Intervention of Phenolic Compounds in Plum Technology. 1. Changes during Drying

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The main simple phenolic compounds in plum likely to have an effect on the quality of the fruit were investigated by HPLC. Evolution of the compounds and of polyphenoloxidase (PPO) was monitored during the first phase of drying under the effect of different temperatures. The d'Ente plum is characterized by a high neochlorogenic acid content. Neochlorogenic acid content is 2.4 times as high in the epidermis. Rutin is largely predominant among the flavonol glycosides and is found only in the epidermis. Anthocyanins—principally rutinosides—are solely epidermic. The degradation of dihydroxycinnamic acids is directly connected to the evolution of PPO activity; they were thus more degraded when the drying temperature was low since PPO was not denatured as soon. In contrast, flavanoids (rutin and anthocyanin) were more degraded when the drying temperature was high, and their reaction to thermal treatment was distinctly different.

Phenolic compounds are very widely distributed in plants; they are particularly important in fruits and vegetables where they contribute to color and flavor. Reports on the subject (Harborne, 1964; Ribereau-Gayon, 1968; Van Buren, 1970) show that hydroxycinnamic derivatives are particularly interesting because of their relatively high concentration in fruits. Their contribution during technological processes, particularly in browning phenomena (enzymic or not), has been demonstrated by several authors (Mathew and Parpia, 1971; Golan et al., 1977; Vamos-Vigyazo, 1981).

The effect of oxidasic activities on phenolic compounds leads to the production of quinones that can form brown polymers. This browning is generally harmful to the quality of the processed produce. This is why it is useful to limit it by controlling phenoloxidase activity. However, enzymic browning may be sought, and a black color is considered a criterion of quality in certain dried products such as black tea, coffee, and prune skins.

Chlorogenic acid losses which may result from polyphenoloxidase (PPO) activity have been observed during the drying of various prune cultivars (De Moura and Dostal, 1965) and in d'Ente plums in particular (Puech and Jouret, 1974). Phenolic compounds in plums are thus modified during drying and in particular in the initial stages. In addition, the epidermis changes color during the first hours in the oven; anthocyanins are rapidly degraded (Moutounet, 1978).

HPLC was used to identify the main simple phenolics in plums likely to affect the quality of prunes. The evolution of these compounds and that of o-diphenoloxidases was monitored during the first phase of drying, which appeared to be decisive for the future of the product. The various temperatures used correspond to the temperatures encountered in practice in tunnel dehydrators (Gentry et al., 1965) or conveyor tunnels (Letang, 1986). The purpose of this work was to relate the disappearance of these potential substrates to the activity of the enzymes that may oxidize them; this was investigated in relation to the drying temperature applied.

MATERIALS AND METHODS

Plant Material. Work was carried out with use of Agen plums, clone 707 (*Prunus domestica*, L. cv. d'Agen), from Casseneuil (Lot et Garonne Department). The fruits were graded to obtain as homogeneous a sample as possible by manual sorting (average weight 20 g) and densimetric baths (density 1.080–1.090) according to Jouret and Maugenet (1967).

Drying Conditions. Drying of the fruit was carried out at three different temperatures in a ventilated oven (capacity 15 kW). Batches of 20 fruits were treated as follows: at 55 °C, 1, 2, 4, 8 h; at 75 °C, 30 min and 1, 2, 4 h; at 95 °C, 15 and 30 min, 1 h, 90 min, 2 h. The exocarp and pulp of each batch were separated and immediately frozen separately in liquid nitrogen, freeze-dried, and stored under vacuum. A batch of nondried plums was treated in the same way.

Extraction of Polyphenols. Five grams of freeze-dried material was ground for 2 min in a Polytron apparatus with petroleum ether. After removal of carotenoids with a Soxhlet apparatus (12 h at 55 °C), the residue was extracted twice with 50 mL of ethanol–ethyl acetate (v/v) under magnetic stirring for 20 min. After centrifugation (10 min at 3000*g*), the residue was resuspended in the same way three times in 50 mL of methanol. The different supernatants were pooled and evaporated to dryness under vacuum at 30 °C. The residue was resuspended in 20 mL of water at pH 3. The mixture was filtered on a Sartorius 0.45-μm filter and formed the crude polyphenol extract.

Separation and Identification of Single Polyphenols by HPLC. Separation of single polyphenols from the extract was carried out with use of HPLC on a Waters Associates apparatus consisting of an AGC 680 controller, a Data Module Model 680 recorder, two pumps (Models 45 and 6000), and a Model 440 double-detection absorption detector. A Spherisorb ODS 2 (particle size 5 μm) 250- × 4.6-mm column was used for the separation of phenolic compounds. The elution curve was linear to reach in 50 min 22% of the solvent acetic acid–acetonitrile–water (5:80:15, v/v) in the initial acetic acid–water solvent (5:95, v/v) with a flow rate of 1.5 mL/min. Peaks were detected simultaneously at 280 and 313 nm after injection of 10 μL of crude extract.

Separation of anthocyanins was carried out with a Bondapak $C_{18}W_3$ column (7.8 × 300 mm) fitted with a Brownlee C_{18} 30 × 4.6 mm precolumn. The initial gradient consisted of 5% solvent A (formic acid–methanol–water, 10:50:40, v/v) and 95% solvent B (formic acid–water, 10:90, v/v). The elution gradient was linear for 20 min to reach 30% A and 70% B and then 100% A at 40 min on curve 7. Detection of peaks was effected at 546 nm after injection of 50 μL of crude extract.

The columns were maintained at a constant 30 °C in a thermostatically controlled oven. Solvents were degassed by ultrasound and then filtered on Sartorius 0.45-μm cellulose filter before use.

Simple polyphenols were identified from the chromatograms by different methods (Ribereau-Gayon, 1968): simultaneous detection at two wavelengths (280 and 313 nm and then 280 and 365 nm for simple polyphenols and 280 and 546 nm for anthocyanins); coinjection with different standards supplied by Extrasynthese, with the exception of 5-caffeoylquinic acid (chloro-

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Table I. Nature and Concentration of the Phenolic Compounds Identified in a Polyphenolic Extract of the Pulp and Exocarp of Fresh Plums

phenolic compd	pulp, mg·g^{-1} dry wt	exocarp, mg·g^{-1} dry wt
neochlorogenic acid	2.6	6.25
chlorogenic acid	0.11	1.37
caffeic acid	0.055	0.036
catechin	0.10	0.74
rutin		2.20
anthocyanins		6.34
proanthocyanins	0.79	0.59

genic acid) from Fluka and 3-caffeoylquinic acid (neochlorogenic acid) available in a laboratory (Puech and Jouret, 1974); and comparison of absorption spectra plotted with a Waters Model 490 programmable multichannel UV/visible light detector with those of the corresponding control compounds plotted by a Kontron-Uvikon 810 spectrophotometer between 200 and 400 nm. The results were expressed in milligrams of the compound per gram of dry matter.

Proanthocyanidin Assay. Proanthocyanidins were determined by colorimetry after separation on Sephadex LH 20 using Moutounet's method (1981) modified. Two milliliters of crude extract was injected at the top of the column, and specific elution of the various groups of polyphenols was carried out by successive passage of different solvents: water containing 0.5% acetic acid; 5%, 20% and 100% methanol; (v/v) and then 60% acetone (v/v) at a flow of 40 mL/h. Polyphenols in the eluate were detected at 280 nm with use of an Isco Model UA5 absorbance monitor UV apparatus. The different fractions recovered, corresponding to the fractions eluted by each solvent, were analyzed with use of a Kontron Uvikon 810 spectrophotometer between 200 and 400 nm. The fraction containing the proanthocyanidins (100% methanol) was evaporated under vacuum, and the anthocyanidins resulting from acid hydrolysis by a butanol–HCl–$FeSO_4$ mixture were assayed by colorimetry at 500 nm (Pompei et al., 1971).

Extraction and Determination of the Activity of Polyphenoloxidases. Enzymic extracts were prepared from freeze-dried pulp and exocarp with the procedure used by Moutounet (1976). Polyphenoloxidase activity was measured by polarography with a Clark-type oxygen electrode (Yellow Springs Instruments, Yellow Springs, OH). The standard reaction mixture contained 15 mL of McIlvaine buffer at pH 4.25 and 2.5 mL of 0.02 M chlorogenic acid in the same buffer. It was equilibrated under air at 30 °C by magnetic stirring until the medium was saturated with oxygen (0.23 mM O_2 dissolved at 30 °C). The enzymic reaction was started by the addition of 0.2 mL of enzymic extract. The O_2 used by the enzymic reaction was calculated in time from the linear portion of the initial curve; the results were expressed in micromoles of O_2 per minute per milliliter of crude enzymic extract.

RESULTS

Type and Amount of the Main Phenolic Compounds. The chromatographic profile of a polyphenolic extract of plum pulp was characterized by a predominance of a phenol acid. This was neochlorogenic acid, which formed 66.5% of total phenols detected (chlorogenic equivalent), i.e., 2.6 mg·g^{-1} of freeze-dried pulp (Table I). Its isomer, chlorogenic acid, formed only 0.11 mg·g^{-1} of the pulp.

The same dihydroxycinnamic derivatives predominated in the exocarp (Figure 1), but the levels were distinctly higher. Neochlorogenic acid was also preponderant (6.25 mg·g^{-1} of dry matter), followed by chlorogenic acid (1.37 mg·g^{-1} of dry matter). These contents were, respectively, 2.4 and 12.4 times higher than in the pulp. Very low concentrations of free caffeic acid were present in both the pulp and exocarp. No dicaffeoylquinic derivatives were found in plum extracts with reference to an isochlorogenic acid standard (Corse et al., 1965) made up of a mixture of monocaffeoyl- and dicaffeoylquinic derivatives.

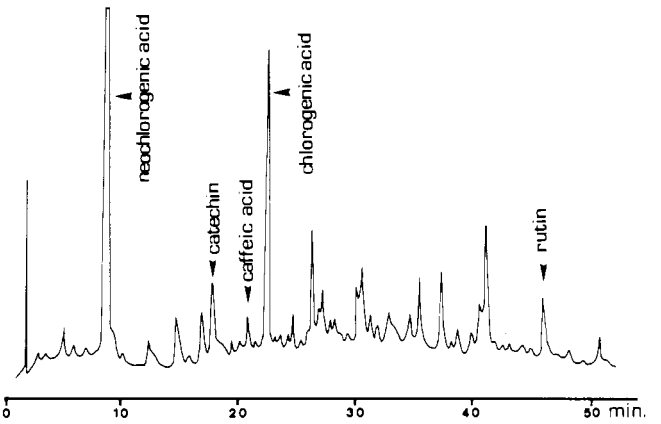

Figure 1. HPLC profile of a polyphenolic extract of d'Ente plum exocarp.

Among flavans, only catechin was identified in the pulp at levels as high as those of chlorogenic acid (0.10 mg·g^{-1} of dry matter). The catechin content was 7 times higher in the same amount of exocarp (0.74 mg·g^{-1} of dry matter). Its isomers epicatechin and gallocatechin, which have been reported in other varieties of plums (Herrmann, 1958), were not identified in d'Ente plums within the limits of sensitivity of our assay.

In flavonol glycosides, rutin (quercetin 3-rutinoside) was found only in plum exocarp; the levels were relatively high, reaching 2.2 mg·g^{-1} of dry matter in fruit before drying. The other flavonol glycosides found in d'Ente plums by other authors (Bate-Smith, 1961; Harborne, 1967), such as quercetin 3-rhamnoside, quercetin 3-glucoside, and kampferol, were not found in the plums studied within the limits of the detection threshold of these compounds (0.02 mg/g of dry weight).

The four anthocyanins previously identified by Van Buren (1970) in Victoria plums were found in the exocarp extracts in the present work. They were 3-glucoside and 3-rutinoside derivatives of cyanidin and peonidin. The total amount was on the order of 6.34 mg·g^{-1} of dry weight. Rutinoside derivatives were predominant: Cyanidin 3-rutinoside and peonidin 3-rutinoside formed 44% and 42%, respectively, of the total anthocyanins, whereas cyanidin 3-glucoside was present in quantities that did not reach the detection threshold of the methods used.

Proanthocyanidins were present in the pulp and exocarp at levels of 0.79 and 0.59 mg·g^{-1} of dry weight (Table I). It can be seen that these compounds form nearly 22% of total polyphenols measured in plum pulp.

Change of the Main Phenolic Compounds during Drying. Evolution of the two caffeoylquinic derivatives was similar at the start of drying (Figure 2). However, neochlorogenic acid seemed to disappear proportionally more rapidly than its isomer. Since it is more plentiful in the pulp, it might become the preferential substrate of oxidases. The rate of degradation of these compounds was high during the first 2 h irrespective of the drying temperature. It then fell and tended to stabilize after 4 h of drying. After 8 h at 55 °C, there remained 27.1% neochlorogenic acid and 36.5% chlorogenic acid. The changes of these two caffeoylquinic derivatives were similar for the three temperatures studied. Nevertheless, it should be noted that degradation was more marked as the temperature fell.

The rate of degradation of these two compounds in the exocarp was much more rapid than in the pulp (results not described). Indeed, whatever the outside temperature, the amounts of these compounds were already lower after 1 h than in the pulp after 2 h of drying.

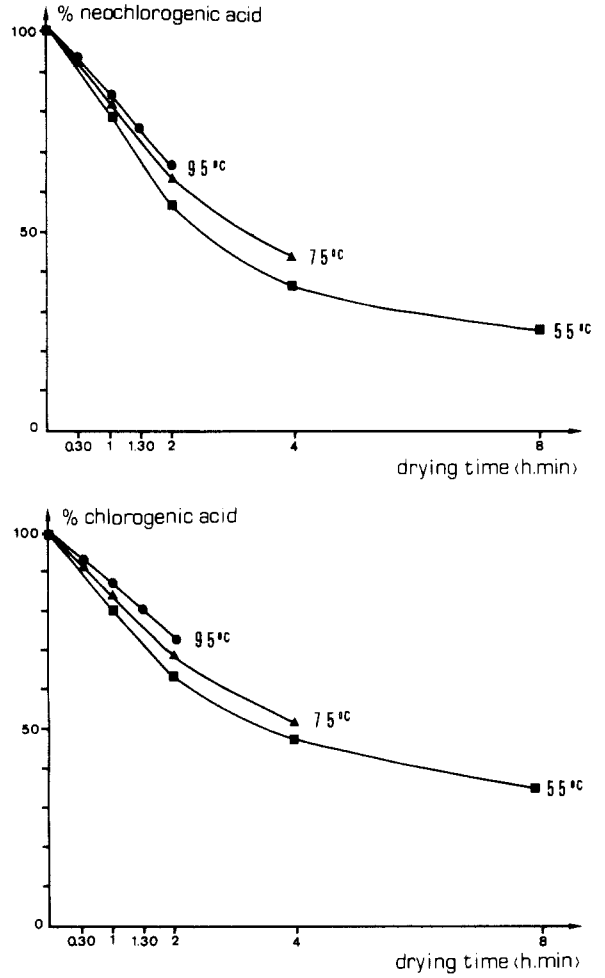

Figure 2. Evolution of neochlorogenic and chlorogenic acids in d'Ente plum pulp during the initial hours of drying at several temperatures.

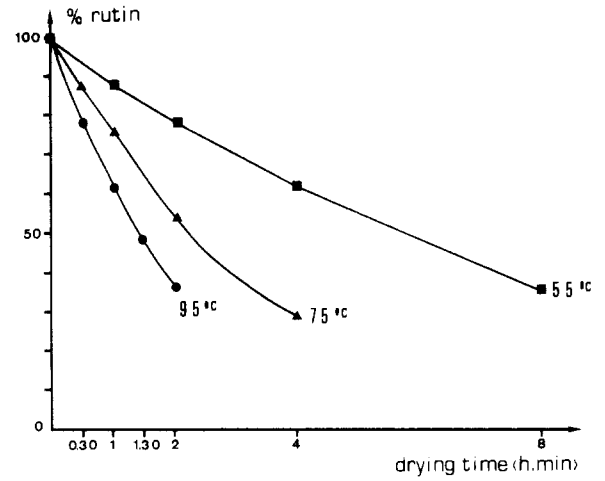

Figure 3. Evolution of rutin in d'Ente plum exocarp during the initial hours of drying at several temperatures.

The evolution of catechin during drying displayed similar features to that of dihydroxycinnamic acids. However, it disappeared more slowly (results not described).

Degradation of rutin was quasi-linear as a function of drying time, particularly at 55 °C (Figure 3). In contrast with the kinetics observed in the case of the compounds above, the rate of degradation of rutin increased as the drying temperature rose. Thus, 36% rutin remained after only 2 h at 95 °C, whereas the same percentage was reached after 8 h at 55 °C.

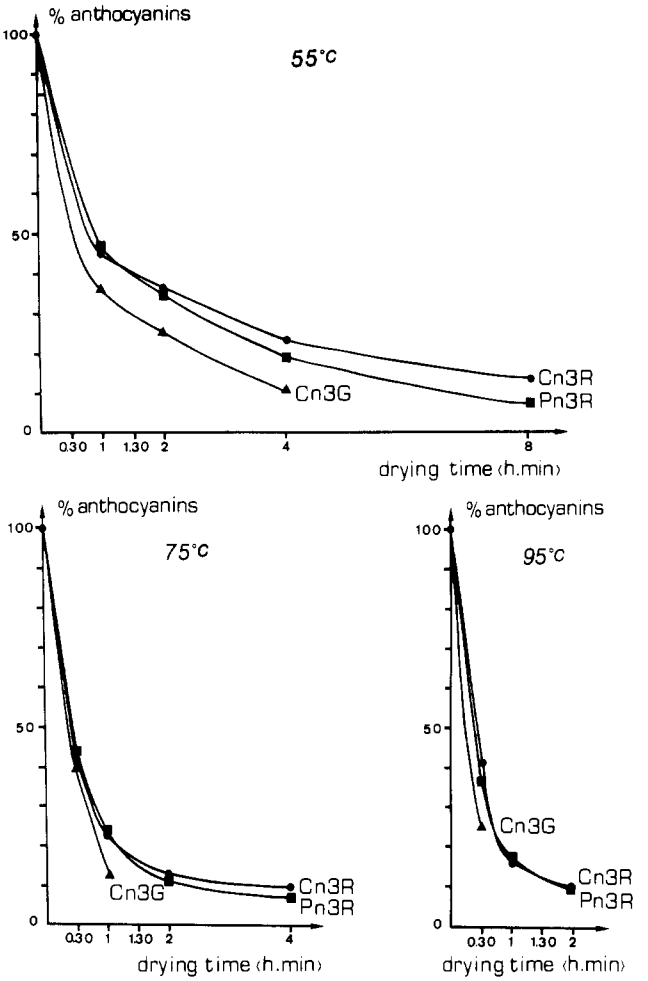

Figure 4. Evolution of anthocyanins in d'Ente plum exocarp during the initial hours of drying at different temperatures: Cn3G, cyanidin 3-glucoside; Cn3R, cyanidin 3-rutinoside; Pn3R, peonidin 3-rutinoside.

The three types of anthocyanins isolated disappeared very rapidly (Figure 4). Indeed, this phenomenon took place essentially during the first hour. It was more marked as the temperature rose. Remaining after 1 h at 95 °C were 14.6% Cn3R and 16.8% Pn3R, whereas 45.6% and 46.9% remained after 1 h at 55 °C. In addition, the glucoside derivative was slightly more sensitive than the rutinoside derivatives at the three temperatures.

Change of Polyphenoloxidase Activities during Drying. During the first hours of drying, PPO activity in the pulp fell strongly when the surrounding temperature was above 55 °C. There were only 14% and 27% residual activities after 2 h at 95 and 75 °C (Figure 5). In contrast, denaturation of PPO was slow and progressive at 55 °C. Residual activity was still 27% after 8 h. The activity of this enzyme after 2 h at this temperature was 85% of the initial activity.

Denaturing of PPO in the exocarp displayed the same variations as the pulp, leading to similar residual activities at the end of treatment at the temperatures used (results not described). Nevertheless, loss of activity was more rapid at 55 °C during the first few hours (70% residual activity after 2 h) than at higher temperatures where denaturation was less pronounced during the first 2 h of drying.

DISCUSSION

The d'Ente plum, like other fruits of the genus *Prunus*, is characterized by a high caffeoylquinic acid content. Whereas chlorogenic acid accumulates preferentially in

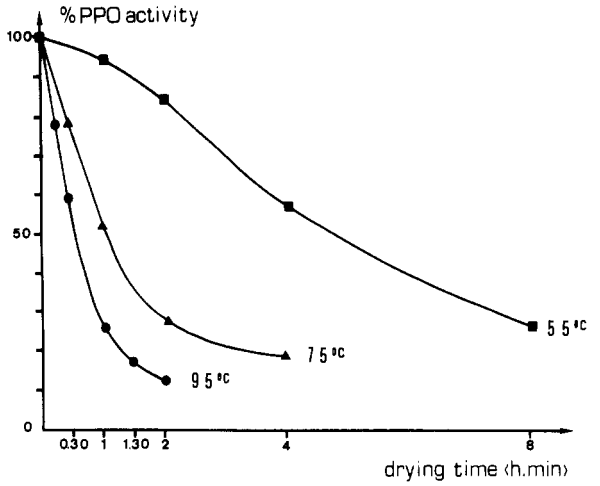

Figure 5. Evolution of PPO activity in d'Ente plum pulp during the initial hours of drying at different temperatures.

numerous fruits, neochlorogenic acid is predominant in many species of *Prunus* (Sondheimer, 1958; Macheix et al., 1977). The d'Ente plum is thus also characterized by a predominance of 3-caffeoylquinic ester (85% caffeoylquinic acids) mainly located in the exocarp.

Free caffeic acid was also found in small quantities in the plum extracts. This acid is very rarely encountered in a free state in fruits. It is possible that in the case studied use of HPLC might make such detection possible.

As in many other fruits, flavans are not plentiful and are mainly located in the exocarp. Predominance of flavans in the exocarp (the concentration was 7 times higher than in plum pulp) is frequent in other fruits such as apples (Van Buren, 1970). The concentration of these compounds, like all the *o*-diphenols, falls during maturation (Vamos-Vigyazo et al., 1984). It is doubtless for this reason that the catechin content is so low, particularly in d'Ente plum pulp since this fruit is harvested after the physiological maturity.

Rutin is clearly the predominant flavonol glycoside and is located only in the exocarp. It is not surprising that rutin (quercetin 3-rutinoside) is present in plums since quercetin derivatives are frequently the most plentiful in fruits, but its predominance is remarkable (2.2 $mg \cdot g^{-1}$ of dry matter). Its presence in such quantities has only been reported in certain varieties of cherries (Swain, 1962; Harborne, 1967) and in tomatoes, where it was found only in the epidermis (Wu and Burrel, 1958). The yellow color of the pulp zone is certainly not caused by flavonols but by carotenoids (Moutounet and Mondies, 1979).

The anthocyanins in d'Ente plums are uniquely epidermic and consist essentially of rutinosides. Cyanidin derivatives (cyanidin 3-glucoside, cyanidin 3-rutinoside) are the most widespread of the anthocyanins listed by Van Buren (1970) in numerous fruits. Peonidin 3-rutinoside, which forms 42% of the total anthocyanins in d'Ente plums, is to the best of our knowledge only found in the genus *Prunus*, except for *Duchesnea chrysantha*; in addition, it is only found in certain varieties: *Prunus cerasus* var. Monmorency (Shrikhande and Francis, 1973), *Prunus avium* var. Bigarreau Napoléon (Melin et al., 1979), *P. domestica* var. Victoria (Harborne, 1967), and *Prunus spinosa* (Harborne, 1967). It should be noted that the four anthocyanins found in d'Ente plums are identical with the four anthocyanins found in Victoria plums and in sloe (*P. spinosa*) (Van Buren, 1970).

Condensed polyphenols, which are polymers connected by covalent bonds, are very disparate compounds. They are condensed flavans, called proanthocyanidins, whose presence has been reported in all fruits. Knowledge of these compounds is less advanced than that of the other polyphenols. Indeed, study using HPLC is still delicate because of the low solubility and high reactivity of polyphenols. In plums, these compounds are generally represented in the pulp (0.79 $mg \cdot g^{-1}$ of dry matter) as reported in the Victoria variety (Hillis and Swain, 1959). Nevertheless, catechin (proanthocyanidin monomer) is only present at 0.1 $mg \cdot g^{-1}$ of dry matter in this part of the fruit. Indeed, the degree of condensation increases during maturation, causing the proanthocyanidin content to increase at the expense of monomers (Van Buren, 1970). The amounts of proanthocyanidin found in plums are doubtlessly underestimated since it is not known whether the high molecular weight compounds are insoluble or bound to the cell wall. It is highly probable according to Gupta and Haslam (1980) that these proanthocyanidins, which are hardly soluble, may often form the major part of the proanthocyanidins present.

Putting into contact cytoplasm oxidases and these phenol acids located in the vacuole can only be achieved by loss of selective permeability or denaturation of membranes. This phenomenon takes place very rapidly at the beginning of drying (Raynal et al., 1985) and oxidation of phenols can therefore take place. The process stops subsequently after denaturation of the enzymic proteins whose intensity increases with the level and duration of application of drying temperature. It is interesting to report that all the conditions are apparently present in plums for the reactions resulting from this contact to be optimal. Indeed, PPO in d'Ente plums stands out from that of other fruits in that its maximum pH for activity is among the lowest (4.25), which is close to the pH of plum juice (3.8). It has a rather high resistance to thermal denaturation (destructuration coefficient z = 16 °C) (Moutounet, 1976), and a remarkable affinity for chlorogenic acids, the most plentiful substrates in plums ($K_{m,app}$ 2.38 mM).

The disappearance of the caffeoylquinic substrates is directly related to residual polyphenoloxidase activity. The internal temperature increases rapidly for the first 30 min, whatever the surrounding temperature, and then tends to stabilize (Raynal et al., 1985). Denaturation of PPO was slow with a surrounding temperature of 55 °C; as a result, oxidation is more pronounced in the polyphenol pool.

Denaturation of PPO is much faster with the surrounding temperatures of 75 and 95 °C. It therefore follows that dihydroxycinnamic acids are decreasingly degraded as the drying temperature rises. Nevertheless, the deviation observed in residual PPO activity between 55 and 75 °C is not repeated in the curves of the rate of oxidation of dihydroxycinnamic acids. This disagreement is probably a result of the simultaneous effect of two phenomena. Firstly, cell destruction takes place much more rapidly at drying temperatures of 75 and 95 °C than at 55 °C. The action of PPO on dihydroxycinnamic acids is therefore much earlier, resulting in acceleration of the rate of oxidation of the substrates. Secondly, denaturation of these enzymes takes place more rapidly at these drying temperatures. As a result, the rate of oxidation of dihydroxycinnamic acids falls more rapidly than that at a drying temperature of 55 °C.

The epidermis was subjected to an external temperature of 55 °C and was at a higher temperature than the pulp; the rate of PPO denaturation was therefore faster even though the enzyme was protected to a certain extent by the cuticle. Cell destruction must also have taken place more rapidly, resulting in greater *o*-diphenol oxidation rates than in the pulp. At drying temperatures of 75 and

95 °C, the cuticle no longer protects PPO; fusion takes place at about 65 °C (McBean et al., 1971). In contrast, it no longer forms an obstacle to the evaporation of water from the fruit. Acceleration of evaporation causes relative diminution of the temperature in the epidermis cells; this results in later denaturation of PPO than in the pulp. Oxidation of *o*-diphenols is therefore more rapid and more extensive than in the pulp.

Degradation of rutin and anthocyanins is not directly connected with the denaturation of PPO since these compounds disappear more rapidly as the temperature rises. Flavonoids are therefore not degraded by the same mechanism as phenolic acids. These compounds are not direct substrates of the oxidases (Baruah and Swain, 1959; Walker, 1964), as PPO does not act directly on glycosides.

Nevertheless, degradation of anthocyanins is very rapid. Anthocyanin molecules are particularly unstable as a rule and are sensitive to technological processing, particularly when heat is involved. During these processes, the balance between the various forms of anthocyanins moves rapidly toward the pseudobase, which is destroyed by oxidation mechanisms (Chichester and McFeeters, 1970). It is therefore difficult to identify the respective roles of the two factors—enzymatic and thermic—that may have an effect on the disappearance of anthocyanins from plum exocarp.

The special behavior of anthocyanins during the first phase of drying raises the problem of understanding the mechanisms involved. Several hypotheses can be put forward in light of the literature on the degradation of anthocyanins. Research on this subject is the subject of the second part of this investigation.

ACKNOWLEDGMENT

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Registry No. PPO, 9002-10-2; neochlorogenic acid, 906-33-2; chlorogenic acid, 327-97-9; caffeic acid, 331-39-5; catechin, 154-23-4; rutin, 153-18-4; cyanidin 3-glucoside, 7084-24-4; cyanidin 3-rutinoside, 18719-76-1; peonidin 3-rutinoside, 27539-32-8.

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