Phenolic Composition, Browning Susceptibility, and Carotenoid Content of Several Apricot Cultivars at Maturity

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Abstract. Phenolic composition and susceptibility to browning were determined for nine apricot (*Prunus armeniaca* L.) cultivars. Chlorogenic and neochlorogenic acids, (+)-catechin and (-)-epicatechin, and rutin (or quercetin-3-rutinoside) were the major phenolic compounds in apricots. In addition to these compounds, other quercetin-3-glycosides and procyanidins have been detected. Chlorogenic acid content decreased rapidly during enzymatic browning, but the susceptibility to browning seemed to be more strongly correlated with the initial amount of flavan-3-ols (defined as catechin monomers and procyanidins). As chlorogenic acid is certainly the best substrate for polyphenol oxidase, the development of brown pigments depended mainly on the flavan-3-ol content.

Numerous studies have been devoted to the enzymatic browning of apricot (Dijkstra and Walker, 1991; Gajago et al., 1979, 1982; Vámos-Vigyazo et al., 1979). Various causes (physiological, mechanical, technological) may induce enzymatic browning in fruits with the development of undesirable color, flavor and a loss of nutrients. Browning can also originate from nonenzymatic reactions occurring in heat-processed fruit products (Maillard reaction).

Enzymatic browning results from oxidation, in the presence of oxygen, of phenolic compounds by polyphenol oxidases. The phenolic compounds are oxidized to quinones which then polymerize into brown products (Amiot et al., 1997; Macheix et al., 1990; Nicolas et al., 1993). The tendency of fruits to brown results from the action of many factors, which vary with the age of the fruit, physiological stage, cultivar, disease and the treatments to which they are subjected (Macheix et al., 1990). In apricot, browning is related to the ortho-diphenolic content (Vámos-Vigyazo et al., 1979), but only for a few cultivars, and these compounds are the limiting factor in enzymatic browning (Vámos-Vigyazo et al., 1981).

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The phenolic content of apricots has been measured by some authors as summarized by Macheix et al. (1990). The hydroxycinnamic acid derivatives were identified as esters of caffeic, coumaric, and ferulic acids (Herrmann, 1973). Coumarin and scopoletin have also been identified (Reschke and Herrmann, 1981). Apricot fruit was characterized by the predominance of chlorogenic acid or 5'-caffeoylquinic acid (Dijkstra and Walker, 1991; Gajago et al., 1977; Garcia-Viguera et al., 1994). Coumaroyl and feruloyl derivatives were present as glucose esters and as quinic isomers (Reschke and Herrmann, 1981; Risch and Herrmann, 1988). The presence of (+)-catechin and (-)-epicatechin has also been reported (Mosel and Herrmann, 1974; Risch and Herrmann, 1988). Flavonols in apricots have been characterized as glucosides and rutinosides of quercetin and of kaempferol (Herrmann, 1979; Garcia-Viguera et al., 1994).

Because there is an increasing demand for apricot products (juices, purées, jams, precut apricots), cultivars with little browning must be selected. The objective of our study was to characterize nine important apricot cultivars at commercial maturity stage for their susceptibility to browning, their phenolic content, polyphenol oxidase activity and carotenoid content. Browning kinetics were studied, and the degradation of phenolic compounds and of carotenoids is discussed in relation to the change of color and the nutritional quality.

Materials and Methods

Plant materials. Fruits were harvested in 1993 and 1994 at the Institut National de la Recherche Agronomique in Manduel (Gard, France); names of cultivars used are given in

Table 1. For each cultivar, 50 fruits were picked at commercial maturity. Fruits were cut into small pieces, immediately frozen in liquid N, freeze-dried and stored at -20 °C until analyzed.

Measurement of browning. Freeze-dried powder (10 g) was homogenized for 15 min in 40 mL distilled water or in 40 mL solution containing enzymic inhibitors (0.1% NaF + 0.1% thiourea). Three small petri dishes were filled with each purée. Reflectance measurements (L*, lightness; a*, green/red; and b*, blue/yellow chromaticity) were carried out with a Minolta CR 300 apparatus. The susceptibility to browning was determined by the difference between the tristimulus coordinates measured on oxidized and nonoxidized purées. For each cultivar, measurements were carried out in three replicates. The data were expressed in DL*, Da*, and Db*. The variability within each parameter was <1%.

Extraction and purification of phenolic compounds. Freeze-dried apricots were finely powdered. Two grams of powder (two replicates per sample) were homogenized in 100 mL cold aqueous ethanol (75%) containing sodium metabisulfite (0.5%) for 1 min using an Ultra-Turrax blender. Three successive extractions with ethanol (75%) were carried out at 4 °C for 30 min. After removing the alcohol under vacuum at 35 °C, ammonium sulfate (20%) and metaphosphoric acid (2%) were added to the aqueous phase. Pigments were eliminated by three successive extractions with petroleum ether (2:1, v/v). Phenolic compounds were then extracted three times with ethyl acetate (1:1, v/v). The three organic phases were combined, filtered through Whatman paper (phase separator silicone treated) to eliminate the aqueous phase, and evaporated to dryness under vacuum at 38 °C. The residue was dissolved in methanol (1 mL). Methanol extracts were filtered through an Acrodisc filter (0.45 μ m) before analysis by high-performance liquid chromatography (HPLC).

Determination of phenolic compounds. Separation and determination of phenolics was performed by HPLC (Varian 5500 connected to a diode array detector Waters 990) using an Chrompack C₁₈ 7 μ m (200 $\times$ 3 mm i.d., Alltech) column. The solvent system used was a gradient of A (water; 2% CH₃COOH) and B (MeOH). The best separation was obtained using the following gradient: at 0% to 7% in 5 min, 7% B for 13 min, then 7% to 40% B in 44 min and constant 40% for an additional 13 min. The solvent flow rate was 0.8 mL·min⁻¹ and the separation was performed at 35 °C. Two detectors were used: a diode array detector (Waters 990) for characterization of each peak, and a monochromatic detection (Varian UV 200) for quantification. Phenolic compounds were assayed by external standard calculation at 320 nm for hydroxycinnamic derivatives and flavonols and at 280 nm for flavan-3-ols. The concentrations of phenolics were expressed in mg·g⁻¹ of dry matter as chlorogenic acid equivalents for hydroxycinnamic derivatives, as (+)-catechin equivalents for flavan-3-ols, and as quercetin-

Table 1. Phenolic content, PPO activity, and carotenoid content of the fruits of nine apricot cultivars at commercial maturity.

Cultivar	Harvest date	Phenolic compounds ^a									PPO ^b	Carotenoids ^c		
		3'CQ	5'CQ	CAT	EPI	RUTIN	HCE	FLA	FLO	FLA/ HCE		beta-car	gamma-car	lyco-pene
		(μg·g ⁻¹ DM)										(nkat·g ⁻¹ DM)	(μg·g ⁻¹ DM)	
1993														
Henderson	30 June	52 c ^a	197 c–c	428 a	205 c	148 bc	427 cd	1089 a	250 b	2.55 a	4971 ab	116 ± 8 ^w	15 ± 1	9 ± 1
Monique	2 July	68 ed	225 cd	0 d	41 fg	100 c–e	360 ed	453 c	133 de	1.26 b	5342 a	5 ± 1	---	---
Rouge de Roussillon	12 July	83 d	103 g	115 c	398 a	119 b–d	324 e	785 b	154 c–e	2.42 a	3770 b–e	34 ± 3	---	---
Rouge de Fourmes	28 June	120 c	390 a	200 b	92 ed	155 bc	771 a	300 d	224 bc	0.39 c	3964 a–d	74 ± 6	21 ± 1	---
Polonais	12 July	87 d	123 fg	80 c	132 d	119 b–d	282 e	390 cd	232 b	1.38 b	3489 c–e	57 ± 4	32 ± 2	19 ± 1
Canino	28 June	277 a	246 c	167 b	337 b	180 b	626 b	818 b	229 b	1.30 b	2074 f	50 ± 6	---	---
Cafona	28 June	144 bc	177 de	0 d	0 g	62 de	411 cd	4 e	190 b–d	0.01 c	2399 ef	29 ± 2	---	---
Bebeco	2 July	51 e	322 b	0 d	4 g	49 e	456 c	47 e	95 e	0.10 c	4528 a–c	5 ± 1	---	---
1994														
Précoce de Tyrinthe	14 June	170 b	159 ef	0 d	70 ef	438 a	468 c	70 e	438 a	0.15 c	3015 d–f	74 ± 5	13 ± 1	---

^a3'CQ: 3'-caffeoylquinic acid (or neochlorogenic acid); 5'CQ: 5'-caffeoylquinic acid (or chlorogenic acid); CAT: (+)-catechin, EPI: (-)-epicatechin. FLA: flavan-3-ols; HCE: hydroxycinnamic esters; FLO: flavonols. HCE, FLA, and FLO data are presented as equivalents of chlorogenic acid, catechins, and rutin, respectively.

^bPPO: polyphenol oxidase activity; car: carotene.

^cMean separation within columns by Tukey's HSD, $P < 0.05$; $n = 2$.

^wMeans $\pm$ SD.

^xNot detected.

3-rutinoside equivalents for flavonols. Three samples were injected for each extract (= total of six per sample).

Extraction and determination of carotenoids. Celite 545 (4 g) was added to 10 g of apricot powder and homogenized with acetone. After filtration, carotenoids were transferred to 10 mL hexane. The hexane was washed with water three times to eliminate acetone, then dried with anhydrous sodium sulfate. Separation of carotenoids was performed according to the method of Saleh and Tan (1991). The analytical apparatus used was a HP1090L chromatograph equipped with a diode array detector. Carotenoids were separated along a Vydac column 201TP54 C₁₈ (250 × 4.6 mm) containing 5-μm particles and a 15 × 3.2-mm Vydac C₁₈ guard column with the following mobile phase: 18% methanol, 80% acetonitrile, and 2% dichloromethane. The flow rate was 0.5 mL·min⁻¹. Peaks were identified by comparison of retention times and spectra with commercial standards (Sigma Chemical Co.) for β-carotene, and lycopene, from Hoffman Laroche for γ-carotene. Carotenoids were determined by external calibration at 440 nm. Only one replicate was used.

Polyphenol oxidase activity. One gram of freeze-dried material was suspended in 10 mL of freshly prepared, cold McIlvaine's buffer at pH 6.5, containing 1% Triton X100 and 25 mM ascorbic acid for 15 s using an Ultra-Turrax blender, and stirred for 15 min at 0 °C. The homogenate was filtered through cheesecloth and centrifuged for 30 min at 15,000 g, at 4 °C; the supernatant was used to evaluate enzyme activity. The polyphenol oxidase (PPO) activity was measured by polarography at 30 °C at pH 6.5 according to Dijkstra and Walker (1991), using an air-saturated 4-methylcatechol (20 mM) solution and 50 μL of the enzyme extract. Activity was expressed as nmol of oxygen consumed per second (nkat). For each cultivar, two replicates were used for extraction and measurements.

Browning kinetics and changes in phenolic composition. Browning kinetics were carried out on the cultivar Canino, the fruits of which

were rich in chlorogenic acid and catechins. Dry powder (2 g) was mixed in 8 mL distilled water for 0, 2, 5, 15, and 30 min; the browned purée was homogenized for 1 min in 100 mL cold aqueous ethanol (75%, containing 0.5% sodium metabisulfite) and stirred for 30 min at 4 °C. Extraction, purification, and determination of phenolics were as described above.

Statistical analyses on phenolic composition, PPO activity, and browning data were performed using SAS software (SAS Inst., 1985).

Results

Cultivar variation in phenolic and carotenoid contents and in PPO activity. Phenolics were identified as 5'-caffeoylquinic acid (chlorogenic acid) and 3'-caffeoylquinic acid (neochlorogenic acid), (+)-catechin, (-)-epicatechin, and quercetin-3-rutinoside (rutin). Among the hydroxycinnamic esters, coumaroyl esters were characterized by their spectra with a maximum at 315 nm and a shoulder at 300 nm. In addition to (+)-catechin and (-)-epicatechin, there were some flavan-3-ol oligomers (procyanidins) that showed the same spectral characteristics as monomers with a maximum at 280 nm, but their structures remain unknown. Two procyanidins have been tentatively identified as procyanidins B2 and C1 (isolated from apples and grapes) (Amiot et al., 1992; Oszmianski and Sapis, 1989), based upon their retention times.

There were great variations in phenolic composition among cultivars (Table 1). Flavan-3-ols (FLA) and hydroxycinnamic esters (HCE) represented ≈80% to 90% of phenolic content for six cultivars ('Henderson', 'Monique', 'Rouge de Roussillon', 'Rouge de Fourmes', 'Polonais', and 'Canino'); in the other cultivars ('Cafona', 'Bebeco', and 'Précoce de Tyrinthe'), flavonols (FLO) and hydroxycinnamoyl esters represented the major classes (90% to 95%). For all the cultivars studied, chlorogenic and neochlorogenic acids, (-)-epicatechin, (+)-catechin and rutin were the main compounds (Table 1). Chlorogenic acid and neochlorogenic acid represented be-

tween 60% and 84%, respectively, of the total hydroxycinnamoyl esters. The presence of these two hydroxycinnamics in high amounts in apricot fruits has been reported previously (Moller and Herrmann, 1983). In two cultivars ('Canino' and 'Précoce de Tyrinthe'), neochlorogenic acid was found at a higher concentration than chlorogenic acid. Among the flavan-3-ols, (-)-epicatechin and (+)-catechin were found in high concentrations as previously reported by Mosel and Herrmann (1974) and Risch and Herrmann (1988). However, for four cultivars ('Monique', 'Cafona', 'Bebeco', and 'Précoce de Tyrinthe'), these two compounds remained very low or were not detected (Table 1). Concerning the flavonols, quercetin-3-rutinoside (rutin) was very high in all the cultivars studied, in agreement with the findings of Garcia-Viguera et al. (1994). This compound represented between 60% and 80% of the flavonol content, except for two cultivars ('Polonais' with 51% and 'Cafona' with 33%). All the cultivars contained low amounts of kaempferol glycosides (tentatively identified as kaempferol 3-rutinoside). These results are in good agreement with previously reported data for other apricot cultivars (Henning and Herrmann, 1980), but differ from results published on American canned apricots in which kaempferol derivatives were detected (El-Sayed et al., 1965). In addition to these two compounds, flavonols were identified by some authors as quercetin-3-glucoside (Garcia-Viguera et al., 1994) and kaempferol-3-glucoside (Henning and Herrmann, 1980). A good parameter to distinguish the cultivars was the ratio FLA : HCE. This ratio varied from 0.01 ('Cafona') to 2.55 ('Henderson'). For four cultivars ('Rouge de Fourmes', 'Cafona', 'Bebeco', and 'Précoce de Tyrinthe'), this ratio was <1.

PPO activity was high in apricot (5342 nkat·g⁻¹ dry mass for the maximum) (Table 1). 'Monique' and 'Henderson' were characterized by a high activity and 'Canino' and 'Cafona' by a lower activity.

Carotenoid content was also different among the cultivars studied. β-Carotene was

the major carotenoid in apricot fruits, as previously reported (Gross, 1987). Its concentration varied from 5 $\mu\text{g}\cdot\text{g}^{-1}$ dry mass ('Bebeco') to 115 $\mu\text{g}\cdot\text{g}^{-1}$ dry mass ('Henderson'). In 'Polonais', β -carotene represented 50% of total carotenoid content. In this cultivar, γ -carotene and lycopene were present in high quantities. Apricots from 'Précoce de Tyrinthe' were characterized by low phenolic and high carotenoid contents.

Cultivar variation in susceptibility to browning. In the presence of inhibitors, L^* of purées varied from 45 to 65, a^* from -2 to 6, and b^* from 22 to 47 (Table 2). These data depended mainly on the concentration of carotenoids. 'Henderson' was characterized by a high concentration of β -carotene and a high b^* value corresponding to the yellow vector. Apricots from 'Polonais' were rich in lycopene, a red carotenoid; thus, the a^* value corresponding to the red vector was particularly high. After oxidation, all the color data were profoundly modified. L^* values decreased corresponding to the darkening of the purées; b^* decreased markedly while a^* increased. The formation of brown pigments modified considerably the chromaticity and the hue value (H^*). However, after oxidation, some cultivars presented a high lightness $L^* > 40$ ('Rouge de Fournes', 'Bebeco', and 'Précoce de Tyrinthe'). 'Précoce de Tyrinthe' presented a higher L^* value after oxidation than 'Cafona' and 'Bebeco' without oxidation. According to our results, 'Précoce de Tyrinthe' and 'Bebeco' appear to be the best cultivars for processing. In fact, when oxidized purées were compared to nonoxidized purées, great differences were apparent among the cultivars studied. The differences in L^* , in a^* and in H^* remained low for 'Précoce de Tyrinthe' and 'Bebeco'. In contrast, purées of 'Monique' and 'Henderson' were very susceptible to browning. 'Monique', characterized by a green flesh [a^* (nonoxidized) = -2.2] presented the highest difference in H^* among the cultivars studied.

Changes in phenolic and in carotenoid content. Browning kinetics were examined during 30 min of oxidation (at 2, 5, 15, and 30) (Fig. 1). Thus, the residual phenolic and carotenoid content could be compared to the initial content of 'Canino' fruits. All the phenolic compounds were affected during oxidation. Hydroxycinnamic derivatives and flavan-3-ols were more rapidly degraded than flavonols. Concentrations of chlorogenic and neochlorogenic acid decreased rapidly during the first two minutes of oxidation (to $\approx 30\%$ of the initial concentrations) and (+)-catechin and (-)-epicatechin to $\approx 50\%$ of the initial concentrations. After 30 min, more than 99% of the hydroxycinnamic derivatives and the flavan-3-ols were degraded, whereas flavonols (rutin) were still detected at $\approx 20\%$ of the initial concentrations. Carotenoids were also affected during oxidation. β -Carotene was less degraded than phenolics during the first 5 min of oxidation (decrease of 25%). After 30 min, carotenoid content remained higher (40%) than phenolic compounds (20% for rutin). Carotenoids can be degraded by enzymatic cooxidation involving lipoxygenase, as shown in tomato by Cabibel and Nicolas (1991).

Discussion

Based on the results presented here, chlorogenic acid, (+)-catechin, and (-)-epicatechin are the major phenolic compounds in apricots. These compounds are also the major phenolic compounds of many other fruits (Macheix et al., 1990). Besides these major compounds, oligomers of catechins (procyanidins) and flavonols were detected in apricots. The phenolic composition differed significantly among the cultivars studied. More recently, Bellagi et al. (1996) found similar significant varietal differences for eight apricot cultivars ('Bebeco', 'Bergeron', 'Cafona', 'Canino', 'Polonais', 'Rouge de Roussillon', 'Rouge de Fournes', and 'Screara'), whereas no significant difference was observed among three maturity stages (turning, ripe and overripe). In this study, 'Bebeco' appeared as the best cultivar with the lowest browning for processing into purées and juices.

All the phenolic compounds are affected by oxidation in apricots, as was previously reported for apples (Amiot et al., 1992). Chlorogenic acid was rapidly degraded in apricot purées. As previously reported in other fruits (Macheix et al., 1990; Nicolas et al., 1993), chlorogenic acid seemed to be a good substrate for polyphenol oxidases. Neochlorogenic (3'-caffeoylquinic acid) was also strongly degraded, but less so than chlorogenic acid (5'-caffeoylquinic acid). As previously reported for cryptochlorogenic acid (4'-caffeoylquinic acid) in apples (Amiot et al., 1992), the isomers of chlorogenic acid were not as good substrates for PPOs as was chlorogenic acid. Stereochemistry can play a major role in the differences among kinetic parameters of PPOs. Cultivar with a higher content of neochlorogenic acid (except 'Canino') tended to show less browning. Catechin monomers were also

easily degraded; they are considered as good substrates for PPOs, and they are also degraded by coupled reactions (Amiot et al., 1995; Cheynier et al., 1988; 1989; Nicolas et al., 1994). Catechin degradation rates are enhanced by chlorogenic acid, mainly by coupled oxidation mechanisms (Oszmianski and Lee, 1990; Singleton, 1987). Caffeoyl esters-orthoquinones that form enzymatically can oxidize catechins to catechin ortho-quinones, thus reducing the caffeoyl quinones into the original phenols. Oligomers of catechins and flavonols, which are considered to be poor substrates for PPOs, are usually degraded by coupled oxidation (Nicolas et al., 1993; Richard-Forget et al., 1992). Rutin and flavan-3-ols in apricot purées were certainly also degraded by cooxidation. The initial amount of enzymatically formed quinones (from chlorogenic acid and catechins) which enter in further cooxidation reactions is dependent on PPO activity. The kinetics of the enzymatic reaction also contributes to the final brown color. Flavonols are poor substrates for polyphenol oxidases (Amiot et al., 1995), and the amount of oxidized flavonols could decrease the amount of quinones resulting from other phenolics, such as flavan-3-ols and hydroxycinnamic (Goupy et al., 1995). Thus, the degradation of phenolic compounds in apricots could be the result of both the direct oxidation by polyphenol oxidases and of coupled oxidation, as was described for others fruits, such as grapes (Cheynier et al., 1988; Cheynier and Ricardo da Silva, 1991) and apples (Oleszek et al., 1989; Richard-Forget et al., 1992). Nonenzymatic reactions depend on the amount of ortho-quinones initially formed enzymatically. The amount of ortho-quinones depends mainly on the concentrations of the best substrates (caffeic acid derivatives and catechins) and on the polyphenol oxidase ac-

Fig. 1. HPLC profiles of the phenolic compounds of apricot fruits. 3'CQ: neochlorogenic acid, 5'CQ: chlorogenic acid, CAT: (+)-catechin, EPI: (-)-epicatechin, RUT: rutin; a: putative procyanidin B2, b: putative procyanidin C1, FLA: flavan-3-ols (catechin oligomeric form or procyanidin), HCE: hydroxycinnamic esters, FLO: flavonols.

Table 2. Enzymatic browning of the fruit of nine apricot cultivars at commercial maturity (reflectance measurements L*, a*, b*).

Cultivar	Color of purées ^a								Browning data ^b			
	Nonoxidized				Oxidized				DL*	Da*	Db*	DH°
	L*	a*	b*	H°	L*	a*	b*	H°				
Henderson	65.2 ± 0.3	1.5 ± 0.2	46.8 ± 0.3	88.2 ± 0.1	38.9 ± 0.9	9.5 ± 0.3	19.8 ± 0.4	64.4 ± 0.3	26.3 a	8.0 b	27.1 a	23.8 b
Monique	59.4 ± 1.0	-2.2 ± 0.1	22.2 ± 0.5	95.6 ± 0.3	37.9 ± 1.3	7.6 ± 0.4	15.6 ± 0.2	64.0 ± 1.1	21.4 b	9.8 a	6.6 c	31.6 a
R. Roussillon	53.9 ± 0.7	2.1 ± 0.5	35.1 ± 0.9	86.6 ± 0.5	36.1 ± 1.6	7.2 ± 0.5	15.9 ± 1.3	65.8 ± 1.2	17.8 c	5.0 c	19.2 b	20.8 c
R. Fournes	60.7 ± 0.3	4.8 ± 0.2	44.6 ± 0.7	83.9 ± 0.2	43.0 ± 0.2	9.4 ± 0.2	25.5 ± 0.3	69.7 ± 0.2	17.8 bc	4.6 cd	19.2 b	14.1 e
Polonais	52.9 ± 0.9	6.3 ± 0.2	41.9 ± 1.1	81.5 ± 0.4	36.1 ± 0.5	9.1 ± 0.3	17.9 ± 0.4	63.1 ± 0.9	16.8 c	2.8 e	24.0 ab	18.4 d
Canino	52.4 ± 0.7	2.7 ± 0.2	37.2 ± 0.8	85.9 ± 0.3	35.7 ± 0.9	7.6 ± 0.4	15.7 ± 0.6	64.2 ± 1.9	16.7 c	4.9 c	21.5 b	21.7 c
Cafona	47.6 ± 0.9	1.5 ± 0.2	30.1 ± 1.1	87.2 ± 0.2	35.9 ± 1.2	4.6 ± 0.3	15.1 ± 0.6	73.2 ± 1.6	11.8 d	3.1 e	15.0 c	14.0 e
Bebeco	45.9 ± 0.7	0.1 ± 0.1	29.0 ± 1.0	89.8 ± 0.7	40.6 ± 1.1	2.5 ± 0.3	17.2 ± 0.5	81.8 ± 1.0	5.3 e	2.4 e	11.8 cd	8.1 f
P. Tyrinthe	52.2 ± 0.7	5.8 ± 0.4	40.5 ± 0.7	81.8 ± 0.3	48.5 ± 0.3	8.6 ± 0.3	31.2 ± 0.7	74.5 ± 0.4	3.7 e	2.8 de	9.3 de	7.3 f

^aMeans ± SD.^bDL*, Da*, Db* = Differences in lightness and in chromaticity between oxidized and nonoxidized purées.^cMeans separation within columns by Tukey's HSD test, $P < 0.05$.

tivity. In addition, carotenoids influence enzymatic browning reaction (Kim et al., 1994). Because oxygen is the first substrate in enzymatic browning reactions (Janovitz-Klapp et al., 1990), β -carotene can influence the velocity of enzymatic reaction by acting as an oxygen quencher.

Hydroxycinnamic esters and flavan-3-ols, the two main classes of phenolic compounds, contributed to browning of apricots. Flavan-3-ols give pigments that are more intensely colored than those produced by chlorogenic acid (Rouet-Mayer et al., 1990). In the present study, the cultivars less susceptible to browning ('Cafona', 'Bebeco', and 'Précoce de Tyrinthe') were characterized by low initial percentages of flavan-3-ols. This suggested that flavan-3-ols (catechin monomers and oligomeric forms) played a prominent role in the development of brown coloration of apricot purées. Recently, Goupy et al. (1995) have described the role of some phenolics in browning. This work has been carried out with synthetic solutions containing chlorogenic acid and (-)-epicatechin. Chlorogenic acid oxidized by apple PPO gave higher a^* values than oxidized (-)-epicatechin. Multilinear regression analysis indicated that both phenolics contributed to the darkening (decrease in L^*), and Goupy et al. (1995) demonstrated that an increase in chlorogenic acid leads to an increase in a^* (redness), whereas (-)-epicatechin has almost no effect. Thus, in pears a high correlation between Da^* and the initial content of chlorogenic acid has been reported (Amiot et al., 1995). In apricots, no correlation has been obtained between the decrease in L^* and the initial content in chlorogenic acid. However, a good correlation ($r^2 = 0.64$) was obtained between the decrease in L^* (darkening of purées) and the initial content of flavan-3-ols (Table 3). In apricots, since chlorogenic acid is certainly a good substrate for PPO, browning depends mainly on the flavan-3-ol content. In addition, Aubert and Amiot (data not published) have shown that apple purées have high acceptability when $L^* > 40$ (high lightness and good texture) and H^* values are close to 90 (yellow purées). At lower L^* and H^* values, purées were rejected by the consumer. For apricot purées, the acceptability could be also related to $L^* > 40$. Sensorial analyses will be needed to specify H^* values (yellow or more orange purées).

Table 3. Correlation coefficients ($\times 1000$) between the browning data (DL*, Da*, Db*, DH°) vs. initial contents of phenolic compounds and polyphenol oxidase (PPO) activity.

Browning data	3'CQ	5'CQ	CAT	EPI	RUTIN	HCE	FLA	FLO	FLA/HCE	PPO
DL*	-230	-69	709*	429	-361	-53	803**	-264	780**	413
Da*	-255	20	394	170	-162	-83	601	-234	571	622
Db*	-14	-138	759*	571	-181	76	658	44	595	144
DH°	-129	-206	330	372	-338	-256	685*	-352	697*	394

*,**Significant at $P \leq 0.05$ or 0.01, respectively.

In conclusion, hydroxycinnamic esters, especially caffeoyl esters, were strongly degraded during oxidation and certainly contributed to a large extent to enzymatic browning. The *ortho*-caffeoyl quinones formed enzymatically may oxidize flavan-3-ols, which appear to be involved in the development of brown pigments. The degradation of carotenoids during oxidation may affect the organoleptic and nutritional qualities of apricot purées. In fact, β -carotene, with two ionone rings, is the provitamin A with the highest provitaminic activity (Gross, 1987). Further studies are needed to clarify the role of carotenoids and other factors, such as ascorbic acid and acidity in apricot browning. Such studies are of value for selecting cultivars with low browning and with high organoleptic and nutritional qualities.

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