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Postharvest Changes in Physicochemical Properties and Volatile Constituents of Apricot (*Prunus armeniaca* L.). Characterization of 28 Cultivars

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To investigate the changes in physicochemical properties and volatile constituents in apricot during postharvest ripening, the volatile compounds of 28 apricot cultivars were investigated by means of liquid−liquid microextraction (LLME), GC-FID, and GC-MS. Fruits picked at their optimal harvestable stage of maturity were analyzed at harvest and after ripening at 20 °C under controlled conditions. Soluble solids (SS), titratable acidity (TA), levels of sugars (saccharose, fructose, and glucose), and organic acids (citric and malic acids) were also determined. Thirty-three volatile compounds, including 6 esters, 5 C_6 compounds, 4 alcohols, 3 carbonyl compounds, 6 terpenic compounds, and 9 lactones, were identified. Changes in the levels of volatiles have been found to increase greatly during postharvest ripening in comparison to the modifications observed for the other physicochemical characteristics. The discrimination of the 28 apricot cultivars into four distinguishable aroma groups was achieved by statistical treatment of the data including ANOVA, principal component, and cluster analyses.

KEYWORDS: Apricot; volatile compounds; aroma; postharvest; ripening

INTRODUCTION

Contrary to what its scientific name suggests, the apricot (*Prunus armeniaca* L.) does not originate from Armenia, but from China, and was introduced in Europe at the beginning of the Roman era (*1*). Apricots are members of the Rosaceae family, along with peach, pear, strawberry, apple, and cherry. They belong to the subfamily Prunoideae and the subgenus *Prunus* of the genus *Prunus*. Botanically, apricots are drupes or "stone fruits"—like peaches, plums, cherries, and mangoes—in which an outer fleshy part (exocarp and mesocarp) surrounds a hard stone (endocarp) with a seed inside. With a world production of ~2.8 Mt in 2005 (FAOSTAT. 2005), apricot is the third most widely grown stone fruit crop. The production is mainly located in the Mediterranean countries which collectively account for 40% of global production. With ~13% of the world production, Turkey, with a production mainly located in the province of Malatya, is the main producer and provides ~85% of the world's dried apricot and apricot kernels. The other main Mediterranean producers are Italy (8%), France (6%), Spain (5%), Algeria (4%), Morocco (3%), and Greece (3%). In the United States, apricot production was about 80000 t in 2005 (~3%), over 90% of which was grown in California.

Harvesting apricot at the proper stage of maturity is essential for its quality. Nevertheless, for commercial reasons (handling, long-distance transport, storage, etc.), apricot is generally harvested at a stage of maturity hardly compatible with rapid consumption. This harvestable maturity stage does not necessarily mean that the product has the maturity requirements for an immediate use, but rather that the fruit "has reached a sufficient stage of development that after harvesting and postharvest handling, its quality will be at least the minimum acceptable to the ultimate consumer" (*2*). Nevertheless, the latter often complains about the low quality of apricot, and two previous surveys have cited the lack of both aroma and sugar in fresh apricots as the main reason for dissatisfaction among consumers (*3*, *4*). However, when they were asked how they kept apricots at home, it appeared that ~20% of them did not allow the fruits to ripen at ambient temperature but rather immediately placed them in the refrigerator (*3*). The formation of the volatile compounds in fruits is a dynamic process, and generally the typical flavor of most of them is not present at harvest but develops after a ripening process. In contrast to other fruits such as apple, strawberry, or peach, the flavor of apricot, although strong and typical, has hardly been investigated (*1*, *5*−*20*). If variability in aroma compounds has been reported to depend on cultivars (*8*, *10*, *11*, *13*, *15*), maturity (*16*), or processing and storage conditions (*7*, *11*, *12*, *17*), the evolution of apricot volatiles during postharvest maturation has, to our knowledge, not been studied. Given the rather low quality level of the apricots that are available to the consumer, and also because the latter is generally confused by the diversity of the marketed varieties available, the aim of this work was (i) to investigate the changes in physicochemical properties and volatile constituents of 28 apricot cultivars during postharvest ripening under controlled conditions and (ii) to compare the levels of volatiles of the different cultivars in order, initially,

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Table 1. Physicochemical Characteristics of the 28 Apricot Cultivars

no.	cultivar	skin color at harvest[a]	harvest date	days to ripen[b]	firmness (ID_{10}) UR[c]	firmness (ID_{10}) R[d]	rate of softening (ID_{10} per day)	titratable acidity (mequiv/100 g) UR	titratable acidity (mequiv/100 g) R	soluble solids (%Brix) UR	soluble solids (%Brix) R	saccharose (g/100 g) UR	saccharose (g/100 g) R	glucose (g/100 g) UR	glucose (g/100 g) R	fructose (g/100 g) UR	fructose (g/100 g) R	citric acid (g/100 g) UR	citric acid (g/100 g) R	malic acid (g/100 g) UR	malic acid (g/100 g) R
1	Early Blush Rutbhart (cov)[e]	4	May 29	2	68	26	21.0	39.5	38.8	11.3	12.1	5.3	6.0	1.0	1.0	0.1	0.1	0.1	0.1	2.8	2.8
2	Spring Blush EA3126TH (cov)	7	May 29	2	74	37	18.5	26.7	25.1	13.0	13.3	5.6	6.1	2.3	2.2	0.7	0.5	1.5	1.5	0.5	0.5
3	PSB 28-58	7	May 29	2	68	35	16.5	32.5	31.3	11.1	11.7	5.4	5.9	1.2	1.3	0.3	0.2	2.1	2.2	0.4	0.4
4	Earlycot 1	5	May 29	2	63	45	9.0	32.8	30.0	13.1	14.6	7.0	7.7	0.6	0.8	0.1	0.1	1.7	1.8	0.7	0.6
5	Flodea (cov)	8	June 5	3	78	43	11.7	27.4	32.1	12.8	14.3	6.5	6.9	1.0	1.5	0.5	0.5	2.0	2.2	0.6	0.6
6	Sylred (cov)	7	June 5	3	73	47	8.7	30.8	31.9	13.3	13.8	6.2	6.2	1.5	1.6	0.8	1.0	2.2	2.1	0.5	0.4
7	Soledane (cov)	4	June 5	3	72	43	9.7	29.6	31.7	11.4	12.3	6.0	6.2	0.9	1.0	0.3	0.2	1.6	1.6	0.9	0.8
8	Red Sylver	8	June 9	3	71	45	8.7	21.5	19.5	13.8	14.9	7.0	7.3	1.7	1.7	0.8	0.9	1.2	1.2	0.5	0.5
9	Lilly Cot (cov)	7	June 9	5	81	49	6.4	34.0	35.2	15.1	16.0	9.0	8.9	0.7	1.1	0.1	0.3	2.2	2.4	0.5	0.4
10	Tom Cot Toyaco (cov)	8	June 12	7	72	35	5.3	33.6	30.1	16.7	17.4	7.9	8.4	1.7	2.5	0.9	1.1	1.9	1.8	0.9	0.7
11	Sweet Cot Toyuda (cov)	6	June 12	4	69	36	8.3	30.5	29.1	12.7	14.2	6.3	7.1	1.4	1.6	0.5	0.5	0.6	0.6	1.7	1.6
12	Latica (cov)	8	June 14	5	77	43	6.8	29.5	28.5	11.5	12.1	6.0	6.3	1.1	1.3	0.3	0.3	1.6	1.6	0.6	0.6
13	Perle Cot (cov)	8	June 14	5	81	44	7.4	27.4	24.9	13.6	15.5	7.2	7.7	1.3	2.0	0.7	0.8	0.7	0.8	1.6	1.5
14	Mascot	8	June 14	5	71	46	5.0	29.8	27.2	13.2	15.1	5.9	6.7	1.4	1.8	0.5	0.5	1.4	1.3	0.5	0.4
15	Robada (cov)	7	June 14	5	73	45	5.6	23.9	22.0	11.8	13.2	7.0	8.3	1.6	1.8	0.4	0.4	1.7	1.6	0.4	0.4
16	Orangered Bhart (cov)	7	June 14	5	83	34	9.8	14.4	14.9	11.8	13.3	6.5	7.2	1.5	1.8	0.4	0.5	0.8	0.9	0.4	0.4
17	Goldstrike Toyesi (cov)	6	June 14	5	77	33	8.8	33.0	29.4	13.9	14.3	5.6	6.7	1.6	1.6	0.6	0.6	1.6	1.6	0.9	0.7
18	Bigred	8	June 16	10	79	44	3.5	27.0	25.9	13.8	15.3	7.6	7.6	1.7	2.1	0.5	0.6	1.4	1.5	0.7	0.6
19	Goldrich	7	June 21	5	69	46	4.6	36.0	33.3	12.7	13.2	6.0	5.9	1.4	1.7	0.5	0.6	1.9	1.8	0.9	0.7
20	Flavor Cot Bayoto (cov)	8	June 23	6	76	45	5.2	23.1	24.6	14.4	15.5	7.1	7.1	2.3	2.4	0.7	0.8	0.2	0.3	1.6	1.4
21	Helor	7	June 23	6	75	50	4.2	14.0	17.7	13.3	14.4	5.5	5.5	3.1	3.4	1.0	1.0	1.0	1.0	0.2	0.2
22	Kioto (cov)	8	June 26	7	72	45	3.9	33.3	33.1	12.1	13.8	5.4	6.2	1.6	2.0	0.7	0.8	2.1	2.1	0.4	0.4
23	Hargrand	7	July 3	4	69	40	7.3	19.0	16.8	14.2	15.9	6.7	8.8	1.4	1.5	0.5	0.5	1.0	0.9	0.6	0.6
24	Royal Roussillon	5	July 3	4	71	45	6.5	20.7	20.2	14.0	14.4	4.8	6.2	3.2	2.8	0.8	0.6	1.2	1.3	0.5	0.5
25	Frisson (cov)	4	July 20	3	76	49	9.0	21.5	20.1	15.5	16.2	6.7	7.6	2.9	2.8	0.6	0.6	1.3	1.3	0.7	0.7
26	Bergeron	4	July 20	4	65	54	2.8	22.7	20.7	10.5	10.6	4.8	4.9	1.7	1.6	0.4	0.3	0.4	0.4	1.3	1.4
27	Vertige (cov)	7	July 20	3	67	45	7.3	13.5	14.3	15.3	15.7	8.2	8.1	1.9	1.7	0.7	0.6	0.7	0.8	0.6	0.6
28	Tardif de Tain (cov)	5	July 20	4	67	53	3.5	18.3	16.6	12.0	12.5	5.0	5.6	2.1	2.1	0.5	0.6	0.6	0.6	1.0	0.9

[a] According to the Ctifl apricot color code. [b] Days to ripen to a firmness of 55 ID_{10} or less. [c] Unripened apricots. [d] Apricot ripened at 20 °C. [e] (cov), varietal denomination.

Table 2. Concentrations[a] of Volatiles in the 28 Apricot Cultivars[b] at Harvest and after Ripening

compound	RI[c]	ID[d]	stage[e]	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27
Esters																														
butyl acetate	1075	A	UR	224	–[f]	1	97	16	11	6	–	8	109	110	–	1	103	–	tr[g]	1	tr	6	164	–	2	10	29	2	113	5
			R	1922	–	6	203	54	69	42	–	32	692	307	–	3	880	–	3	333	2	575	2688	–	52	81	208	35	301	74
3-methylbutyl acetate	1115	A	UR	1	–	1	tr	–	tr	–	1	1	–	1	1	1	1	1	1	1	–	–	1	tr	6	tr	tr	tr	tr	tr
			R	7	–	1	tr	–	1	–	1	1	–	1	1	1	1	1	1	2	–	–	1	3	tr	tr	1	1	2	2
pentyl acetate	1152	A	UR	2	–	2	3	–	tr	–	–	1	3	2	–	–	4	–	–	–	–	tr	6	tr	1	1	2	6	8	1
			R	10	–	3	4	–	tr	–	–	1	12	5	–	–	11	–	–	–	–	3	47	tr	3	3	7	1	8	3
hexyl acetate	1275	A	UR	12	1	1	15	3	tr	6	–	9	35	22	–	–	41	–	tr	1	–	1	73	–	1	5	12	1	56	3
			R	54	2	3	32	5	3	19	–	23	121	63	–	–	139	–	2	4	–	16	578	–	11	48	75	27	73	50
(*Z*)-3-hexenyl acetate	1321	A	UR	6	1	2	7	2	–	2	–	1	7	4	–	–	11	–	–	–	–	2	3	tr	2	3	2	3	13	3
			R	5	2	2	5	1	–	3	–	1	8	1	–	–	20	–	–	–	–	1	5	tr	1	2	6	2	8	2
(*E*)-2-hexenyl acetate	1338	A	UR	10	2	1	1	–	–	–	–	–	–	2	–	–	5	–	–	–	–	–	–	–	–	–	1	1	–	3
			R	3	2	2	3	–	–	–	–	–	–	1	–	–	3	–	–	–	–	–	–	–	–	–	4	1	–	1
total			UR	255	4	8	123	21	11	15	1	19	153	142	1	1	164	1	1	3	tr	9	247	1	11	19	47	12	190	14
			R	2002	6	15	246	61	73	65	1	58	833	378	1	4	1054	1	7	338	2	594	3319	4	66	135	300	67	392	132
relative %			UR	27	1	2	19	6	3	5	<1	4	26	26	<1	1	33	1	1	1	<1	7	27	1	15	8	17	6	60	8
			R	58	1	2	36	8	7	10	<1	5	42	34	<1	1	66	<1	1	33	<1	58	68	1	23	27	32	9	46	29
C_6 Compounds																														
hexanal	1080	A	UR	11	9	15	32	4	5	5	3	–	9	5	–	4	7	2	2	7	2	3	10	–	3	6	2	5	3	5
			R	11	6	23	16	5	4	7	3	–	5	6	–	3	2	2	3	7	2	3	10	–	1	6	3	7	3	4
(*E*)-2-hexenal	1220	A	UR	123	69	120	283	57	48	75	19	28	84	47	8	61	63	11	9	82	6	12	97	–	–	55	15	76	29	68
			R	133	59	153	130	42	24	58	11	10	47	56	8	18	17	9	13	73	4	7	47	–	–	43	25	117	33	69
hexanol	1355	A	UR	18	6	10	4	3	4	3	3	7	15	6	3	6	6	2	1	6	1	1	22	3	1	3	3	2	5	2
			R	11	5	12	10	3	4	5	5	11	56	14	3	4	16	1	4	2	5	5	174	16	4	11	15	18	13	11
(*Z*)-3-hexen-1-ol	1386	A	UR	10	4	16	5	8	4	1	2	–	8	2	–	–	4	1	tr	5	–	–	–	–	–	1	tr	2	1	1
			R	4	3	10	3	3	1	1	1	–	4	1	–	–	2	tr	1	1	–	–	–	–	–	1	1	3	2	1
(*E*)-2-hexen-1-ol	1409	A	UR	70	12	23	4	5	8	2	2	–	7	5	–	–	3	2	1	13	–	–	–	–	–	1	tr	2	2	1
			R	20	9	21	4	2	4	2	2	–	3	1	–	–	tr	tr	2	1	–	–	–	–	–	tr	1	4	2	1
total			UR	232	100	183	328	77	69	85	29	35	124	66	10	71	83	17	12	113	9	16	129	3	4	67	20	86	40	96
			R	179	83	218	163	55	36	74	22	22	115	78	11	25	38	13	22	84	10	14	232	16	5	62	44	148	53	87
relative %			UR	24	18	45	49	20	21	25	8	7	21	12	4	27	17	10	5	45	7	12	14	2	5	27	7	41	13	55
			R	5	11	23	23	8	4	11	4	2	6	7	2	3	2	3	3	8	2	1	5	4	2	12	5	19	6	19
Alcohols																														
butanol	1125	A	UR	10	–	1	17	2	6	3	3	4	10	4	1	3	3	tr	1	1	1	1	8	tr	tr	2	1	1	9	1
			R	88	–	2	40	5	23	8	3	6	51	14	4	14	12	1	2	34	9	20	69	28	4	8	5	25	12	7
2-methylbutanol	1208	A	UR	3	–	1	1	–	1	–	–	–	–	–	–	–	–	–	–	tr	–	–	–	–	–	–	–	–	–	–
			R	18	–	1	2	–	3	–	–	–	–	–	–	–	–	–	–	9	–	–	–	–	–	–	–	–	–	–
6-methyl-5-hept-en-2-ol	1575	A	UR	5	5	7	–	7	5	tr	5	5	7	7	7	7	9	5	4	2	2	3	6	3	3	–	–	–	–	–
			R	10	6	7	–	10	8	1	5	5	7	7	9	9	10	6	8	2	5	4	7	3	5	–	–	–	–	–
benzyl alcohol	1880	A	UR	4	2	5	4	–	–	–	4	–	4	–	3	2	5	3	2	5	3	2	16	–	1	10	3	–	–	–
			R	7	5	4	5	–	–	–	3	–	13	–	3	3	12	2	2	4	5	6	17	–	2	3	2	–	–	–
total			UR	22	5	9	18	9	12	3	8	9	17	11	8	10	11	5	5	3	3	4	15	3	4	2	1	1	9	1
			R	123	6	10	42	15	33	9	8	11	58	21	13	22	22	7	9	45	14	25	76	31	9	8	5	25	12	7
relative %			UR	2	1	2	3	2	3	1	2	2	3	2	3	4	2	3	2	1	3	3	2	2	5	1	<1	<1	3	1
			R	4	1	1	6	2	3	1	1	1	3	2	3	3	1	1	1	4	3	2	2	7	3	2	1	3	1	2
Carbonyl Compounds																														
2-octanone	1287	A	UR	tr	6	6	–	7	6	7	1	6	1	9	7	10	6	6	6	tr	1	tr	9	6	7	7	6	8	9	7
			R	1	6	6	–	8	6	7	2	7	2	11	6	26	6	6	6	tr	2	1	14	7	8	13	12	9	9	8
6-methyl-5-hept-en-2-one	1341	A	UR	6	1	5	1	1	1	1	1	1	1	2	1	1	1	1	1	1	1	tr	1	1	1	2	1	1	–	1
			R	9	10	2	2	2	1	1	1	1	1	2	1	1	1	1	1	1	1	1	2	1	1	5	1	1	–	1
benzaldehyde	1520	A	UR	18	20	11	92	13	12	27	12	9	116	95	13	14	19	11	19	73	20	27	248	13	6	61	77	22	5	16
			R	23	31	6	93	17	12	47	15	15	311	205	22	21	33	38	44	128	29	34	860	17	16	123	96	33	9	25
total			UR	23	27	22	94	22	18	35	14	17	118	106	21	25	26	18	27	74	22	28	258	20	14	70	84	31	14	24
			R	32	47	14	94	28	18	54	18	23	314	218	30	48	40	45	52	129	31	36	877	24	25	140	109	43	18	34
relative %			UR	2	5	5	14	6	5	10	4	3	20	20	8	10	5	11	12	29	17	21	28	14	17	29	30	15	4	14
			R	1	6	1	14	4	2	8	3	2	16	20	6	6	3	10	7	13	7	3	18	6	9	28	12	6	2	7
Terpenic Compounds																														
linalool	1531	A	UR	72	226	31	34	34	29	51	100	153	65	79	109	41	76	59	112	27	37	37	113	56	22	32	20	17	5	7
			R	80	256	43	36	50	40	64	123	189	79	61	127	65	80	107	185	26	39	33	61	39	29	23	26	21	8	8
β-cyclocitral	1603	A	UR	1	1	1	–	–	–	–	–	–	2	–	1	1	2	1	1	–	2	1	4	1	2	–	–	–	–	–
			R	1	2	1	–	–	–	–	–	–	1	–	2	1	3	1	1	tr	1	1	1	tr	3	–	–	–	–	–
α-terpineol	1696	A	UR	19	56	9	11	12	11	17	22	40	23	21	30	12	21	16	22	–	12	9	34	16	6	10	6	6	3	4
			R	22	63	11	12	16	15	20	28	53	27	19	34	18	23	30	48	–	12	9	20	9	9	8	9	6	3	3
geraniol	1865	A	UR	14	34	6	10	8	6	11	12	25	16	13	24	8	15	13	11	7	9	1	24	15	6	12	8	–	–	–
			R	16	39	7	12	10	11	11	15	31	19	13	26	12	–	23	22	9	11	5	16	11	11	6	9	–	–	–
linalool hydrate	1996	B	UR	4	27	2	1	2	3	3	10	12	7	5	16	9	7	10	10	–	–	–	–	–	–	–	–	–	–	–
			R	3	20	1	1	3	7	5	7	12	6	4	13	4	8	12	13	–	–	–	–	–	–	–	–	–	–	–
dihydroactinidiolide	2291	B	UR	11	10	9	2	8	2	1	65	11	13	35	12	21	66	18	10	4	15	6	37	7	2	2	11	2	4	2
			R	15	12	10	3	12	6	1	80	10	23	51	11	26	79	25	22	7	19	14	28	2	6	1	11	5	7	5
total			UR	120	353	57	58	63	52	81	210	240	126	153	193	92	188	118	165	37	74	54	213	96	39	56	45	26	12	12
			R	137	391	73	64	91	78	102	254	295	155	149	214	126	193	198	290	43	63	62	127	62	57	39	55	33	18	16
relative %			UR	13	62	14	9	17	15	24	57	47	21	29	76	36	38	68	73	15	58	41	23	64	50	23	16	12	4	7
			R	4	51	8	9	13	8	15	40	24	8	13	42	17	12	42	42	4	18	6	3	14	20	8	6	4	2	4
Lactones																														
γ-hexalactone	1703	A	UR	36	24	20	9	36	38	37	17	33	29	16	6	17	10	4	4	7	5	5	13	8	3	11	14	11	11	6
			R	108	46	85	24	147	221	158	51	223	337	71	136	161	134	99	88	135	218	66	95	185	79	60	113	55	92	32
γ-octalactone	1916	A	UR	41	14	17	8	21	19	19	17	22	12	15	5	7	4	2	3	6	3	5	16	6	1	6	20	10	15	5
			R	79	19	69	15	45	46	36	29	67	52	43	25	37	16	13	31	53	28	35	58	22	12	13	65	41	36	27

Table 2 (Continued)

Compound	RI[c]	ID[d]	stage[e]	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
																Lactones															
δ-octalactone	1965	A	UR	6	tr	5	–	1	1	tr	2	4	–	–	–	1	–	–	1	1	tr	1	tr	tr	1	–	1	1	tr	–	tr
			R	30	2	12	–	6	6	7	3	15	–	–		6	–	–	4	2	1	4	1	10	tr	–	7	1	tr	–	tr
γ-nonalactone	2028	A	UR	3	–	2	–	–	1	1	2	2	tr	–	–	1	–	tr	i	1	1	tr	tr	1	tr	tr	1	–	–	–	–
			R	6	–	5	–	–	5	3	4	6	2	–	–	5	–	1	4	3	2	2	1	1	1	tr	3	–	–	–	–
γ-decalactone	2144	A	UR	148	28	59	19	89	84	41	52	86	14	18	4	16	7	4	3	4	5	6	12	8	1	10	36	25	19	9	11
			R	454	105	281	35	178	350	106	182	316	71	115	39	212	56	45	120	125	26	116	82	49	21	27	176	230	134	89	85
γ-jasmolactone	2181	A	UR	17	6	6	3	12	13	11	9	11	4	6	4	7	3	3	2	3	4	3	2	3	1	4	3	3	3	3	2
			R	52	14	23	5	40	86	45	20	79	36	30	41	66	25	42	35	38	38	22	5	8	14	8	16	12	38	7	12
δ-decalactone	2192	A	UR	43	5	18	4	23	14	4	8	28	2	1	1	8	2	tr	1	1	tr	tr	2	1	tr	tr	6	3	2	1	1
			R	227	35	131	4	48	69	17	42	81	8	6	2	34	7	3	27	15	3	41	28	20	1	1	37	117	47	24	22
(Z)-7-decen-5-olide	2255	B	UR	2	tr	1	tr	1	1	tr	–	2	–	–	1	3	1	tr	tr	–	tr	tr	tr	tr	–	1	tr	3	2	2	2
			R	24	1	8	tr	6	9	5	–	13	–	–	1	7	2	2	4	–	2	4	tr	3	–	8	10	7	15	3	4
γ-dodecalactone	2372	A	UR	4	1	2	–	1	1	tr	–	–	–	–	–	–	–	–	–	–	–	–	8	–	–	–	–	tr	1	tr	tr
			R	13	3	6	–	2	1	1	–	–	–	–	–	–	–	–	–	–	–	–	10	–	–	–	–	2	6	2	tr
total			UR	300	78	126	44	185	173	114	105	186	60	57	21	60	27	14	15	23	18	20	54	26	7	33	81	56	53	26	32
			R	993	226	623	84	471	792	377	331	800	506	265	244	528	239	205	314	372	318	292	261	298	129	117	429	466	367	184	190
relative %			UR	32	14	31	7	49	52	34	29	37	10	11	8	23	5	8	7	9	14	15	6	17	9	13	29	26	17	15	24
			R	29	30	65	12	65	77	55	52	66	26	24	48	70	15	14	45	37	70	29	6	16	44	23	45	60	43	40	47
total			UR	952	567	405	665	376	335	334	367	506	597	535	253	259	499	173	225	253	127	131	316	148	76	286	278	212	318	174	131
			R	3465	760	954	694	721	1030	680	634	1210	1981	1109	512	753	1588	469	694	1012	458	1022	4911	436	291	501	942	781	860	460	406

[a] Values expressed in μg/kg equivalent of 2-octanol. [b] For code see Table 1. [c] Linear retention index on DB-Wax Etr (J&W Scientific) based on a series of *n*-hydrocarbons. [d] A, identified by mass spectrum and linear retention index of reference compounds; B, tentatively identified by mass spectrum and linear retention index similar to mass libraries or published data. [e] Unripened apricots (UR) and apricots ripened at 20 °C (R). [f] –, not detected. [g] tr, <1 ppb.

to constitute references and databases, which may subsequently allow consumer expectations to be met.

MATERIALS AND METHODS

Solvent and Chemicals. Analytical grade chloroform (Chromasolv Plus, 99.9%) and *n*-propyl gallate (≥98%) were, respectively, from Sigma and Fluka (Saint Quentin Fallavier, France). Ammonium sulfate $(NH_4)_2SO_4$ (puriss. p.a., ≥99%), and *n*-alkane standards (C_8–C_{40}) were from Riedel-de Haën (Saint Quentin Fallavier, France). Reference compounds were obtained from Sigma-Aldrich (Saint Quentin Fallavier, France) [butyl acetate, 3-methylbutyl acetate, pentyl acetate, hexyl acetate, (*Z*)-3-hexenyl acetate, (*E*)-2-hexenyl acetate, hexanal, (*E*)-2-hexenal, (*E*)-2-hexen-1-ol, butanol, 2-methylbutanol, 6-methyl-5-hepten-2-ol, benzyl alcohol, 2-octanone, 6-methyl-5-hepten-2-one, benzaldehyde, linalool, β-cyclocitral, α-terpineol, geraniol, γ-octalactone, γ-nonalactone, and γ-decalactone], Interchim (Montluçon, France) (γ-hexalactone, δ-octalactone, δ-decalactone, and γ-dodecalactone), and Fluka [hexanol, (*Z*)-3-hexen-1-ol, and γ-jasmolactone].

Samples. Apricots (*P. armeniaca* L.) of different maturities, according to their period of production in France, were collected during the 2006 season over a 3-month period during the peak of normal harvest (May–July) in the experimental orchard of the Ctifl (Balandran, Gard, France). Among the main apricot cultivars available in France, 28 were selected (see Table 1). Cultivars 1–4 were very early apricots; cultivars 5–16 were early varieties; cultivars 17–19 were midseason apricots; cultivars 20–24 were full-season varieties; and cultivars 25–28 were late apricots. The stage of maturity was measured by external color and firmness. The harvest date was determined by skin ground color changes from green to orange. Measurements were performed using the Ctifl apricot color chart that provides 10 shades from 1 (green) to 10 (red-orange) (*21*). The exact yellowish green color at harvest being dependent on the variety, most of them were in accordance with those recommended by professionals. Fruits were hand-picked and immediately transported to the laboratory. For each cultivar, healthy fruits (~10–15 kg) were immediately selected for their skin color uniformity and size and divided into two batches. Physicochemical measurements and volatile analysis were performed on the fruits at harvest (batch I) and after ripening (batch II). For each cultivar, fruits from batch II were placed in trays and stored in ripening chambers maintained at 20 °C and 60–70% relative humidity until complete maturity (up to 10 days depending on the cultivar, see Table 1). Firmness measurement of 30 fruits, randomly picked in each ripening sample, was performed daily as described below. Maturity was considered to be complete when the average firmness of the ripened samples was 55 ID_{10} or less.

Firmness Determination. Firmness was determined on two opposite sides of 30 apricots using an electronic Durofel (licensed by Copa-Ctifl) with a 0.10 cm^2 tip. Durofel is a nondestructive dynamometer that provides a measure of the force used to press a spring-loaded pawl against the fruit surface (*22*, *23*). The measurements are expressed in ID_{10} on a scale of 0 (very soft) to 100 (very hard).

Chemical Analyses. Thirty apricots from each cultivar were sliced, pitted, and homogenized in a Waring Blendor. Soluble solids (SS) were determined on the purée with an Atago PR-101 digital refractometer. Titratable acidity (TA) was determined by diluting 5 g of the purée with 50 mL of deionized water and titrating to pH 8.1 with 0.1 N NaOH using an automatic titrator Crison Compact II with autosampler. After centrifugation of the purée (14000*g*, 5 min, 4 °C), the individual sugars (glucose, fructose, and sucrose) and organic acids (malic and citric) were simultaneously determined from 1 mL of supernatant, diluted 20-fold with deionized water, by HPLC as described by Doyon et al. (*24*). All measurements were performed in triplicate.

Isolation of Volatiles. Thirty apricots from each cultivar were sliced and pitted, and flesh cubes (~1 cm^3) were prepared. Cubes were then immediately frozen with liquid nitrogen and stored at −25 °C until analysis. Isolation of volatiles was performed according to the liquid–liquid microextraction (LLME) method previously described by Aubert et al. (*25*) with some modifications. One hundred grams of frozen apricot, 100 mL of *n*-propyl gallate (10 mM), 40 g of $(NH_4)_2SO_4$, and 100 μL of 2-octanol (401.5 μg/mL) (internal standard) were homogenized in a Waring Blendor for 90 s. The mixture was centrifuged (14000*g*, 5 min, 4 °C) and the supernatant filtered through a Whatman paper filter (grade 113v) and centrifuged again (21000*g*, 5 min, 4 °C). Forty milliliters of supernatant, filtered again through a Whatman paper filter (grade 113v), was introduced into a 50-mL screw-capped conical centrifuge tube (34 × 98 mm glass borosilicate) containing a magnetic stir bar (15 × 6 mm). Two hundred and fifty microliters of chloroform was added, and the mixture was extracted for 60 min under magnetic stirring at room temperature. After removal of the magnetic stir bar, the tube was sonicated for 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. Concentrations of volatiles (Table 2) are given as the average of data from three isolations. The average standard deviation was 15.5% for concentrations ranging from 1 to 10 ppb and 7.7% for higher concentrations.

Table 3. One-Way ANOVA Results for Physicochemical Characteristics and Volatile Compounds between Unripened and Ripened Apricots

	unripened		ripened			
	mean	range	mean	range	t_{27}[a]	p[b]
Physicochemical Characteristics						
firmness (ID_{10})	72.8	63.0–83.0	42.9	26.0–54.0	18.65	***
TA (mequiv/100 g)	26.6	13.5–39.5	25.9	14.3–38.8	1.95	
SS (%Brix)	13.1	10.6–16.7	14.1	10.6–17.4	−9.63	***
saccharose (g/100 g)	6.36	4.80–9.04	6.90	4.89–8.92	−5.50	***
glucose (g/100 g)	1.64	0.64–3.19	1.81	0.79–3.44	−3.35	**
fructose (g/100 g)	0.53	0.09–0.95	0.56	0.03–1.05	−1.35	
citric acid (g/100 g)	1.32	0.07–2.19	1.33	0.08–2.40	−1.01	
malic acid (g/100 g)	0.81	0.24–2.80	0.76	0.22–2.82	4.30	***
Volatile Compounds[c]						
butyl acetate	36.9	nd[d]–223.8	308.0	nd–2687.6	−2.53	*
3-methylbutyl acetate	0.7	nd–6.0	1.1	nd–7..	−1.17	
pentyl acetate	1.5	nd–7.8	4.5	nd–47.0	−1.98	
hexyl acetate	10.8	nd–73.2	49.4	nd–577.8	−2.15	*
(*Z*)-3-hexenyl acetate	2.7	nd–13.0	2.8	nd–20.1	−0.23	
(*E*)-2-hexenyl acetate	0.9	nd–9.6	0.6	nd–3.6	0.98	
sum of esters	53.5	0.3–254.7	366.5	0.7–3318.6	−2.52	*
hexanal	5.8	nd–31.9	5.2	nd–23.0	0.82	
(*E*)-2-hexenal	56.9	nd–283.5	44.5	nd–152.7	1.89	
hexanol	5.2	0.7–22.1	16.0	1.3–174.3	−1.97	
(*Z*)-3-hexen-1-ol	2.7	nd–15.8	1.6	nd–9.7	2.92	**
(*E*)-2-hexen-1-ol	5.8	nd–69.9	2.9	nd–21.3	1.61	
sum of C_6 compounds	76.4	2.6–328.1	70.2	5.3–231.5	0.74	
butanol	3.3	nd–16.9	17.7	nd–87.9	−3.98	***
2-methylbutanol	0.2	nd–2.7	1.2	nd–18.1	−1.57	
6-methyl-5-hepten-2-ol	3.7	nd–8.8	4.8	nd–10.2	−4.00	***
benzyl alcohol	2.8	nd–16.2	3.5	nd–17.1	−1.25	
sum of alcohols	10.1	0.7–30.8	27.1	3.1–123.1	−3.93	***
2-octanone	5.5	nd–10.4	7.1	nd–25.9	−2.67	*
6-methyl-5-hepten-2-one	1.2	nd–5.6	1.8	nd–10.3	−1.70	
benzaldehyde	38.8	5.1–243.1	83.1	5.8–860.5	−1.98	
sum of carbonyl compounds	45.5	13.7–257.9	92.0	13.5–877.2	−2.06	*
linalool	59.0	5.2–225.8	68.0	6.1–255.6	−2.12	*
β-cyclocitral	0.7	nd–3.5	0.7	nd–2.7	0.14	
α-terpineol	16.1	nd–56.1	18.9	nd–62.7	−2.21	*
geraniol	11.0	nd–33.6	12.4	nd–39.1	−1.48	
linalool hydrate	4.5	nd–26.6	4.3	nd–20.5	0.62	
dihydroactinidiolide	14.0	0.5–66.3	17.8	0.9–80.1	−3.62	**
sum of terpenic compounds	105.3	11.8–352.7	122.2	16.2–391.3	−2.48	*
γ-hexalactone	15.6	2.7–38.1	116.2	23.8–336.6	−7.89	***
γ-octalactone	11.6	1.1–41.5	37.2	12.4–79.5	−10.01	***
δ-octalactone	0.9	nd–6.3	4.2	nd–30.2	−3.33	**
γ-nonalactone	0.6	nd–2.9	2.0	nd–6.5	−4.84	***
γ-decalactone	29.2	0.8–148.1	136.7	21.0–453.8	−7.18	***
γ-jasmolactone	5.4	1.3–16.6	30.7	5.3–85.8	−7.06	***
δ-decalactone	6.4	0.1–42.8	39.2	0.9–226.5	−4.18	***
(*Z*)-7-decen-5-olide	0.8	nd–2.6	5.0	nd–23.9	−4.43	***
γ-dodecalactone	0.7	nd–8.1	1.7	nd–12.9	−2.48	*
sum of lactones	71.1	6.7–300.0	372.9	83.9–992.9	−9.80	***
total	361.9	79.6–952.1	1050.9	292.9–4928.0	−4.51	***

[a] t_{27} is the paired Student's *t*-test value. Plus sign means a larger amount in unripened apricots. Minus sign means a larger amount in ripened apricots. [b] *, $p < 0.05$; **, $p < 0.01$; ***, $p < 0.001$. [c] Values expressed in μg/kg equivalents of 2-octanol. [d] Not detected.

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 (Linde) carrier gas was 1.3 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 using a 1079 PTV injector from Varian under the following injection program: initially 20 °C for 0.1 min, then programmed to 250 °C at 200 °C/min, and kept at 250 °C. Injections were performed 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.

GC-MS Conditions. A Varian 3800 gas chromatograph was used with the same DB-Wax Etr capillary column as above. The oven and injector temperature programs were as above. Injections (1 μL) were performed using a CombiPAL autosampler (CTC Analytics). The flow of helium 6.0 (Linde) carrier gas was 1 mL/min. 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, 45, and 250 °C. Mass spectra were scanned in the range of m/z 30−350 amu at 1 s intervals. Compounds were first identified using NIST/EPA/NIH MS Search 2.0 and our own mass spectra libraries. The identities of most of them were then confirmed by comparison of their linear retention indices and EI mass spectra with those of reference compounds.

HPLC Conditions. A Varian ProStar 230 liquid chromatograph was used with a photodiode area (Varian PDA detector 330) and a refractometer (Varian RI detector 350) connected in series. The PDA was set at 210 nm. Twenty microliters of each sample was injected using a Varian 410 autosampler on a 300 mm × 7.8 mm i.d. cation exchange ICSep ICE-ION-300 column equipped with an ICSep ICE

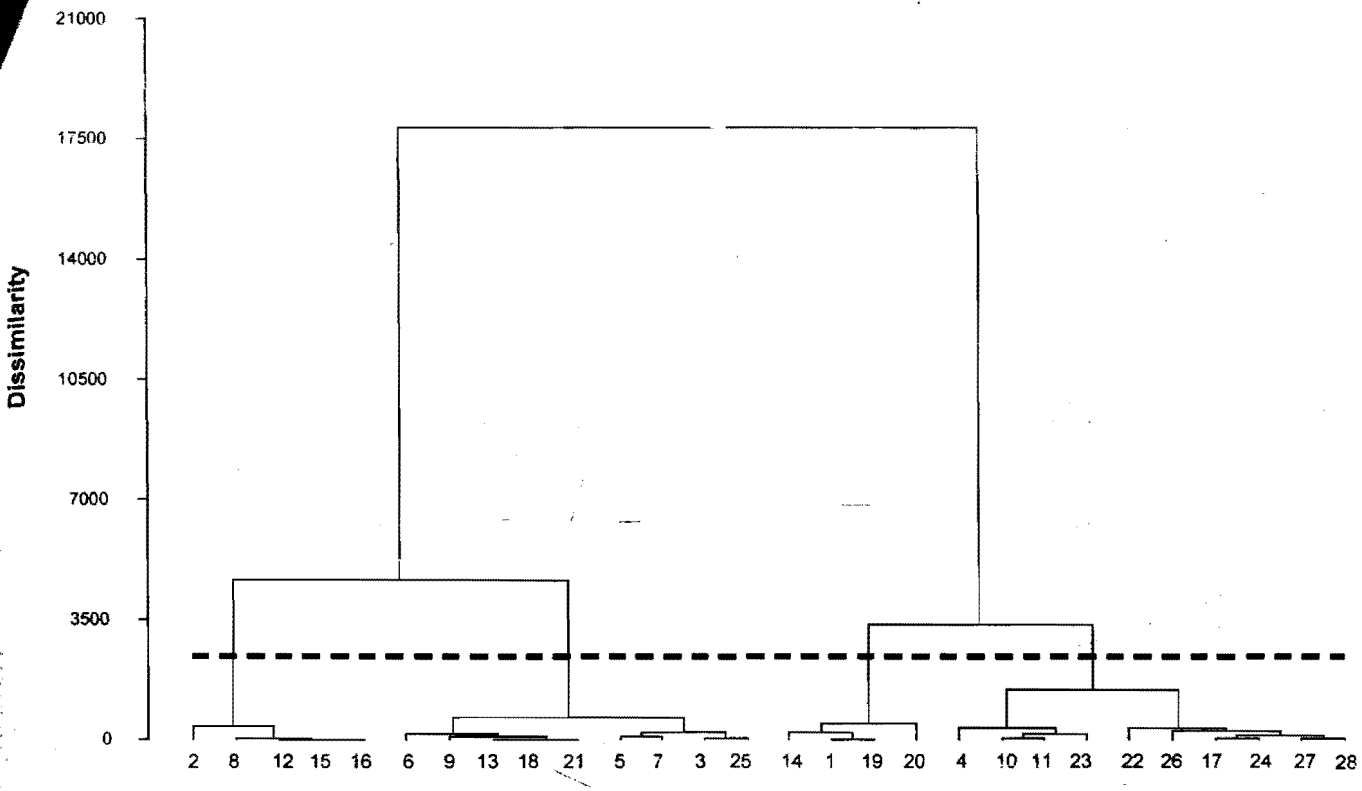

Figure 1. Dendrogram resulting from cluster analysis. The dotted horizontal line separates the main clusters (for cultivar codes see **Table 1**).

GC-801/C guard column (Transgenomic, San Jose, CA). The column oven temperature was set at 30 °C. The flow of mobile phase (0.008 N H_2SO_4) was 0.4 mL/min.

Statistical Analysis. Analyses of variance, principal component analysis (PCA), and ascendant hierarchical classification (AHC) were performed using Statbox 6.7 (Grimmersoft, Paris, France). In the cluster analysis the distances between pairs of samples were compared on the basis of the squared Euclidean distance. The resulting clusters were then connected using Ward's method, which merges the two clusters for which the total sum-of-square error is smallest (*26*).

RESULTS AND DISCUSSION

The effects of postharvest ripening on the physicochemical characteristics and volatile constituents of 28 apricot cultivars of different maturities were investigated during the 2006 season. Fruits were picked at their "optimal harvestable" stage of maturity as advised by the professional organizations (*21*) and ripened at 20 °C and 60−70% relative humidity until complete maturity. Maturity was considered to be complete when the firmness of the fruit was 55 ID_{10} or less, that is, when the apricot is "ready-to-eat". Firmness, SS, TA, organic acids (malic and citric acids), sugars (glucose, fructose, and saccharose), and the levels of the main volatiles were determined at harvest and after ripening. Thirty-three volatile compounds, including 6 esters, 5 C_6 compounds, 4 alcohols, 3 carbonyl compounds, 6 terpenic compounds, and 9 lactones, were extracted by LLME (*25*) and analyzed by GC-FID and GC-MS. The effects of postharvest ripening on the physicochemical characteristics and volatile compounds of the 28 apricot cultivars are summarized in **Tables 1** and **2**. A one-way analysis of variance, using the paired Student's t test, was performed to determine the effect of ripening on the physicochemical characteristics and the levels of volatile compounds (**Table 3**). The discrimination of the 28 cultivars after ripening in four groups, based on the relative abundances (percent) of the main volatile classes, was performed by cluster and principal component analyses (**Figures 1** and **2**). Finally, **Table 4** shows the results of the one-way analysis of variance using the GLM procedure and the Newman−Keuls test (SNK) performed on the levels of volatiles in the four different groups of apricots after ripening.

Changes during Ripening. As indicated in **Table 1**, the skin color at harvest was greatly different according to the cultivar, from yellow-green (color grade 4) for Early Blush (1), Soledane (7), Frisson (25), and Bergeron (26) to orange (color grade 8) for Flodea (5), Red Sylver (8), Tom Cot (10), Latica (12), Perle Cot (13), Mascot (14), Bigred (18), Flavor Cot (20), and Kioto (22). As indicated in **Tables 1** and **3** the most significant change in physicochemical characteristics due to postharvest ripening at 20 °C was a decrease in firmness. Ripening softened the fruit to a mean firmness of 43 ID_{10}, whereas the mean firmness at harvest was 73 ID_{10}. The average time for the apricots to ripen was 4 days at 20 °C; nevertheless, the rate of fruit ripening varies considerably among cultivars. As indicated in **Table 1**, Early Blush (1), Spring Blush (2), and PSB 28-58 (3) required only 2 days to ripen at 20 °C and have a high rate of softening (loss of firmness higher than 15 ID_{10} per day), whereas Bigred (18), Goldrich (19), Helor (21), Kioto (22), Bergeron (26), and Tardif de Tain (28) required up to 10 days and have a low rate of softening (loss of firmness lower than 5 ID_{10} per day). No significant correlation has been observed between the skin color at harvest and the number of days to ripen ($r^2 = 0.2381$). As for other physicochemical characteristics, although some results were statistically different between unripened and ripened samples (**Table 3**), the changes were relatively small and the levels in samples after ripening were found to be similar overall to those observed at harvest (**Table 1**).

As indicated in **Table 2**, the total volatile contents generally highly increased with ripening. Except for Earlycot 1 (4), the levels of total volatiles in ripened samples were ~1.4−8-fold higher than those observed in unripened apricots. As shown in **Table 3**, the results obtained from the analysis of variance and

cultivars, particularly for compounds which contribute most to the apricot aroma such as terpenic compounds, esters, and lactones. Nevertheless, although the results have demonstrated that the 28 apricot cultivars could be discriminated into four different aroma groups, it would be particularly relevant, in further investigations, to characterize these cultivars from a sensory point of view (descriptive analyses, consumer preferences) and to identify the genetic components involved in the quality of these fruits to facilitate breeding of new cultivars meeting the consumer's expectations.

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