methylbutyrate, ethyl butyrate, ethyl hexanoate, hexyl acetate, and butyl acetate and sulfur compounds such as ethyl 2-(methylthio)acetate, 2-methylthioethanol, ethyl 3-(methylthio)propanoate, 3-(methylthio)propyl acetate, and 3-(methylthio)propanol with low odor values were 2–30-fold lower in long shelf life cultivars than in the others. Discrimination of long shelf life cultivars from wild and mid shelf life melons was achieved by statistical treatment of the data by principal component and variance analysis.

KEYWORDS: Charentais melon; *Cucumis melo*; volatiles; aroma; sulfur compounds

INTRODUCTION

Melon (*Cucumis melo* L.) belongs to the Cucurbitaceae family and has been divided into seven different varieties: *C. melo* var. *cantalupensis* Naud., *C. melo* var. *flexuosus* Naud., *C. melo* var. *conomon* Mark, *C. melo* var. *chito* Naud., *C. melo* var. *dudaim*, *C. melo* var. *reticulatus* Naud., and *C. melo* var. *inodorus* Naud. (1, 2).

The Charentais cantaloupe (*C. melo* var. *cantalupensis* Naud.) is the most important melon produced in France. Its orange-fleshed fruits are highly prized for their strong aromatic flavor. Contrary to American cantaloupes (*C. melo* var. *reticulatus* Naud.), also called rockmelons in Australia, Charentais melons have poor storage capabilities and a short shelf life (~3–4 days) usually due to a rapid ripening associated with a sharper climacteric phase (2, 3). In recent years, to improve storage and handling properties, breeders have generated, by traditional breeding methods, hybrids of Charentais cantaloupe with a shelf life more or less extended: mid (MSL) and long shelf life (LSL) melons. Nevertheless, if the shelf life has been greatly extended, up to 14 days for LSL fruits, the consumer often complains about the low quality of the latter, which are generally recognized as having less aromatic flavor compared to the others (4, 5).

Although the melon volatiles have been extensively investigated (6–16), the aroma composition of Charentais melon (*C. melo* var. *cantalupensis* Naud.) has been hardly studied (17–

20). Moreover, previous works have shown that transformed melons, expressing an antisense ACC oxidase (21), exhibited a considerable reduction in total volatile production (19, 20), but no report has focused on the volatile compounds of mid and long shelf life varieties obtained by conventional breeding methods. The aim of this study is to investigate the aroma composition of wild, mid, and long shelf life cultivars of Charentais melons and to discriminate them according to their storage life by using their levels of volatile compounds.

MATERIALS AND METHODS

Solvent and Chemicals. Analytical grade dichloromethane and *n*-alkane (C₈–C₄₀) standards were, respectively, from Riedel-de Haën and Fluka. All of the reference compounds were from Aldrich except (Z)-3-hexenyl acetate, methyl 3-(methylthio)propanoate, ethyl 3-(methylthio)propanoate, 3-(methylthio)propyl acetate, and 3-(methylthio)propanol (Interchim).

Samples. Charentais cantaloupe melons (*Cucumis melo* var. *cantalupensis* Naud.) used in this study were grown using standard horticultural practices. Wild (Figaro, Cézanne, and Nogaró) and mid shelf life melons (Escrito, Anasta, and Lunabel) were harvested when they exhibited a yellow rind and a fruit abscission. For long shelf life cultivars (Sirio, Person, Stromboli, Aneto, Colt, Dalton, Etna, Kousto, and Tobbia), whose fruits do not show these characteristics, melons were picked when judged fully ripe by an experienced agronomist as in commercial practice. Melons were obtained from the experimental orchards of Ctifl (Baladrán, Gard, France) except for the Aneto, Colt, Dalton, Etna, Kousto, and Tobbia cultivars (Aprel, Saint-Rémy-de-Provence, Bouches-du-Rhône, France).

Sample Preparation. Fruits, ~15 melons for each cultivar, were first washed, and then the stem and blossom portions (~4 cm) were

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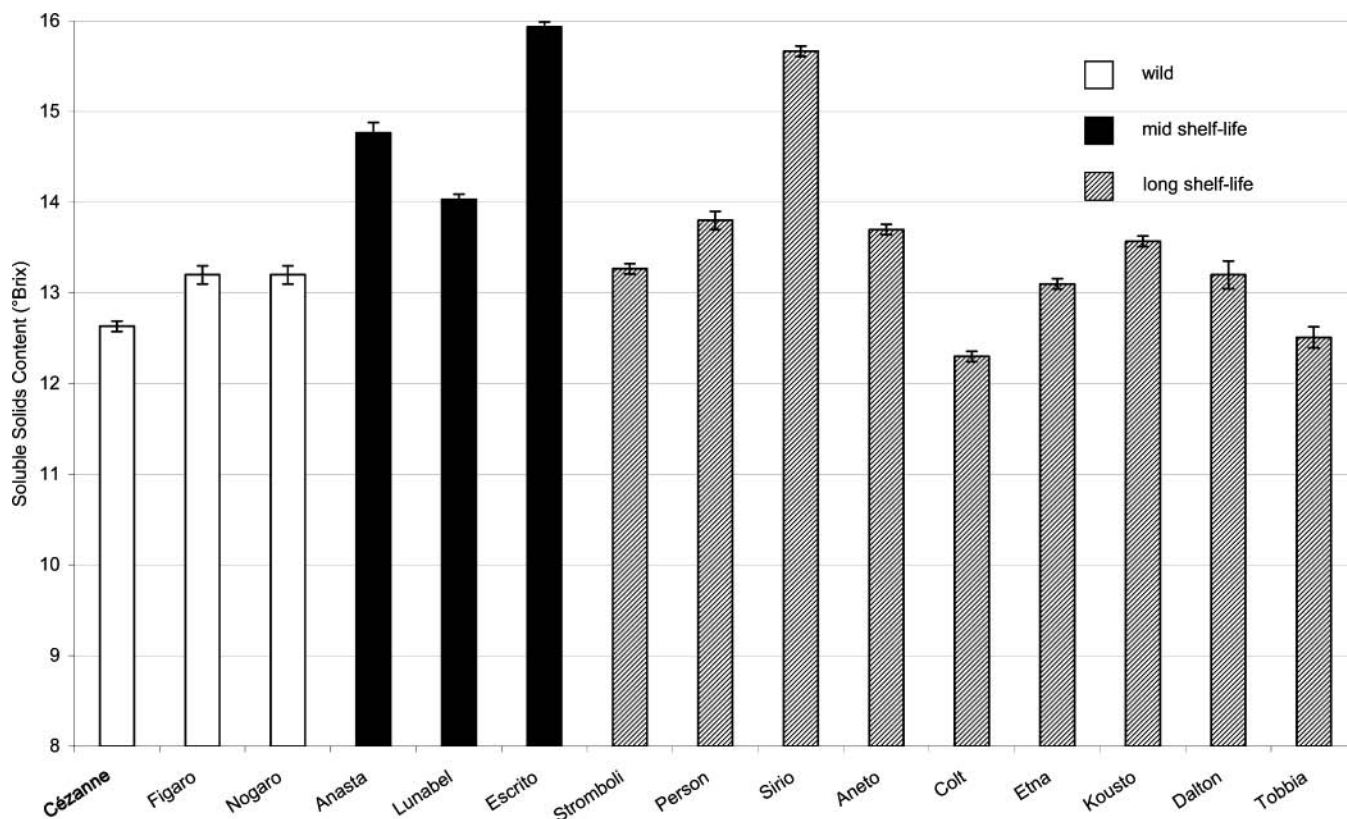


Figure 1. Soluble solids content of the different Charentais melon cultivars

cut off. After removal of the skin, cubes (~2 cm × 2 cm) were prepared, immediately frozen with liquid nitrogen, and stored at -25 °C until analysis.

Soluble Solids. Soluble solids (°Brix) were measured with an Atago PR-101 digital refractometer on the juice obtained from 100 g of fruit after homogenization and centrifugation (8500g, 20 min, 4 °C). Analyses were performed in triplicate.

Volatile Analysis. Three hundred grams of frozen fruits, 300 mL of saturated NaCl solution, and 100 μ L of 4-nonanol (3.28 mg/mL) (internal standard) were homogenized in a Waring blender for 3 min. The pulp was then centrifuged (8500g, 20 min, 4 °C), and the clear juice was filtered through glass wool. One hundred milliliters of clear juice was extracted in batches with 50 mL of analytical grade dichloromethane (further purified by distillation before use) for 30 min under magnetic stirring at 4 °C. Then, the mixture was centrifuged (8500g, 10 min, 4 °C) and transferred to a 250 mL separatory funnel. The aqueous phase was then re-extracted twice as mentioned above. After centrifugation and separation, both organic extracts were dried over anhydrous sodium sulfate, filtered through glass wool, and concentrated to ~1 mL using a small Vigreux column at 45 °C. One microliter of each sample was then injected at 220 °C in the injection port (splitless 3 min) of a GC-FID and GC-MS. All analyses were performed in triplicate.

GC-FID Conditions. A Varian 3800 gas chromatograph equipped with a DB-Wax (J&W Scientific, Folsom, CA) capillary column (30 m × 0.25 mm i.d., 0.25 μ m film thickness) was used. The flow of hydrogen carrier gas was 1 mL/min. The oven was kept at 40 °C for 3 min, then programmed to 250 °C at 3 °C/min, and kept at 250 °C for 20 min. The FID detector was kept at 250 °C. The levels of the volatile compounds were expressed as 4-nonanol equivalents (assuming all the response factors to be 1). The concentrations are to be considered as relative data because recovery after extraction and calibration factors related to the standard were not determined.

GC-MS Conditions. A Varian 3800 gas chromatograph was used with the same DB-Wax capillary column as above. The flow of helium 6.0 carrier gas was 1 mL/min. The oven and injector temperature programs were as above. A Saturn ion-trap mass spectrometer was used. Mass spectra were recorded in electronic impact (EI) ionization mode.

Table 1. Levels of Soluble Solids (°Brix) of Different Shelf-Life Melons

F ^a	wild ^b		mid shelf life ^b		long shelf life ^c		
	mean	range	mean	range	mean	range	
SS	12.1	13.0 z	12.6–13.3	14.9 y	14.0–16.0	13.5 z	12.3–15.7

^a $F_{(0.05; 2; 42)} = 3.2$; $F_{(0.01; 2; 42)} = 5.2$; $F_{(0.001; 2; 42)} = 8.2$. ^b Three samples. ^c Nine samples.

The ion trap, the manifold, and the transfer line temperatures were set, respectively, at 150, 45, and 250 °C. Mass spectra were scanned in the range of m/z 29–350 amu at 1 s intervals. Identifications were carried out by comparison of linear retention indices and EI mass spectra with data from authentic compounds.

Statistical Analysis. Analyses of variance using the general linear model procedure and principal component analysis (PCA) were performed, respectively, using Statbox 6.3 (Grimmersoft) and Statlab 3.0 (SLP Infoware).

RESULTS AND DISCUSSION

Because sweetness and aroma are known to be the most important quality parameters of melon for the consumer, soluble solids and volatile constituents of 15 commercial melon cultivars differing by their storage life—wild, mid (MSL), and long shelf life (LSL)—were determined. Volatile compounds were isolated by direct dichloromethane extraction and analyzed by means of GC-FID and GC-MS. More than 40 compounds were identified by GC-MS, and 28 of them were quantified by GC-FID.

As shown in Figure 1, the soluble solids contents (°Brix) of samples ranged from 12.3 °Brix for Colt to 16 °Brix for Escrito. It is noteworthy that in all samples, the levels of soluble solids were >10 °Brix, which is the minimum recommended by the European Community for Charentais melons [*Off. J. Eur. Communities* 2001, L 214 (Aug 8)]. Globally, the levels of soluble solids for MSL melons were found to be significantly

Table 2. Concentrations^a of Volatile Compounds in Charentais Melon Cultivars

code	component ^b	RI ^c	wild			mid shelf life			long shelf life								
			Cezanne	Figaro	Nogaro	Anasta	Lunabel	Escrito	Stromboli	Person	Sirio	Aneto	Colt	Etna	Kousto	Dalton	Tobbia
A1	2-methylpropanol	1093	316 ± 36	454 ± 25	503 ± 92	411 ± 58	483 ± 39	754 ± 120	294 ± 21	129 ± 1	82 ± 11	305 ± 47	124 ± 3	220 ± 27	136 ± 2	213 ± 6	532 ± 50
A2	2-methylbutanol	1206	238 ± 6	733 ± 20	464 ± 50	540 ± 83	282 ± 5	790 ± 137	133 ± 23	56 ± 1	30 ± 2	81 ± 5	71 ± 4	71 ± 8	84 ± 1	27 ± 2	405 ± 25
A3	hexanol	1348	75 ± 5	174 ± 5	278 ± 20	217 ± 31	52 ± 6	232 ± 52	23 ± 1	8 ± 0	— ^d	16 ± 1	17 ± 3	20 ± 2	16 ± 0	—	88 ± 2
A4	(Z)-3-hexen-1-ol	1374	85 ± 3	206 ± 2	172 ± 10	437 ± 61	186 ± 5	497 ± 99	28 ± 1	—	23 ± 2	34 ± 5	5 ± 0	20 ± 2	8 ± 0	—	74 ± 2
A5	benzyl alcohol	1857	239 ± 27	1280 ± 40	838 ± 12	845 ± 80	484 ± 27	991 ± 178	951 ± 47	175 ± 6	53 ± 3	211 ± 34	100 ± 12	275 ± 33	182 ± 13	42 ± 6	531 ± 17
A6	2-phenylethanol	1890	46 ± 9	232 ± 8	127 ± 7	162 ± 13	81 ± 6	140 ± 24	90 ± 1	23 ± 3	65 ± 9	48 ± 13	42 ± 6	62 ± 10	102 ± 15	32 ± 3	241 ± 21
	sum of alcohols		999 ± 46	3079 ± 100	2383 ± 153	2613 ± 321	1569 ± 80	3404 ± 606	1518 ± 2	393 ± 7	255 ± 25	695 ± 105	358 ± 22	669 ± 54	526 ± 31	321 ± 19	1870 ± 117
C1	3-hydroxy-2-butanone	1271	518 ± 6	1942 ± 27	2102 ± 228	7268 ± 1220	1578 ± 105	10594 ± 1946	15 ± 1	12 ± 1	44 ± 2	620 ± 89	35 ± 3	21 ± 6	13 ± 0	15 ± 2	134 ± 4
C2	β-cyclocitral	1598	42 ± 6	58 ± 8	49 ± 1	55 ± 3	44 ± 5	61 ± 4	50 ± 4	37 ± 0	45 ± 11	49 ± 9	28 ± 2	38 ± 2	36 ± 10	42 ± 1	29 ± 1
C3	β-ionone	1937	18 ± 4	41 ± 2	95 ± 19	49 ± 4	77 ± 15	23 ± 3	64 ± 8	65 ± 7	24 ± 2	24 ± 4	12 ± 1	42 ± 9	6 ± 2	22 ± 2	18 ± 2
	sum of carbonyl compounds		578 ± 15	2040 ± 33	2246 ± 208	7373 ± 1221	1699 ± 109	10678 ± 1940	129 ± 5	115 ± 9	113 ± 11	693 ± 102	76 ± 0	101 ± 14	54 ± 12	79 ± 5	181 ± 6
E1	2-methylpropyl acetate	1022	2212 ± 112	2100 ± 228	1970 ± 205	1550 ± 252	2017 ± 105	1869 ± 356	959 ± 0	852 ± 36	2302 ± 107	2076 ± 121	1221 ± 52	1990 ± 173	2525 ± 22	2056 ± 152	1816 ± 79
E2	ethyl butyrate	1037	1935 ± 81	1454 ± 47	1899 ± 232	1716 ± 228	1824 ± 45	2222 ± 426	—	116 ± 2	55 ± 10	274 ± 11	199 ± 5	154 ± 15	105 ± 16	151 ± 18	249 ± 1
E3	ethyl 2-methylbutyrate	1052	719 ± 14	757 ± 12	324 ± 36	811 ± 97	1037 ± 15	1556 ± 249	—	11 ± 0	19 ± 1	95 ± 4	35 ± 1	28 ± 4	18 ± 5	29 ± 3	96 ± 4
E4	butyl acetate	1075	1439 ± 74	931 ± 6	2010 ± 133	1608 ± 235	1084 ± 32	1364 ± 274	110 ± 2	217 ± 5	440 ± 37	523 ± 42	244 ± 11	524 ± 50	407 ± 4	445 ± 44	396 ± 7
E5	2-methylbutyl acetate	1125	2767 ± 63	3398 ± 82	2677 ± 272	2669 ± 334	2735 ± 26	2548 ± 500	633 ± 13	616 ± 2	826 ± 53	1380 ± 122	687 ± 89	1179 ± 98	1593 ± 40	1365 ± 83	1125 ± 30
E6	pentyl acetate	1175	85 ± 3	90 ± 0	90 ± 7	60 ± 9	62 ± 1	77 ± 2	33 ± 3	35 ± 1	40 ± 4	56 ± 8	22 ± 3	76 ± 1	58 ± 2	56 ± 5	31 ± 3
E7	ethyl hexanoate	1232	224 ± 1	246 ± 2	212 ± 10	148 ± 12	171 ± 5	314 ± 20	—	8 ± 0	22 ± 0	45 ± 3	16 ± 0	4 ± 1	23 ± 1	23 ± 2	31 ± 2
E8	hexyl acetate	1277	1325 ± 7	971 ± 33	2510 ± 82	1210 ± 49	982 ± 11	2325 ± 427	162 ± 7	254 ± 0	341 ± 4	474 ± 46	246 ± 2	617 ± 13	534 ± 2	228 ± 153	337 ± 9
E9	(Z)-3-hexenyl acetate	1313	545 ± 14	94 ± 3	148 ± 4	566 ± 44	426 ± 4	86 ± 14	120 ± 7	26 ± 0	29 ± 2	29 ± 3	8 ± 1	314 ± 21	92 ± 0	196 ± 5	87 ± 1
E10	benzyl acetate	1754	825 ± 97	1423 ± 43	1643 ± 69	1137 ± 72	1898 ± 110	895 ± 148	1605 ± 75	1360 ± 78	1212 ± 39	1017 ± 203	284 ± 32	1439 ± 156	900 ± 83	960 ± 14	440 ± 19
E11	2-phenylethyl acetate	1804	94 ± 15	205 ± 5	163 ± 17	142 ± 1	188 ± 22	136 ± 18	166 ± 5	55 ± 7	128 ± 13	151 ± 44	92 ± 15	221 ± 47	416 ± 61	258 ± 4	193 ± 24
	sum of esters		12169 ± 452	11670 ± 367	13648 ± 894	11618 ± 1303	12422 ± 312	13392 ± 2391	3788 ± 72	3551 ± 46	5414 ± 166	6120 ± 604	3054 ± 207	6546 ± 258	6670 ± 221	5769 ± 460	4801 ± 186
S1	methyl 2-(methylthio)acetate	1402	11 ± 0	19 ± 1	10 ± 0	6 ± 0	14 ± 1	8 ± 0	—	—	—	—	—	—	—	—	—
S2	ethyl 2-(methylthio)acetate	1451	301 ± 16	327 ± 17	272 ± 14	221 ± 12	361 ± 19	481 ± 25	—	—	27 ± 1	42 ± 2	34 ± 2	—	29 ± 2	—	39 ± 1
S3	2-(methylthio)ethyl acetate	1503	543 ± 24	347 ± 15	920 ± 41	608 ± 27	833 ± 37	521 ± 23	—	95 ± 4	247 ± 11	88 ± 4	35 ± 2	—	122 ± 5	78 ± 3	102 ± 4
S4	methyl 3-(methylthio)propanoate	1510	9 ± 1	9 ± 1	—	—	8 ± 1	—	—	—	—	—	—	—	—	—	—
S5	2-(methylthio)ethanol	1515	57 ± 4	115 ± 9	170 ± 13	186 ± 14	116 ± 9	232 ± 18	5 ± 0	11 ± 1	—	9 ± 1	10 ± 1	6 ± 0	10 ± 1	—	34 ± 1
S6	ethyl 3-(methylthio)propanoate	1569	100 ± 5	66 ± 3	43 ± 2	39 ± 2	79 ± 4	54 ± 3	—	—	—	42 ± 2	14 ± 1	—	—	—	11 ± 0
S7	3-(methylthio)propyl acetate	1620	601 ± 19	322 ± 10	533 ± 17	394 ± 13	529 ± 17	202 ± 7	91 ± 3	130 ± 4	43 ± 1	123 ± 4	168 ± 5	144 ± 5	101 ± 3	192 ± 6	137 ± 3
S8	3-(methylthio)propanol	1714	43 ± 3	74 ± 4	80 ± 5	58 ± 3	47 ± 3	76 ± 5	19 ± 1	6 ± 0	38 ± 2	55 ± 3	27 ± 2	7 ± 0	—	—	43 ± 2
	sum of sulfur compounds		1664 ± 14	1280 ± 11	2032 ± 13	1516 ± 8	1988 ± 1	1576 ± 12	117 ± 2	246 ± 1	362 ± 10	362 ± 3	291 ± 5	160 ± 4	269 ± 1	281 ± 3	368 ± 0
	total volatiles		15410 ± 506	18069 ± 425	20309 ± 1263	23119 ± 2847	17677 ± 481	29050 ± 4943	5553 ± 68	4305 ± 62	6144 ± 209	7870 ± 814	3779 ± 232	7475 ± 297	7519 ± 263	6450 ± 472	7221 ± 309

^a Values expressed in $\mu\text{g}/\text{kg}$ of fresh weight are given as average \pm standard deviation ($n = 3$). ^b Identified by linear retention index and mass spectra of authentic standards. ^c Linear retention index based on a series of n -hydrocarbons. ^d Concentration $< 5 \mu\text{g}/\text{kg}$.

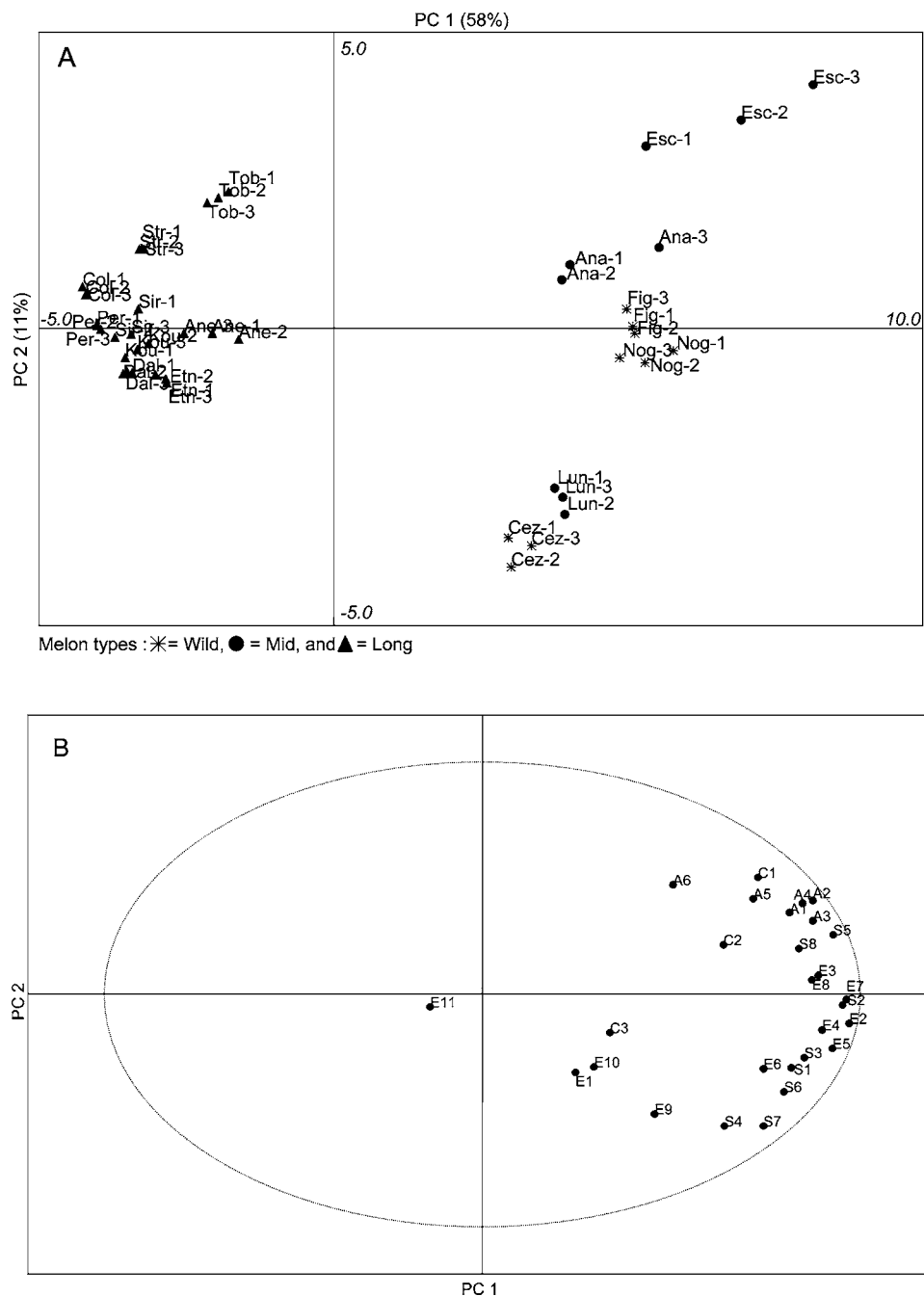


Figure 2. Results from PCA analysis: (A) projection of the samples (Cez, Cézanne; Fig, Figaro; Nog, Nogararo; Ana, Anasta; Lun, Lunabel; Esc, Escrito; Str, Stromboli; Per, Person; Sir, Sirio; Ane, Aneto; Colt, Colt; Etn, Etna; Kou, Kousto; Dal, Dalton; Tob, Tobbia); (B) distribution of variables (for codes, see Table 2).

higher than in others, whereas no significant difference was observed between wild and LSL melons (Table 1).

Table 2 reports the mean concentrations of the 28 components in the 15 melon cultivars. Except for Anasta and Escrito, for which the levels of 3-hydroxy-2-butanone were found to be very high, esters were the main compounds identified in the samples, ranging from 46% (Escrito) to 89% (Dalton) of the total volatile compounds quantified. Among them, 2-methylpropyl acetate, ethyl butyrate, ethyl 2-methylbutyrate, butyl acetate, 2-methylbutyl acetate, benzyl acetate, and hexyl acetate were the most abundant. Wyllie et al. (14) and Bauchot et al. (19) also reported these compounds to be predominant in melon, respectively, in Makdimon (*C. melo* var. *reticulatus*) and Védrantais (*C. melo* var. *cantalupensis*) cultivars. Nevertheless, except for the levels of 2-methylpropyl, benzyl, and 2-phenylethyl acetates, a con-

siderable reduction in the levels of esters was observed in the LSL cultivars. The total of esters was 43–77% lower in LSL melons than in others. The main differences were observed for compounds with low odor values such as ethyl 2-methylbutyrate (0.006 $\mu\text{g}/\text{kg}$), ethyl butyrate (1 $\mu\text{g}/\text{kg}$), ethyl hexanoate (1 $\mu\text{g}/\text{kg}$), hexyl acetate (2 $\mu\text{g}/\text{kg}$), and butyl acetate (2 $\mu\text{g}/\text{kg}$) (22). These results are similar to those reported by Bauchot et al. (19) in transformed Charentais melons with an ACC oxidase antisense gene.

Eight sulfur compounds were detected in our samples including six thioether esters [methyl 2-(methylthio)acetate, ethyl 2-(methylthio)acetate, 2-(methylthio)ethyl acetate, methyl 3-(methylthio)propanoate, ethyl 3-(methylthio)propanoate, and 3-(methylthio)propyl acetate] and two thioether alcohols [2-(methylthio)ethanol and 3-(methylthio)propanol]. Thioether

Table 3. Concentrations ($\mu\text{g}/\text{kg}$) of Volatile Compounds in Shelf-Life Type of Charentais Melon

component	F^a	wild ^b			mid shelf life ^c			long shelf life ^d		
		mean	SD	range	mean	SD	range	mean	SD	range
2-methylpropanol	21.5	424y	98	282–595	550y	171	353–877	226z	135	70–582
2-methylbutanol	32.3	478y	216	234–752	537y	234	278–913	106z	112	26–430
hexanol	34.9	176y	88	71–297	167y	92	48–273	21z	25	1–91
(Z)-3-hexen-1-ol	78.7	155y	54	82–208	373x	154	182–589	22z	22	0–76
benzyl alcohol	13.6	786y	453	214–1320	773y	246	466–1166	280z	280	37–998
2-phenylethanol	2.8	135	81	39–240	128	39	76–178	78	64	20–262
sum of alcohols	28.9	2154y	922	956–3179	2528y	869	1507–3982	734z	551	229–1987
3-hydroxy-2-butanone	41.0	1521z	764	514–2329	6480y	4112	1479–12498	101z	192	11–709
β -cyclocitral	10.8	50y	9	36–66	53y	8	38–65	39z	9	25–58
β -ionone	2.3	51	36	15–114	50	25	21–91	31	21	4–73
sum of carbonyl compounds	41.6	1621z	795	566–2454	6583y	4097	1587–12577	171z	193	42–795
2-methylpropyl acetate	1.7	2094	194	1765–2338	1812	305	1400–2138	1755	582	816–2547
ethyl butyrate	399.5	1763y	263	1407–2131	1920y	335	1584–2615	145z	85	0–285
ethyl 2-methylbutyrate	131.2	600y	209	288–769	1135x	357	749–1778	37z	34	0–100
butyl acetate	82.4	1460y	473	926–2143	1352y	291	1052–1879	367z	141	108–581
2-methylbutyl acetate	136.7	2947y	370	2406–3480	2651y	312	2011–3054	1045z	356	598–1632
pentyl acetate	34.2	89y	4	82–97	67y	9	53–80	45z	17	19–77
ethyl hexanoate	161.0	227y	16	202–247	211y	79	140–335	19z	13	0–47
hexyl acetate	40.9	1602y	700	938–2592	1506y	659	975–2743	355z	155	75–625
(Z)-3-hexenyl acetate	11.3	262y	213	92–559	360y	215	71–617	100z	96	8–338
benzyl acetate	2.3	1297	372	746–1713	1310	464	757–2024	1024	433	252–1680
2-phenylethyl acetate	0.7	154	50	82–210	156	28	117–213	187	105	48–477
sum of esters	169.1	12496y	1038	11303–14542	12477y	1572	10842–15583	5079z	1319	2847–6882
methyl 2-(methylthio)acetate	79.4	13x	5	10–20	9y	4	6–15	1z	1	0–4
ethyl 2-(methylthio)acetate	185.0	300y	28	256–341	355y	114	208–502	19z	18	0–43
2-(methylthio)ethyl acetate	82.9	603y	253	337–967	654y	142	505–876	85z	72	0–260
methyl 3-(methylthio)propanoate	33.0	7x	3	3–11	5y	3	2–9	2z	1	0–3
2-(methylthio)ethanol	105.1	114y	50	53–183	178x	52	108–250	10z	9	4–35
ethyl 3-(methylthio)propanoate	59.0	70y	25	41–105	57y	18	37–83	8z	14	0–44
3-(methylthio)propyl acetate	65.8	485x	127	311–619	375y	143	195–545	125z	42	42–198
3-(methylthio)propanol	29.9	66y	18	41–86	61y	13	45–81	22z	18	3–58
sum of sulfur compounds	310.8	1658y	326	1268–2046	1693y	223	1506–1989	273z	85	115–373
total volatiles	139.7	17929y	2240	15036–21577	23281x	5697	17230–33732	6257z	1438	3544–8684

^a $F_{(0.05; 2; 42)} = 3.2$; $F_{(0.01; 2; 42)} = 5.2$; $F_{(0.001; 2; 42)} = 8.2$. ^b Three samples. ^c Nine samples. Values with different letters are significantly different.

esters were both qualitatively and quantitatively predominant and represented 79–97% of the total isolated sulfur compounds. As previously reported by Wyllie and Leach (1), 3-(methylthio)propyl acetate and 2-(methylthio)ethyl acetate were the dominant sulfur compounds in all of the cultivars. Ethyl 2-(methylthio)acetate was also found as a dominant compound for wild and mid shelf life cultivars but was frequently absent, or present at low levels, in long shelf life cultivars. The flavor impact of sulfur compounds on the aroma of melon (1, 8, 12, 17, 18) or in many fruits such as Asian pear (22), apple (23), pineapple (24, 25), or strawberry (26) is well established. In our study, marked quantitative differences were observed between the various cultivars. A considerable reduction in the levels of sulfur compounds was observed in the LSL cultivars. The total levels of sulfur compounds were 4–17-fold higher in wild or mid shelf life melons than in long shelf life cultivars. The main differences between LSL melons and the others were observed for thioesters with low odor values, such as ethyl 3-(methylthio)propanoate (7 $\mu\text{g}/\text{kg}$), 3-(methylthio)propyl acetate (30 $\mu\text{g}/\text{kg}$), and ethyl 2-(methylthio)acetate (25 $\mu\text{g}/\text{kg}$) which would have a major impact on the musky note of melon aroma (1, 12, 17, 18).

Besides esters and sulfur compounds, six alcohols and three carbonyl compounds were identified in our extracts. Among alcohols, two C_6 compounds were isolated. The limited number of these compounds identified in this study, and the lack of C_9 compounds, are mainly due to the isolation method chosen (enzyme deactivation with saturated NaCl solution during homogenization) (27–29), inhibiting their formation from lipids during the crushing of the fruits. Thus, their levels can be

considered as representative of the endogenous levels of the fruit. Generally, levels of alcohols were higher in wild or MSL melons than in LSL, except for 2-phenylethanol in Tobbia. Among carbonyl compounds, levels of 3-hydroxy-2-butanone (acetoin) were generally higher in wild or MSL melons, particularly in Anasta and Escrito.

To summarize graphically the changes in the volatile concentrations in the different cultivars, a principal component analysis (PCA) was performed using 45 samples (15 cultivars \times 3 replications) and 28 variables (Figure 2). To compare differences between wild, MSL, and LSL cultivars, data were also analyzed by one-way analysis of variance using the GLM procedure. Results are given in Table 3.

As shown in Figure 2A, 69% of the total variance was explained by the two first axes. The first axis (58% of the variance explained) mainly discriminates the LSL melons from the others, whereas the second axis (11% of the variance explained) mainly discriminates Escrito from Cézanne and Lunabel. The distribution of variables is shown in Figure 2B. Except 4 variables from the 28 (E1, E10, E11, and C3), most of the volatile compounds are well correlated on the first two axes. Wild and MSL melons, positively located on the first axis, are particularly characterized by greater contents of 2-methylpropanol (A1), 2-methylbutanol (A2), hexanol (A3), (Z)-3-hexen-1-ol (A4), ethyl butyrate (E2), ethyl 2-methylbutyrate (E3), butyl acetate (E4), 2-methylbutyl acetate (E5), hexyl acetate (E8), methyl 2-(methylthio)acetate (S1), ethyl 2-(methylthio)acetate (S2), 2-(methylthio)ethyl acetate (S3), 2-(methylthio)ethanol (S5), ethyl 3-(methylthio)propanoate (S6),

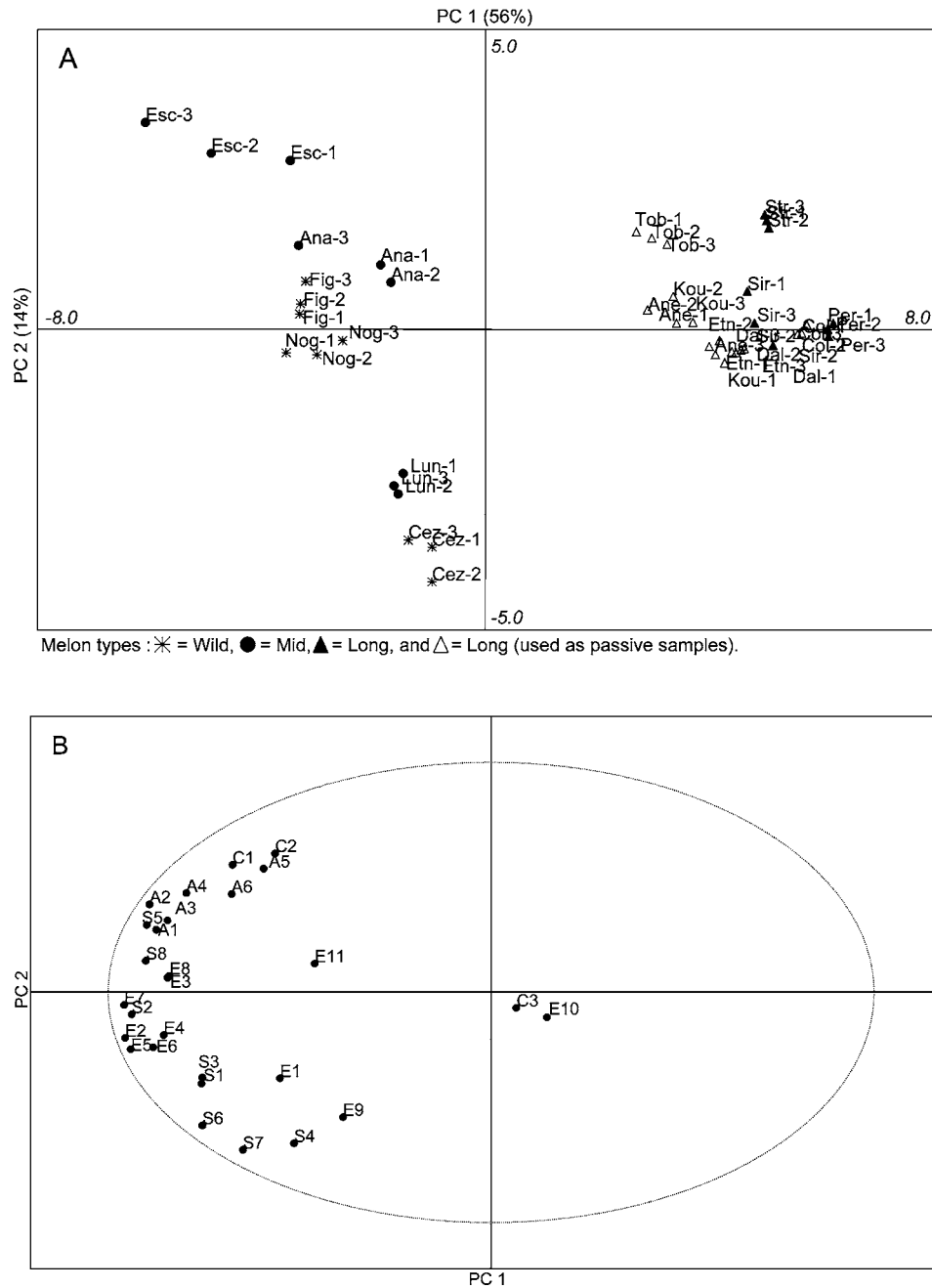


Figure 3. Results from PCA analysis: (A) projection of the samples (Cez, Cézanne; Fig, Figaro; Nog, Nogar; Ana, Anasta; Lun, Lunabel; Esc, Escrito; Str, Stromboli; Per, Person; Sir, Sirio; Ane, Aneto; Colt, Colt; Etn, Etna; Kou, Kousto; Dal, Dalton; Tob, Tobbia); (B) distribution of variables (for codes, see Table 2).

and 3-(methylthio)propanol (S8). Cézanne and Lunabel, negatively located on the second axis, are mainly discriminated from Escrito by a greater content of (*Z*)-3-hexenyl acetate (E9), methyl 3-(methylthio)propanoate (S4), and 3-(methylthio)propyl acetate (S7) and a lower content of 2-phenylethanol (A6) and 3-hydroxy-2-butanone (C1). As shown in Table 3, previous observations were confirmed by analysis of variance. Except for 5 volatiles (2-phenylethanol, β -ionone, 2-methylpropyl acetate, benzyl acetate, and 2-phenylethyl acetate) from the 28, all of the compounds were highly significantly different ($p < 0.001$). The highest amounts of volatile compounds were observed for wild and MSL melons, and generally their levels were found to be similar, except for 3-hydroxy-2-butanone. Most of the volatiles showing the highest *F* values were esters and sulfur compounds with low odor thresholds [ethyl butyrate, ethyl 2-(methylthio)acetate, ethyl hexanoate, 2-methylbutyl acetate,

ethyl 2-methylbutyrate, butyl acetate, 3-(methylthio)propyl acetate, and ethyl 3-(methylthio)propanoate].

Because LSL melons had been obtained from two different locations, a supplementary PCA, using melons from the second location as unknown samples, was carried out to evaluate if a location effect on volatile constituents could be noted (Figure 3). PCA was performed using 27 active samples (9 cultivars from Ctifl orchards \times 3 replications), 28 variables, and 18 passive samples (6 cultivars from Aprel orchards \times 3 replications). As seen in Figure 3, the results showing the differentiation of LSL melons from the others cultivars were very similar to those observed previously. Moreover, no location effect was noted because LSL melons, used as passive samples, were strongly correlated with the LSL active samples.

These results clearly demonstrate that volatile compounds discriminate the long shelf life melons from the others. Results

also indicate that wild and mid shelf life melons are very close from an aroma composition point of view. A considerable reduction in total volatile composition was observed for the LSL melon type, especially esters and thioesters. Although in this study no sensory analysis was carried out, the low levels of esters and thioesters certainly explain why informal evaluation of the aroma of the melons, by the laboratory staff, have shown that all long shelf life melons had less aroma than the others. Because aroma development in melon is closely associated with ethylene biosynthesis, and esters and thioesters are, or are thought to be, amino acid derivatives (7, 13, 19, 30), C₂H₄ production and amino acid profiles of different shelf life types of Charentais melons will be the subject of further investigations.

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