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Physical pre-treatment of plums (*Prunus domestica*). Part 2. Effect on the quality characteristics of different prune cultivars

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Abstract

The effects of an alternative physical pre-treatment for enhancing the drying rate of different plums (*Stanley, Angeleno*®, and Empress), are evaluated by means of the principal chemical parameters and by skin colour. The pre-treatment consists of the superficial abrasion of the plums' peels using an inert abrasive material to remove the cuticular waxy layer, the limiting factor for moisture loss. The drying process was carried out at 60 °C to reduce the plums' quality loss, the latter being assessed by analysing the changes in skin colour, sugars by HPLC, total phenols, total anthocyanins, and reactive substances to the vanillin–HCl reagent. The proposed physical pre-treatment, without significantly altering the other qualitative characteristics of the plums, markedly reduced the dehydration time and, as a result, caused a smaller loss of sugars in *Empress* and *Angeleno* than *Stanley* plums.

Keywords: Colours; Dehydration; Phenols; Plums; Prunes; Sorbitol

1. Introduction

Drying is a means of extending food shelf-life by avoiding microbial spoilage, minimising packaging requirements and economising on shipping cost. At the same time, consumer demand requires the development of operations which minimise the adverse effects of processing, such as decreases in nutritional value and changes in colour (Nijhuis, Torringa, Muresan, Yuksel, Leguijt, & Kloek, 1998). In some instances, for example in plums, the dried product achieves a characteristic flavour (Sabarez, Price, & Korth, 2000), which means that it reaches a different market from the fresh fruit. Thus, in addition to the traditional fresh fruit market, the use of prunes in the confectionery industry has increased notably. The varieties utilised to produce plums, and especially the American hybrids, are characterised by their great size, high sugar levels and intense colour (Crivelli, Cortellino, Genna, & Citro, 1998; Newman, Price, & Woolf, 1996). Few varieties of European plums are still cultivated, for their large dimensions are destined mainly for fresh consumption; while the use of plums for double purposes (fresh and dried consumption) is becoming widespread (Sansavini & Lugli, 1998). Changes in glucose, fructose, sucrose, and sorbitol were studied during dehydration of *d'Agen* prunes at different temperatures (70–90 °C) (Wilford, Sabarez, & Price, 1997). The sorbitol content, peculiar to fruits of the Rosaceae family, is one of the criteria used when choosing the variety for drying (Forni, Erba, Maestrelli, & Polesello, 1992). In fact, sorbitol, in addition to possessing a good laxative effect at low doses (70 g/day), is not easily caramelised and is not a reactant molecule in the Maillard reaction, thereby preventing excessive browning in prunes.

Phenolic compounds contribute to colour and flavour; moreover, flavonoid substances, presence of which has been already observed in prunes (Risch & Hermann, 1988; Donovan, Meyer, & Waterhouse, 1998; Arts, van de Putte, & Hollman, 2000), are potentially beneficial to human health.

During drying, usually carried out at temperature close to 80 °C, the degradation of phenolics is very rapid, due to both enzymatic and thermal reactions that

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induce browning phenomena (Raynal, Moutounet, & Souquet, 1989). The mathematical model of the dehydration of pretreated prunes constitutes the object of our first research paper (Part 1).

In this paper, the effects of physical and chemical pretreatments, which, briefly, consist of a preliminary abrasion of the plum peel and dipping into an alkaline solution containing ethyl oleate (usually adopted for the drying of grapes), so as to accelerate the drying rate, were evaluated in different plums, dehydrated at 60 °C. The European cultivars, *Stanley*, excellent for drying, *Empress*, usually produced for the fresh market, and the chinese-japanese hybrid *Angeleno®*, were compared.

2. Materials and methods

2.1. Sampling

Samples of three cultivars of plums (*Prunus domestica*) at commercial maturity (*Stanley*, *Angeleno®* and *Empress*), were obtained from the public "Fruit Tree Research Institute" orchards in the Campania region, Italy. The plums were evaluated for pH, titratable acidity, skin colour, sugars by HPLC, total phenols, total anthocyanins, and substances reactive to vanillin–HCl. The same analyses, except for the first two, were repeated on the plums after drying. All values reported are calculated on a dry weight (dw) basis and represent the average value of five repetitions of the analyses. A one-way analysis of variance (ANOVA) was used for statistical comparison, and multiple comparison within these was performed by means of the Bonferroni test; the data in the tables sharing a common letter were not significantly different ($P < 0.05$).

2.2. Drying experiments

Drying experiments were carried out in a convection oven at 60 °C, with an air speed of 0.5 m/s, so as to reduce the average moisture of plums to about 0.25% w/w. Before drying, samples of about 20 plums for each variety (code: St = *Stanley;* Em = *Empress;* An = *Angeleno*) were submitted to one of the following pretreatments (TR): (1) abrasion in a pilot plant (Part 1) for 15 min (Abr); (2) immersion in an aqueous solution at 2% (v/v) ethyl oleate and 2.5% (v/v) K_2CO_3 at 40 °C for 5 min (EtOl) (Di Matteo, Cinquanta, Galiero, & Crescitelli, 2000); and (3) untreated samples as reference (UT).

2.3. Standard quality evaluation

Skin colours (L^*, a^*, b^*) of 20 prunes were assessed with a CR-200 Chromameter (Minolta, Japan) having an aperture size of 10 mm. The chroma $[(a^*)^2+(b^*)^2]^{1/2}$ and hue, attributes of chromaticity, indicate a measure of the colour intensity and of the visual property normally regarded as colour, respectively. The hue (degree) was calculated as $[(\arctan b^*/a^*)\times 360°/(2\times 3.14)]$. Titrable acidity was measured by titration with 0.1 N NaOH to pH 8.1 and expressed as malic acid; pH was carried out with a glass-electrode pH-meter (Hanna Instruments).

2.4. Sugars

Sugars were determined by HPLC in a Waters 600 apparatus (Milford, MA, USA) with a refractometric detector (Waters 470), and with a 300×4 (id) mm column Sugar-Pak-(Waters), at 85 °C; the flow rate of the eluate was 0.6 ml/min, according to AOAC (1989).

2.5. Analysis of phenols

A random selection of 100 g of fruit pulp were frozen in nitrogen and ground in a Waring blender, after removal of carotenoids with a Soxhlet apparatus (10 h at 55 °C).

About 5 g of the residue were extracted twice with 50 ml of water–methanol (40:60, v/v) under magnetic stirring for 30 min at 4 °C; the first sub-sample was analysed for its total phenol content and the second for substances reactive to the vanillin–HCl reagent.

2.6. Total phenols

Total phenols were determined colorimetrically at 760 nm (spectrophotometer Perkin Elmer, mod. Lambda Bio 40) and expressed as gallic acid equivalents. After dilution, the samples were added to 5 ml of the Folin-Ciocalteu reagent, 15 ml of a $CaCO_3$ solution (10% w/w), and placed in darkness for 90 min at 30 °C before spectrophotometric analysis.

2.7. Compounds sensitive to vanillin–HCl

Compounds sensitive to the vanillin–HCl reagent were determined with the method described by Price, Van Scoyoc, and Butler (1978). To a portion of methanolic extract was added a 5 ml solution of 0.5% vanillin in methanol, with 4% of HCl. The absorbance of the resulting mixture was measured at 500 nm after 20 min at 30 °C. The results were expressed as (+)-catechin equivalents.

2.8. Total anthocyanin

About 5 g of the powder were poured into 15 ml of a HCl/water/ethanol solution (1/29/70) and stirred for 15 min at 4 °C. The extraction was performed three times. Duplicates of all samples were analysed for pigment content. Sub-samples were diluted, filtered and recorded

Table 1
Main chemical composition and dimensions of fresh plums

	Angeleno®	*Stanley*	*Empress*
Moisture (%)	84.0±3.3	78.6±4.1	79.3±3.2
pH	3.1±0.08	3.4±0.06	3.7±0.06
Acidity (g malic acid×100 g)	0.71±0.02	0.72±0.01	0.5.3±0.02
Weight of fruit (g)	61.6±3.1	46.7±2.2	75.2±4.3
Length of fruit (m)	4.8±0.2 (10^{-2})	5.4±0.3 (10^{-2})	6.0±0.4 (10^{-2})
Width of fruit (m)	4.6±0.2 (10^{-2})	3.9±0.1 (10^{-2})	4.7±0.3 (10^{-2})
Weight of stone (g)	1.2±0.1	1.6±0.2	2.1±0.2
Stone/fruit ratio (w/w)	0.019	0.034	0.028
Length of stone (m)	1.5±0.1 (10^{-2})	3.1±0.2 (10^{-2})	3.2±0.1 (10^{-2})
Width of stone (m)	1.1±0.1 (10^{-2})	0.9±0.1 (10^{-2})	0.9±0.1 (10^{-2})

in a spectrophotometer DS100S (Varian, Australia) using 1 cm path length quartz cells. The total anthocyanin content was expressed as cyanidin-3-rutinoside. The $E_{\text{molar abs}}$ of cyanidin-3-rutinoside was equal to 32,800 at $\lambda_{\max}$ absorbance (about 534 nm), in HCl/water/ethanol (1/29/70) at 20 °C, on known dilutions of cyanidin-3-rutinoside chloride. For purposes of molar absorptivity calculations, the molecular weight did not include the weight of a chloride counterion.

2.9. Chemicals and reference compounds

The reagents (Carlo Erba, Milan, Italy) were analytical or HPLC grade, as required. Cyanidin 3-glucoside chloride, and (+)-catechin were purchased from Extrasynthèse (Genay, France); gallic acid and sugars were purchased from Sigma Chemical Co. (St. Louis, USA).

3. Results and discussion

Table 1 shows the main chemical and physical parameters of about 20 plums for each variety considered (*Angeleno, Stanley,* and *Empress*). The *Empress* showed the greatest dimensions, while the ratio between the diameters of fruits was almost identical among the varieties. Moreover, the incidence of the stone was always less than 3.5% (w/w). Finally, the *Angeleno* showed the lowest pH values. At the end of the drying process, the original structure of all prunes was maintained, independently of the pre-treatment used. The abrasion did not involve any loss of juice since not one crack was observed either after the physical pre-treatment or after drying. The behaviours of the different cultivars during the dehydration tests were different. The *Stanley* showed small differences between the drying times of untreated (UT = 30 h) and treated samples (EtOl = 25 h; Abr = 24 h). The *Empress* showed the longest dehydration times (UT = 45 h; EtOl = 35 h; Abr = 30 h), underlining in a more evident manner the positive effect of the pre-treatment, above all the physical one. The experimental drying values of pre-treated and untreated *Angeleno* plums are shown in Fig. 1. A more in-depth analysis of the drying kinetics and the effect of the pre-treatments on *Angeleno* plums constitute the main subject of another research paper.

Stanley plums had the greatest concentrations of total sugars, correlated with a greater amount of sorbitol (Table 2), the latter confirming what has been reported by Wilford et al. (1997). The cultivars with a larger amount of sorbitol in the fresh fruit were the following: *Stanley* 203 g kg^{-1} (dw), and *Empress* 161 g kg^{-1} (dw), which retained their sorbitol content entirely, after drying, without significant differences between samples. In the same way the *Angeleno* plums, having the lowest sorbitol content 104 g kg^{-1} (dw), preserved this content after drying, thus indicating the good stability of sorbitol in plums dried at 60 °C.

The sucrose content was highest in *Stanley* plums and lowest in *Angeleno* plums. After drying, the sucrose disappeared entirely, except in *Stanley* prunes; this different behaviour between varieties during drying has already been reported (Crivelli et al., 1998), as has been the co-occurence of thermal degradation and hydrolysis of sucrose, which yields glucose and fructose. In all the varieties studied, glucose was the most representative

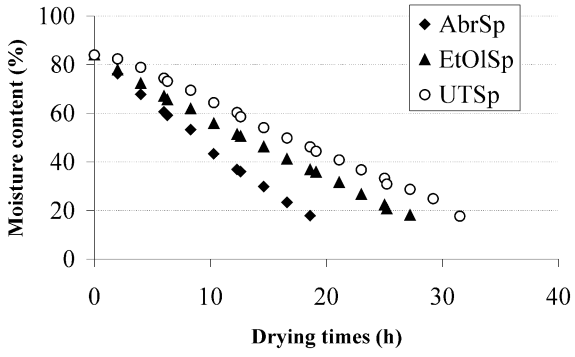

Fig. 1. Experimental (Sp), values of moisture changes (%) vs drying times for *Angeleno* plums, the peel of which was untreated (UT), or pre-treated by dipping into ethyl oleate (EtOl), or by abrasion (Abr).

sugar, with a low variability among them. The fructose content, on the other hand, varied significantly among varieties, with the highest concentration in *Angeleno* plums: 221 g kg^{-1} (dw), and the lowest values in *Empress* plums: 65 g kg^{-1} (dw). After drying, the glucose and fructose contents increased in *Stanley* plums, without differences between samples, while the concentrations of both sugars increased only in the *Angeleno* and *Empress* pre-treated samples.

The pre-treatments caused the final contents of glucose and fructose to be higher than those found in the untreated samples, except in *Stanley,* due to the lowest dehydration times. Prolonged exposure to the high temperatures of the untreated product favoured the loss of the two monosaccharides, due to the onset of caramelisation reactions, which only occur at very low moisture content. On the other hand, insignificant differences were found between sugar contents of samples submitted to chemical or physical pre-treatments.

Stanley and *Empress* plums showed quite similar L^* (lightness), and a^* (redness) values, both in fresh and dried products (Table 3). In the prunes, the L^* values decreased significantly (indicating increased darkness), without significant differences between the samples. The *Angeleno* prunes had the lowest L^* values, which did not vary significantly in the physical and chemical pre-treated prunes, while they approximately halved in untreated samples. The a^* values were highest in *Angeleno* plums and decreased significantly in all dried samples, to a lesser extent in the EtOl samples. The *Empress* prunes were more stable with regard to the a^* values. The b^* (yellowness) values decreased significantly in *Stanley* and *Empress* prunes, without differences between samples, while *Angeleno* prunes showed different b^* values. After drying, the significant decreases in L^* and a^* values in *Angeleno* untreated prunes can be explained by the variety's sensitivity to the prolonged heating time.

Generally, the drying process induces the formation of a dark purple colour that reduces the noticeable differences in the original products and does not change in relation to the pre-treatments or in UT.

Table 2
Sugar content (% dry weight) in plums as fresh product or dried when using no pre-treatment (UT), ethyl oleate dipping (EtOl) or abrasion (Abr)

Varieties	Samples	Pre-treatment	Glucose[a]	Fructose[a]	Sorbitol[a]	Sucrose[a]
Angeleno	Fresh	–	25.3±1.2a	22.1±1.6a	10.4±0.8a	8.1±0.6
Angeleno	Dried	UT	26.4±1.5a	25.8±2.0a	9.1±0.6a	–
Angeleno	Dried	EtOl	29.6±2.1b	28.1±1.8b	9.5±0.7a	–
Angeleno	Dried	Abr	29.7±1.9b	29.0±2.1b	9.4±0.5a	–
Stanley	Fresh	–	25.7±1.3a	9.9±0.5a	20.3±0.9a	15.8±1.8a
Stanley	Dried	UT	31.6±2.5b	13.8±0.8b	18.4±0.8a	0.7±0.03b
Stanley	Dried	EtOl	34.8±2.1b	16.1±0.8b	18.9±0.5a	1.4±0.2c
Stanley	Dried	Abr	34.2±2.2b	14.9±0.9b	19.5±0.9a	3.8+0.4d
Empress	Fresh	–	26.1±1.9a	6.5±0.5a	16.1±0.9a	14.6±1.1
Empress	Dried	UT	31.2±2.3a	10.1±0.7a	15.1±0.8a.	–
Empress	Dried	EtOl	35.2±2.4b	13.1±0.8b	15.9±0.6a	–
Empress	Dried	Abr	34.1±2.2b	12.2±0.3b	14.8±0.5a	–

[a] Mean±standard deviation of five analyses. Means for each cultivar within a column sharing common letter were not significantly different ($P<0.05$).

Table 3
Colour parameters of plums as fresh product or dried when using no pre-treatment (UT), ethyl oleate dipping (EtOl) or abrasion (Abr)

Varieties	Samples	Sample pre-treatment	L^*[a]	a[a]	b[a]	Hue (degree)	Chroma
Angeleno	Fresh	–	35.3±4.2a	37.3±2.4a	2.9±0.4a	4.4±0.3a	37.4±2.4a
Angeleno	Dried	UT	16.1±2.5b	2.8±0.3b	1.8±0.6b	32.6±11.3b	3.4±0.1b
Angeleno	Dried	EtOl	30.2±4.8a	14.7±1.2c	5.7±0.7c	21.3±4.0ab	15.8±0.9c
Angeleno	Dried	Abr	31.4±5.2a	5.4±0.5b	−1.2±0.1d	347.3±2.2c	5.5±0.5b
Stanley	Fresh	–	40.3±6.2a	2.2±0.3a	−11.4±0.9a	280.8±0.6a	11.6±0.9a
Stanley	Dried	UT	24.5±2.5b	3.2±0.3b	−3.7±0.3b	310.8±0.4b	4.9±0.4b
Stanley	Dried	EtOl	28.1±2.8b	3.6±0.2b	−4.2±0.3b	310.6±3.6b	5.5±0.1b
Stanley	Dried	Abr	25.1±3.2b	3.1±0.2b	−3.9±0.2b	308.4±0.4b	5.0±0.3b
Empress	Fresh	–	40.4+3.7a	3.0±0.4a	−6.8±0.7a	296.2±15.7a	7.6±1.9a
Empress	Dried	UT	26.5±2.5b	3.0±0.3a	−4.2±0.4b	305.3±4.3a	5.2±0.5a
Empress	Dried	EtOl	27.3±2.8b	3.1±0.2a	−4.6±0.3b	304.4±3.5a	6.5±0.2a
Empress	Dried	Abr	29.9±3.2b	3.7±0.2b	−5.4±0.4b	304.6±2.7a	5.5±0.2a

[a] Mean±standard deviation of five analyses. Means for each cultivar within a column sharing common letter were not significantly different ($P<0.05$).

Table 4
Total phenols, catechins, and anthocyanins (mg/g dry weight) of plums as fresh product or dried when using no pre-treatment (UT), ethyl oleate dipping (EtOl) or abrasion (Abr)

Varieties	Samples	Sample pre-treatment	Total phenols[a] (as gallic acid)	Reactive subst. to the vanillin–HCl (as catechin)	Anthocyanins (as cyanidin-3-rutinoside)
Angeleno	Fresh	–	7.5±0.3a	2.2±0.2a	5.2±0.4
Angeleno	Dried	UT	6.1±0.2b	3.1±0.3b	–
Angeleno	Dried	EtOl	7.0±0.3ac	3.5±0.2b	–
Angeleno	Dried	Abr	6.8±0.3c	3.1±0.3b	–
Stanley	Fresh	–	5.2±0.2a	1.0±0.1a	3.2±0.2
Stanley	Dried	UT	3.4±0.2bc	1.8±0.3b	–
Stanley	Dried	EtOl	3.6±0.2b	1.9±0.2b	–
Stanley	Dried	Abr	3.1±0.2c	1.8±0.1b	–
Empress	Fresh	–	5.6±0.3a	1.1±0.1a	2.6±0.2
Empress	Dried	UT	3.7±0.2b	1.8±0.2b	–
Empress	Dried	EtOl	3.8±0.4b	1.9±0.1b	–
Empress	Dried	Abr	3.0±0.2c	1.8±0.2b	–

[a] Mean±standard deviation of five analyses. Means for each cultivar within a row sharing common letter were not significantly different ($P<0.05$).

Therefore, as concerns colour, abrasion does not cause changes in the peel different from those caused by UT and ETOl.

The content of total phenols proved to be greatest in the *Angeleno* plums (Table 4), with values equal to 7.5 mg g^{-1} (dw); notable differences were not found between the other two cultivars, with values of slightly greater than 5 mg g^{-1} (dw). The most marked reduction was detected in the dried samples of the varieties with a small initial content of total phenols (*Stanley* and *Empress*) while, in the *Angeleno*, the reduction was less marked, with significant differences between UT and pre-treated samples. The drying process influenced the final content of total phenols in a different way, causing significant differences between the varieties.

In *Angeleno* plums, the compounds reactive to the vanillin–HCl reagent were equal to 2.2 mg g^{-1} (dw), i.e. about twice greater than the other two varieties. These compounds were nearly 29% of the total phenols in *Angeleno* plum pulps. After drying, the compounds reactive to the vanillin test increased significantly, with no differences between the samples. This finding, in contrast to the findings of Donovan et al. (1998), who did not find flavan-3-ol in plums after drying, is the result of the increase in polymeric forms due to the high temperature of drying. Moreover, the vanillin assay in methanol is more sensitive towards polymeric tannins than monomeric flavan-3-ols. These results, considering the limits of the method used, correlate with the sensorial characteristics of the product. In fact, flavan-3-ols and their polymers (condensed tannins), elicit persistent bitterness and astringency: as molecular size increased (within a limited number of monomers), bitterness decreased and astringency increased (Peleg, Gacon, Schlich, & Noble, 1999).

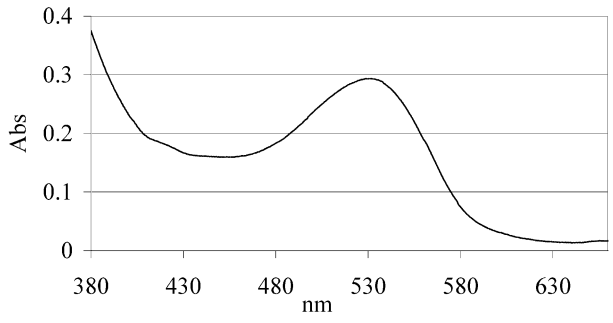

Fig. 2. Spectrum of the HCl/water/ethanol extract of the *Angeleno* plums due to absorption of anthocyanins.

The anthocyanin content was higher in *Angeleno* plums: 5.2 mg g^{-1} (dw) compared to *Stanley:* 3.2 mg g^{-1} (dw) and *Empress* plums 2.6 mg g^{-1} (dw). Fig. 2 shows the visible spectrum of the HCl/water/ethanol extracts of the *Angeleno* plums due to absorption of anthocyanins. The HCl/water/ethanol extracts in the dried samples did not lead to the detection of red pigments, due to the degradation of anthocyanins by the mechanism of oxidation, in which enzymatic and thermal factors are involved.

4. Conclusions

The physical pre-treatments, as well as the chemical ones, caused the final contents of glucose and fructose in *Stanley* and *Empress* prunes to be higher than those found in the untreated samples. Prolonged exposure to high temperatures in the untreated product, favoured the loss of the two monosaccharides, due to the onset of caramelisation reactions. As expected, the *Stanley* prunes demonstrated the best characteristics for drying

in terms of total sugar and sorbitol content. The *Angeleno* plums showed the greatest content of phenols, above all anthocyanins, as confirmed by the higher a^* values. The proposed physical pre-treatment, without significantly altering the other qualitative characteristics of the plums, most importantly reduced the dehydration time and, as a result, caused a smaller loss of sugars in *Empress* and *Angeleno* prunes.

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