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Original Article

Investigation on the Changes in Color Parameters and Turbidity of Cornelian Cherry (*cornus mass L*) Produced by Microwave and Conventional Heating

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ABSTRACT

Background and Objectives: Red colored fruits such as cornelian cherry (*Cornus mas L*) are recognized as being healthy. The color of these fruits is an important sensory property in assessment of product quality; therefore, minimizing the loss of color in the process is very important.

Materials and Methods: In this study, comparison of the color, turbidity, degradation rate of anthocyanin, and rate of evaporation in cornelian cherry (*cornus mass L*) juice produced from microwave and conventional heating at different operational pressures (12, 38.5 and 100 K Pa) was investigated.

Results: The final brix juice 42° was obtained in 137, 125, and 93 min by conventional heating at 100, 38.5 and 12 K Pa, respectively. Applying microwave energy decreased the required times to 115, 90 and 75 min at 100, 38.5 and 12 K Pa, respectively. In both methods, the heating temperature at pressures of 12, 38 and 100 K Pa was 50, 75 and 100 ° C, respectively. The results also showed that hunter lab values (L, a, and b) were decreased with increasing the time of process, turbidity, and degradation rate of anthocyanin.

Conclusions: The heating method affects the color, degradation rate of anthocyanins and evaporation rate of cornelian cherry concentrate. Also the results indicated that temperature and time of process are higher in conventional heating than in microwave. Degradation of anthocyanins and color of cornelian cherry juice was more evident in rotary evaporation as compared to microwave heating method. Thus according to the results, microwave energy could be successfully used in production of cornelian cherry juice concentrate.

Keywords: Cornelian cherry, Heating method, Color, Anthocyanins

Introduction

Cornelian cherry (*Cornus mas L*) belongs to the family Cornaceae, and is naturally grown in temperate regions of the Northern hemisphere, Peru and in large areas of Europe, Armenia, Caucasus, and Iran (1). Cornelian cherry fruits are a considerable source of phenolic compounds, anthocyanins, whole flavonoids, and ascorbic acids. Cornelian cherry could be considered as a good supply of organic antioxidants (2).

The cornelian cherry fruits can be eaten fresh or used to make syrups, juices, jams and other traditional products (3). Since cornelian cherry is obtained in a few months in year, some techniques should be applied for production of its concentrate (4). Furthermore, fruits contain high amounts of water, which makes them susceptible to enzymatic and microbial deterioration; thus the extracted juice is concentrated for long-term storage and easier transportation (5).

Juice is traditionally concentrated by multi-stage vacuum evaporator which has a great effect on the quality and degradation of certain natural anthocyanins, the loss of amino acids, and color of the final product (6). Different methods have been used for fruit juice concentration, including evaporation, as well as membrane and freeze concentration (7). Evaporation method is superior to other methods due

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to the possibility of achieving higher concentrations, greater production capacity and economy (4).

Nowadays, new technologies like microwaves are being investigated in order to find actual alternatives to the conventional treatments (8). Microwave heating appears a very suitable heating method, owing to its well-known advantages over conventional heating: microwave heats directly without the need of intermediate fluid; therefore, fast, efficient and economical treatments are possible (9). Moreover, vacuum evaporation was done to prevent high temperature, juice quality change, and color quality changes, which are more evident in conventional thermal and long- time processing (10).

The color is an important sensory property in assessment of product quality. Minimizing the loss of pigments in the process is the main concern (11). It has been reported that numerous reactions may affect the color during the thermal processing of fruits and their derivatives. One of the most common ones are pigment deterioration, particularly carotenoids and chlorophyll, and browning reactions such as Maillard (12). Hunter color parameters (L, a, and b) and change color (Total Color Difference) are used to specify the color changes throughout the thermal processing of fruit and vegetable products and their derivatives. It has been reported that these parameters change during thermal processes in concentrated pomegranate juice (5). Furthermore, similar results have been reported for the concentration of mango puree, peach puree, and tomato paste (13, 14).

Anthocyanins have polyphenol structure, and are useful for antidiabetic purposes (15). Anthocyanins are polyphenol components and the largest group of water-soluble plant pigments accountable for the color of several fruits including cherries (16). Seeram *et al*. (2002) revealed that anthocyanins of cornelian cherry are the blend of three compounds: delphinidin 3-O-galactoside, cyanidin 3-O-galactoside, and pelargonidin 3-O-galactoside (17). Most significant is that *cyanidin 3-O-galactosid* has the highest oxygen radical absorbance capacity (18). These polyphenolic substances are glycosides of polyhydroxy and polymethoxy-derivatives of 2-phenylbenzopyrylium or flavilium salts (19, 20). Stability of anthocyanins depends on several factors including light, pH, and temperature during storage, and particularly heat processing (21). Degradation of anthocyanins results in conversion to colorless derivatives, and consequently, to insoluble brown pigments (22).

Shao-qian *et al*. (2011) reported that anthocyanins degradation and visual color change increased by increasing the heating temperature and time (11). Thermal degradation of anthocyanins has been reported for red cabbage (23), sour cherry (24), raspberry (25), pomegranate (26), grape (27) and strawberry (28).

The objective of this work was to comparison of evaporation rate and quality attributes of cornelian cherry juice produced from conventional and microwave heating, at different operational pressures.

Materials and Methods

Cornelian cherry juice preparation: Cornelian cherry (*cornus mass L*) was obtained from a local market in Karaj, Iran. Fruit was selected in terms of appearance. After appropriate washing and cleaning, the fruits were soaked in water overnight. The juice was extracted manually by pressing, and then a fabric filter was used to separate the skin and pyrene. The single-strength clarified juice was frozen at -18˚C and used for further experiments.

Heating system: Cornelian cherry juice was concentrated using two methods of heating from an initial brix juice 7° to a final brix juice 42° as following:

Microwave heating system: A programmable microwave (Butane MR-1, Iran, using a maximum output of 900 W at 2450 MHz) and a vacuum pump (Robin-air -Owatonna, MN, USA) were used to produce cornelian cherry juice concentrate at pressures below atmospheric (Fig. 1). System power (wattage) supply and the time of processing could be adjusted in the oven. 400 ml sample of the juice was poured into hermetic jar, which was connected to a vacuum pump, and was placed inside the microwave. Microwave heating was conducted at three operational pressures 100 (atmospheric), 38.5 and 12 k Pa. The samples were taken periodically and replaced after measurement of brix. The microwave vacuum evaporator was set at 300W which was the most suitable power because above 300 W, foaming and charring of juice may occur. The schematic diagram vacuum is shown in Figure 1.

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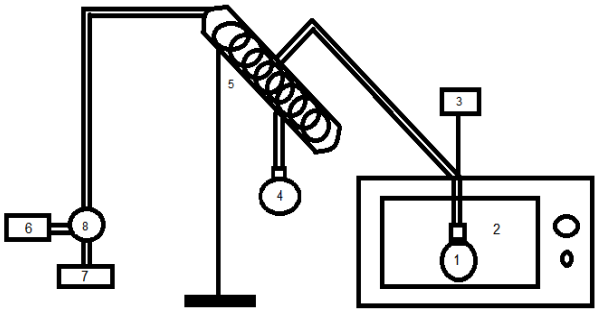


Fig. 1: The schematic diagram of microwave vacuum: 1) Airtight jar; 2) Microwave heating chamber; 3) Thermometer; 4) Collectors jar; 5) Condenser; 6) Vacuum pump; 7) Pressure controller; 8) Vacuum control valve.

Rotary evaporation system: A rotary vacuum evaporator (Heidolph, Heizbad HB Contr, Germany) and vacuum pump were used. In rotary evaporation system, heat transfer was carried out by soybean oil (because of its high boiling temperature, 120˚C). After reaching the final brix juice 42° and after recording the temperature of the sample and the time of process, concentrates were collected for further experiments. An electromagnetic heater was used to concentrate the juice at atmospheric pressure. During the concentration, stirring was performed by magnetic system.

The concentration rate constant (k): The total soluble solids' (TSSs) content for the juice was determined in brix using a hand refractometer (Atago Rx-7000a, Tokyo, Japan). The following equation was used to obtain the coefficient concentration (5):

$$K=\ln(C_t/C_0)/t \quad (1)$$

Where, C_0 is the initial soluble solid content, and C_t is the soluble solid content after t minutes of concentrating at a given pressure (or temperature).

Total anthocyanin content (TAC): The total anthocyanin content of the juice was determined by the pH-differential method using Spectrometer (PerkinElmer Lambda 25 Spectrometer) (29).

Degradation rate of anthocyanins: Kinetics data on anthocyanin degradation were calculated by the following equation (30):

$$\mathrm{Ln}\,(A/A_0) = -Kt \quad (2)$$

Where, A represents the residual anthocyanins' concentration (mg/100 mL) after processing; A_0 represented initial anthocyanins concentration (mg/100 mL); and t and k represented time (min) and reaction rate constant (1/min) at a particular pressure (or temperature) respectively.

Physicochemical properties: The pH of samples was measured using a pH meter (JENWAY pH meter model 3510). Acidity was measured by titration of NaOH (0/1N) (31).

Nephelometric turbidity method was used to measure the turbidity of concentrate (32). Turbidometer (AQUALYTIC Turbidity Meter modle AL450T-IR) was used with an incident light through a 25 mm path and a scattering angle of 90˚C.

The color parameters of concentrates were measured by Hunter Lab (A-60-1010-615 Model Colorimeter, HunterLab, Reston, VA) (33). By putting the parameters in the following equation, other parameters (Total Color Difference(TCD), Chroma) were calculated:

$$TCD=\sqrt{(L_0-L)^2+(a_0-a)^2+(b_0-b)^2} \quad (3)$$

$$\text{Chroma}=\sqrt{a^2+b^2} \quad (4)$$

Where, a_0, b_0 and L_0 show the initial amounts of juice color before concentration.

Statistical analysis: The results were reported as an average of three replicates (7 treatment, N=21). Data were expressed as mean ± standard deviation (SD). Statistics on a completely randomized design (CRD) was performed with the analysis of variance (ANOVA) procedure using SPSS software (Version 16.0. Chicago, SPSS Inc). Duncan tests were used to compare the difference among the mean values at the level of 0.05.

Results

The concentration rate constant (k): Table 1 shows that the heating time to reach the final brix (42°) in microwave heating method is smaller to the conventional heating method (in equal pressure). As a result, according to Eq. [1], the rate constant (K) of microwave heating is higher than that of normal heating.

Degradation rate of anthocyanins: The influence of heating methods and different operational pressures on the stability of anthocyanins in cornelian cherry concentration during heating was investigated. The anthocyanin content (expressed in cyanidin-3-glucoside) of raw cornelian cherry juice was calculated to be 20.0460 ±01942 (mg cyanidin-3-glucoside/100 mL). The determined values are summarized in Table 2. The different heating methods led to different degradation rates for anthocyanins. The degradation rate of anthocyanins in conventional heating was higher than that for microwave method.

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Table 1. Outlet temperature and rate constant of the thermal concentration of cornelian cherry juice

Heating method	Pressure (K Pa)	Time (min)	Outlet temperature (°C)	K (min^{-1})
Control	100	152	95	0.0117 ± 0.0002^{f}
Rotary evaporator	12	93	49	0.0192 ± 0.0002^{b}
	38.5	125	76	0.0143 ± 0.0001^{d}
	100	137	97	0.0130 ± 0.0003^{e}
Microwave	12	75	60	0.0238 ± 0.0013^{a}
	38.5	90	82	0.0198 ± 0.0006^{b}
	100	115	102	0.0155 ± 0.0002^{c}

Similar letters in each column in the level of P ≤0.05 were not significantly different. Response shows as mean ± standard deviation for 3 replications.
K= The concentration rate constant

Table 2. Thermal degradation of anthocyanins using different concentration methods

Heating method	Pressure (K Pa)	A (mg cyanidin-3-glucoside/100 mL)	Rate constant (min^{-1})
Control	100	6.39 ± 0.2804^{d}	0.00746 ± 0.00020^{a}
Rotary evaporator	12	15.10 ± 0.6433^{b}	0.00314 ± 0.00039^{b}
	38.5	8.9 ± 0.5261^{c}	0.00698 ± 0.00048^{a}
	100	7.12 ± 0.0235^{d}	0.00754 ± 0.00018^{a}
Microwave	12	18.58 ± 0.2391^{a}	0.00100 ± 0.00010^{c}
	38.5	18.19 ± 0.3565^{a}	0.00104 ± 0.00021^{c}
	100	14.40 ± 0.3684^{b}	0.00377 ± 0.00135^{b}

Similar letters in each column in the level of P ≤0.05 were not significantly different. Response shows as mean ± standard deviation for 3 replications.
A= The anthocyanin content

pH, acidity, density: Figure 2 shows acidity data for the samples concentrated by evaporator and microwave methods at different operational pressures. The results revealed that the acidity of microwave processed samples was generally less than that of the samples processed by the conventional method. Fig. 2 shows that higher pressures and temperatures lead to increased acidity of the samples.

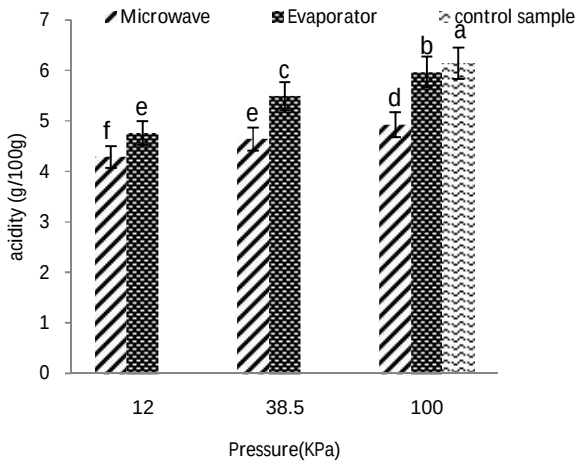


Fig 2. Variation of the acidity during the concentration of cornelian cherry juice; Similar letters in each form or shape in the level of P <0.05 were not significantly different.

Table 3 shows that by increasing the pressure and temperature, in contrast to the increased acidity, no significant differences (P≤0.05) were observed in pH of the samples. Also density of the samples showed no significant difference (P≤0.05).

Turbidity: The results revealed that applying microwave method instead of conventional heating method can decrease the turbidity of samples (Fig. 3). Also, by increasing the pressure and temperature, turbidity of the samples was significantly increased (P≤0.05).

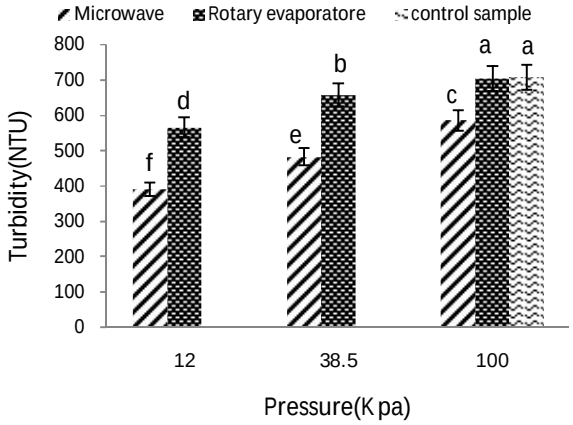


Fig 3. Comparison of the turbidity from the cornelian cherry juice concentrated with microwave and rotary evaporator; Similar letters in each form or shape in the level of P ≤0.05 were not significantly different.

Color: The results of color parameters obtained from the concentration processes are presented in Table 4. Initial amounts of juice color before concentration for a, b and L were 12.33, 3.61, 24.32, respectively. L-value during the process decreased with increasing

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the pressure. Conventional heating of cornelian cherry juices resulted in significant degradation in L-value in comparison with microwave heating. Comparing to its initial amount, b-value was reduced in both heating methods. The a-values were reduced during the treatment by increasing the pressure. Reduction of this value was more evident in the rotary evaporator. The results showed that ΔE was changed as a consequence of changes in the color parameters, changed (Equation 3). The value of ΔE was increased with time during all concentration processes significantly ($P \leq 0.05$).

Chroma index of microwave-heated products were evidently higher than conventionally heated ones. Also increasing of pressure in both heating methods increased the processing time and reduced the Chroma index.

Table 3. pH and density of cornelian cherry juice concentrated with microwave and rotary evaporator

Heating method	Pressure (K Pa)	Density	pH
Control	100	1.2170 ± 0.0025^{a}	3.30 ±0.01^{a}
Rotary evaporator	12	1.2179 ± 0.0150^{a}	3.40±0.01^{a}
	38.5	1.2168 ± 0.0047^{a}	3.30±0.01^{a}
	100	1.2084 ± 0.0029^{a}	3.30±0.01^{a}
Microwave	12	1.2317 ± 0.0409^{a}	3.40±0.01^{a}
	38.5	1.2130 ± 0.0064^{a}	3.40±0.01^{a}
	100	1.2240 ± 0.0039^{a}	3.30±0.01^{a}

Similar letters in each column in the level of P ≤0.05 were not significantly different. Response shows as mean ± standard deviation for 3 replications.

Table 4. Comparison of the color from the cornelian cherry juice concentrated with microwave and rotary evaporator

Heating method	Pressure (K Pa)	L^*	a^*	b^*	TCD	Chroma
Control	100	21.25 ± 0.0264^{d}	8.13± 0.0001^{e}	2.07± 0.230^{c}	5.42± 0.2396^{a}	8.3910±0.0057^{e}
Rotary evaporator	12	22.55 ± 0.0781^{b}	10.87 ± 0.1212^{b}	3.01 ± 0.2165^{b}	2.38 ± 0.0775^{e}	11.280± 0.0689^{b}
	38	21.93 ± 0.0057^{c}	9.92 ± 0 .7621^{c}	2.43 ± 0.2740^{c}	3.63 ± 0.4220^{c}	10.218± 0/7010^{c}
	100	21.90 ± 0.2193^{c}	8.74 ± 0 .2451^{d}	2.15 ± 0.0001^{c}	4.56 ± 0.3057^{b}	9.158± 0.4970^{d}
Microwave	12	23.04 ± 0.2971^{a}	12.03 ± 0.3536^{a}	3.50 ± 0.3251^{a}	1.36 ± 0.3579^{f}	12.530± 0.4051^{a}
	38	22.94 ± 0 .0458^{a}	11.05 ± 0 .0871^{b}	3.22 ± 0.2478^{ab}	1.93 ± 0.0617^{e}	11.512± 0.1206^{b}
	100	22.48 ± .1342^{b}	10.16 ± .1113^{c}	2.93 ± 0.0700^{c}	2.92 ± 0.0831^{d}	10.574± 0.0907^{c}

Similar letters in each column in the level of P ≤0.05 were not significantly different. Response shows as mean ± standard deviation for 3 replications.

Discussion

The concentration rate constant (k): Microwave heats the food directly without the need for intermediate fluid. So microwave heating is rapid, effective and economical (9). Microwave heating is based on the transformation of alternating electromagnetic field energy into thermal energy by affecting the polar molecules of a material. The most important characteristic of microwave heating is volumetric heating (34). Conventional heating occurs by convection followed by conduction where heat must diffuse in from the surface of the material. Volumetric heating means that materials can absorb microwave energy directly and internally, and convert it into heat. In microwave heating, the heat is generated throughout the material, leading to faster heating rates, compared to conventional heating where the heat is usually transferred from the surface to the interior (35).

Successful application of microwave vacuum technology in drying of food products has been reported for many food products including cranberries (36, 37) and carrots (38).

At the operational pressures of 12, 38 and 100 k Pa, the boiling point of the solutions was 50, 75 and 100° C, respectively. During the concentration, the boiling point of the solution increased by increasing the time, which can be explained by an increase in the soluble solid concentration. But in the microwave method, increase of the boiling point is more evident because of the superheating phenomenon. Superheating

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phenomenon is described as a heated liquid at a temperature more than its boiling point, without boiling. This phenomenon is more evident towards the end of the evaporation process when there is higher TSS and lower water content. It reduces the specific temperature of the juice, and the temperature of the concentrated juice undergoes a greater change (5). These results are in agreement with those reported by Yousefi *et al.*

(2012) (39).

Degradation rate of anthocyanins: As expected, the increasing pressure and temperature resulted in an accelerated degradation of anthocyanins. The rate of anthocyanin destruction could be related to several mechanisms. Speedy destruction of anthocyanins at higher temperature may be due to hydrolyzation of 3-Glycoside structure, which has a protective effect in unstable anthocyanin. Another presumption is that hydrolyzation of the pyrilium ring triggers generation of chalkons, which are accountable for brown color developed in the food containing anthocyanins (40).

The high ascorbic acid content of cornelian cherry fruits (17) can accelerate the degradation of anthocyanins. The increasing loss of anthocyanins due to ascorbic acid occurs due to the free radical oxidative cleavage of pyrilium where ascorbic acid acts as molecular oxygen activator. At high temperatures, amino acid undergoes a degradation process, generating degradation products, which may also be responsible for anthocyanins' degradation (41). These results are similar to those reported by Scalzo et al. (2008) (42). Several studies have investigated thermal degradation of anthocyanins (43, 44). Yousefi et al. (2013) also reported that degradation rate of anthocyanins in microwave heating was lower comparing to conventional heating; so microwave heating is better for maintenance of anthocyanins present in raspberry juice (39). This may be explained by the fact that in microwave heating, the heat as controlled is generated throughout the material, leading to faster heating rates, compared to conventional heating where the heat is usually transferred from the surface to the interior (45).

pH, acidity, density: Following the development process and concentration, accumulation of organic acids in the samples was increased. It is suggested that increased acidity is due to bond breaking and release of organic acids during the heating. And since higher temperature and time of heating at 100 k Pa pressure were obtained by Rotary, acidity content at 95% with the same concentration of the sample is significantly higher due to exposure to high temperature and longer time of process**.**

Citric acid, malic acid, tartaric acid and citric acid are the main organic acids in bayberry juice (46). These acids and their salts may form the main buffering system in the juices (47). Therefore, in contrast to increased acidity, in pH of the samples, no significant differences were occurred. It can be caused by the presence of certain compounds in the buffer to act as a tampon. Hojjatpanah et al. (2011) found similar results for acidity in the production of black mulberry concentrates; however, the pH of the samples decreased with increasing the acidity (32).

Turbidity: Although many factors affect the turbidity of beverages, the most frequent cause is protein-polyphenol interaction. Even in products initially free of turbidity, for various reasons, proteins and polyphenols form insoluble complexes that scatter light. When the complex grows to a sufficient size and becomes insoluble, it results in turbidity (48).

As cornelian cherry is a rich source of tannin (15), another reason for the increased turbidity in high pressure and temperature can be attributed to tannin-protein complex. Heat treatment will aid in the increasing loss of protein tertiary structure, resulting in the exposure of extra hydrophobic sites of proteins and increased accessibility of the sites to tannin (49) leading to turbidity (50). The results correspond with those of Hojjatpanah et al. (2011) in production of black mulberry concentrate (32).

Color: Since the amount of L-value shows darkness and lightness, its reduction indicates that the samples are darker (5). Similar results have been reported by different authors. It has been described that L-value is correlated well with increase in the browning of food components and color destruction (51, 52).

Decrease of b-value indicates the disappearance of yellow color. Similar results were observed by decreasing the b-value for kiwi. In this study, the L-value and b-value were decreased as a result of the breakdown of carotenoids and chlorophyll as well as the formation of brown pigments (53).

Reduction of a-value was observed in grape juice (54) and Carrots (55). Also the reduction of the Hunter L and a-value was due to diminishing the red color of anthocyanin pigments (thermal degradation) which are vulnerable in fruit juice (54) and

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polymerization of anthocyanins with different phenolics (28). The results of Chutintrasri and Noomhorm (2007) on color change in pineapple puree confirm that brightness of the samples is reduced by heating (56).

The difference in the color of samples (TCD) was more significant at higher temperatures and longer heating times that correspond to the results of Rattanathanalerk *et al*. (2005) (57). The largest color change was observed in rotary evaporator. It indicates that more color change has occurred due to this process.

The study results showed that by reducing the heating time, the Chroma index of samples and hence the color quality of concentrates will be increased.

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