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Assessing Physicochemical Properties of Different Red Hot Pepper Paste 'Harissa' Commonly Consumed in Tunisia

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ABSTRACT

Pepper is one of the main vegetable crops grown and consumed in Tunisia and is therefore of economic importance. Interest in assessing physicochemical and bioactive compounds with antioxidant capacity and potential health benefits in pepper and pepper based products is increasing. Besides some physicochemical characteristics, the variability of lycopene and total carotenoid contents of 11 red hot pepper pastes (RHPP) covering almost of the commercial types available in Tunisian hypermarkets were determined. Soluble solid content, Titratable acidity, pH, the color index (L^*), (a^*), (b^*) and the calculated coefficients (a^*/b^*) and $(a^*/b^*)^2$ varied significantly among the studied (RHPP). Significant differences were found also in lycopene and total carotenoid contents between the studied (RHPP). Total carotenoids varied from 121.30 mg β-CaE/kg fw in H6 to 463.23 mg β-CaE/kg fw in H11. Lycopene content in H11 was more than 3-fold higher than that in H6. In the present study, lycopene content ranged from 80.39 mg/kg fw in H6 to 182.62 mg/kg fw in H5. Correlation study showed that only lycopene was best correlated with the ratio (a^*/b^*) (R = 0.529 $P < 0.01$) and $(a^*/b^*)^2$ (R = 0.343 $P < 0.05$) indicating that the ratio (a^*/b^*) can be used particularly for the rapid estimation of the lycopene content and screening work in (RHPP) but not for accurate determinations. This study has demonstrated the variability in the physicochemical attributes in different red hot pepper pastes consumed in Tunisia. However, the determination of all the bioactive compounds and the antioxidant activity in such products is required in order to develop new marketing and convincing labels.

Keywords: color indexes, lycopene, soluble solid content, titratable acidity, total carotenoids

INTRODUCTION

The pepper (*Capsicum annuum* L.) is one of the main vegetable crops grown and consumed in Tunisia and is therefore of economic importance. In fact, in 2006, 200,000 ha were dedicated to this crop and its production amounted to 256,000 t (DGPA 2007).

Due to their versatility to be consumed as fresh vegetable in salads, cooked meals or dehydrated powder for spice, pepper fruits are considered of great importance for human diet. Traditionally, pepper fruit were harvested at the mature green stage; however, recently more interests were dedicated to red mature pepper fruits for their increased health benefit, flavor and nutritional quality (Frank *et al*. 2005).

Red mature pepper fruits represent an important source of carotenoids primarily capsaicin and caposorubin both responsible for the red color of the fruit. Its powder is used as food colorant (Hornero-Méndez *et al*. 2002). However, recently Ha *et al*. (2007) reported that besides capsanthin and capsorubin, pepper fruits can also accumulate other types of carotenoids such as lycopene since it harbour the most evolved carotenoid biosynthesis pathway among plant species. Moreover, red-ripe pepper fruits contain high levels of vitamin C and phenols (Marín *et al*. 2004).

The presence of these types of antioxidant in pepper fruits is of great importance. In fact, phytochemical compounds, particularly carotenoids, vitamin C, flavonoids and other phenolics, have attracted much interest because of their antioxidant activity against free radicals, suggesting protective roles in reducing the risk of certain types of cancers, cardiovascular diseases and age-related degenerative pathologies (Rice-Evans *et al.* 1996; Sies and Stahl 1998; Giovanucci 1999; Robards *et al*. 1999; Karakaya *et al*. 2001; Edwards *et al*. 2003; Rao 2006).

Although literature exists on the physicochemical attributes of pepper fruits such as weight, colour, soluble solids and acidity (Tadesse *et al*. 2002; Martínez *et al*. 2007). In addition information on the bioactive compounds with antioxidant properties were widely reported (Fox *et al*. 2005; Materska and Perucka 2005; Navarro *et al*. 2006; Searrano *et al*. 2010). However, as far as we are aware no information is available regarding pepper-based products, particularly red hot pepper pastes.

In Tunisia, red hot pepper paste is prepared from fresh mature red-ripe peppers and is considered among the most appreciated products in the Tunisian diet. Its production was maintained almost constant between 1990 and 2000 at about 10,000 t and reached a peak in 2007 with about 22,500 t (GICA 2008). This product is also becoming increasingly appreciated by the international market. In fact in the recent years, exportation of pepper paste reached 5000 t destined for more than 20 countries mainly in Europe, the United States, Japan, and some other Arabic countries (GICA 2008).

Therefore, and based on these facts, the aim of this study was to evaluate different red hot pepper paste 'Harissa' commonly consumed in Tunisia for their physicochemical properties. Correlations between color indexes/coefficients and lycopene/total carotenoids were also examined.

MATERIALS AND METHODS

Red hot pepper paste sampling

The different red hot pepper pastes (RHPP) were purchased from different local hypermarkets and covered almost all of the com-

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Table 1 Color indexes and calculated coefficients of the different studied red hot pepper pastes (RHPP).

Red hot pepper pastes	*L**	*a**	*b**	(*a**/*b**)	(*a**/*b**)²
H1	40.51 ± 0.11 c	20.02 ± 0.13 ab	18.48 ± 0.19 cde	1.08 ± 0.00 ab	1.16 ± 0.01 a
H2	43.94 ± 0.23 a	17.52 ± 0.45 c	22.84 ± 0.61 a	0.76 ± 0.02 h	0.57 ± 0.00 d
H3	40.35 ± 0.10 c	17.22 ± 0.03 c	15.40 ± 0.10 g	1.11 ± 0.00 a	1.23 ± 0.01 a
H4	40.33 ± 0.17 c	17.13 ± 0.18 c	16.53 ± 0.15 f	1.03 ± 0.01 c	1.06 ± 0.02 ab
H5	40.52 ± 0.15 c	19.41 ± 0.07 b	19.45 ± 0.05 bc	0.99 ± 0.00 d	0.98 ± 0.00 abc
H6	41.07 ± 0.15 b	14.53 ± 0.20 de	17.86 ± 0.11 e	0.81 ± 0.00 g	0.65 ± 0.01 d
H7	40.39 ± 0.36 c	20.73 ± 0.94 a	18.90 ± 0.75 bcd	1.05 ± 0.00 bc	1.12 ± 0.08 a
H8	41.26 ± 0.13 b	16.64 ± 0.34 c	17.95 ± 0.31 de	0.91 ± 0.00 e	0.82 ± 0.33 bcd
H9	39.44 ± 0.10 d	17.17 ± 0.01 c	19.64 ± 0.16 b	0.86 ± 0.01 f	0.73 ± 0.01 cd
H10	39.60 ± 0.33 d	13.62 ± 0.17 e	15.13 ± 0.10 g	0.89 ± 0.00 ef	0.79 ± 0.01 bcd
H11	40.51 ± 0.19 c	14.75 ± 0.14 d	16.58 ± 0.08 f	0.88 ± 0.00 ef	0.77 ± 0.00 bcd
Significance	**	**	**	**	**

Significance: ** Probability level of 1%; ns: not significant. Values in the same column followed by the same letters do not differ significantly (LSD test, P<0.05).

mercial pepper pastes consumed in Tunisia. Different (RHPP) were coded as H1 to H11 to insure anonymity.

Chemicals

Sodium hydroxide and butylated hydroxytoluene (BHT) were obtained from Sigma-Aldrich, Chemical Co., Milan. Other reagents were of analytical grade.

Physicochemical properties determination

Soluble solids content in pepper paste (°Brix) was measured by taking a small sample of the homogeneous paste and squeezing the juice into a digital refractometer (Atago PR-100, NSG Precision Cells Inc., Farmingdale, NY) calibrated with a 10% sucrose solution. The pH was carried out directly on the paste using an electronic pH-meter (WTW, Microprocessor pH Meter, PH 539, Weilheim, Germany). Titrable acidity was estimated after titration at a pH of 8.1 with a sodium hydroxide solution (0.1 M) and results were expressed as percentage of citric acid. Colour measurements were made at different place of the paste surface using a Minolta CR-300 chromameter.

Total carotenoids and lycopene extraction and determination were conducted as described by Lee (2001) and Fish *et al.* (2002), respectively. The method uses a mixture of hexane/ethanol/acetone (2: 1: 1, by volume) containing 0.05% butylated hydroxytoluene (BHT). During the extraction process, some precautions were taken, like working in a reduced luminosity room and wrapping glass materials in aluminium foil to avoid lycopene loss by photooxidation. For total carotenoid and lycopene quantification, the absorbance of the hexane extract was read at 450 and 503 nm respectively using a Beckman DU 650 spectrophotometer (Beckman Coulter, Fullerton, CA, US). Total carotenoids were expressed as mg β-carotene equivalents per kg of fresh weight (mg β-CaE/kg fw). Lycopene molar extinction ε=17.2 10^4 $M^{-1}cm^{-1}$ in *n*-hexane was used for lycopene content determination and results were expressed as mg/kg fw.

Statistical analysis

The analysis of variance was carried out according to the General Linear Models (GLM) procedure developed by the Statistical Analysis Systems Institute (SAS, V6.0, Cary, NC). Means and standard errors were calculated. Correlations were done using Person's correlation coefficient, $P < 0.05$. LSD test was also used for testing significant differences between means with a confidence level of 95%.

RESULTS AND DISCUSSION

Soluble solids contents of the different studied red hot pepper paste (RHPP) are shown in **Fig. 1**. The obtained data showed that soluble solid content values varied significantly between studied (RHPP) ($P < 0.01$). Soluble solid content reached very high levels (>19 °Brix) and varied from 16.06 °Brix in H5 to 19.43 °Brix in H10. The statistical analysis divided the studied (RHPP) into 2 groups. The fist included H6, H8, H9 and H10 with a soluble solid content ≥ 18. The second included the rest of the (RHPP) samples with a soluble solid content < 18 °Brix. Although information on the soluble solid content of the pepper paste are lacking, the obtained values are in line with the Tunisian standards for pepper paste industries (≥ 14 °Brix) (NT52-07, 2005). Increased values of soluble solid content are preferred in the fresh pepper since in reduce the cost of the processing and increase the financial income.

Titratable acidity and pH values of the different studied red hot pepper paste (RHPP) are shown in **Figs. 2** and **3**, respectively. The obtained data showed that titratable acidity and pH values varied significantly between studied (RHPP) ($P < 0.01$). Titratable acidity varied from 0.50 in H6 to 0.81 in H8. The (RHPP) H4 H5 and H10 had similar titratable acidity values with 0.70, 0.70, and 0.69 citric acid %. Although the physicochemical characteristics of the red pepper pastes were poorly reported, the obtained values are in line with those of Bozkurt and Erkman (2005) for different hot pepper paste produced using different techniques ranging from 0.25 to 3.06 citric acid %.

Regarding pH, values ranged from 4.45 in H5 to 4.82 in H3. The (RHPP) H3 had similar value to H3 and H10 had statistically similar pH value to H11. Although these facts were poorly documented in the literature, the obtained values fall within the range reported by Bozkurt and Erkman (2005) ranging from 3.80 to 8.80 in different prepared hot pepper paste. The titratable acidity and pH values are important parameters for food industries. In fact, low pH and high values of titratable acidity of the fresh material are preferred not only to reduce the processing cost and increase the income but also to increase the shelf life of the final product.

Color indexes (L^*, a^* and b^*) as well as the calculated coefficients (a^*/b^*) and $(a^*/b^*)^2$ of the different studied red hot pepper paste (RHPP) are presented in **Table 1**. The obtained data showed that the color indexes (L^*), (a^*), (b^*), (a^*/b^*) and the coefficients $(a^*/b^*)^2$ values varied significantly between studied (RHPP) ($P < 0.01$). The color index (L^*) varied from 39.44 in H9 to 43.94 in H2. The (RHPP) H8 and H6 had statistically similar (L^*) values with 41.26 and 41.07, respectively. H5, H4, H3, H7, H1 and H11 had also similar (L^*) values. The color index (L^*) indicates the intensity of the sample luminosity. This means that increased (L^*) values designate higher luminosity and is therefore more appreciated by the consumers.

Regarding the color index (a^*), values ranged from 13.62 in H10 to 20.73 in H7. The (RHPP) H2, H3, H4, H8 and H9 obtained similar (a^*) values. The color index (a^*) indicate the intensity of the red color. This means that increased (a^*) values indicate increased maturity of the fresh pepper used for the preparation of the different commercial (RHPP) under the study. Concerning the color index (b^*), values ranged from 15.13 in H10 to 22.84 in H2. The color index (b^*) indicate the intensity of the yellow color in the different studied (RHPP). The higher is the index the higher is the intensity of the yellow color. The calculated coeffici-

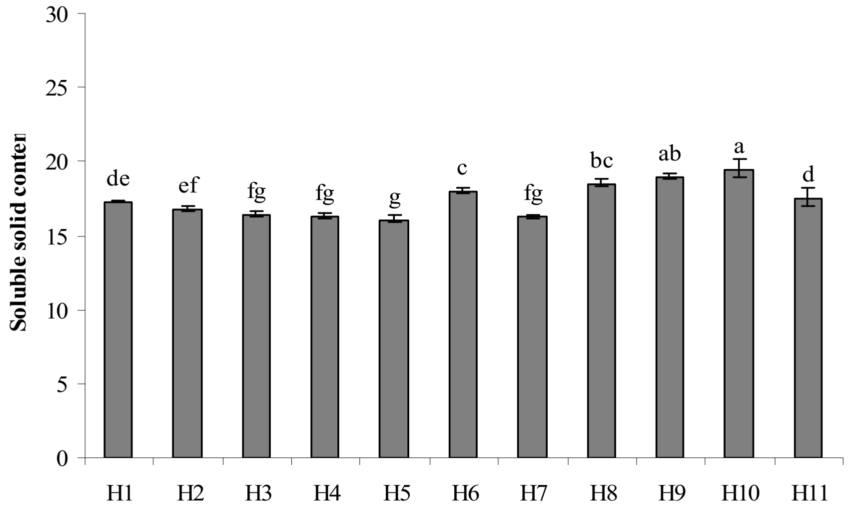

Fig. 1 Soluble solid (°Brix) content of the different studied red hot pepper pastes. Data are means of three replicates ± standard error. Bars marked with the same letters are not significantly different (LSD test, $P < 0.05$).

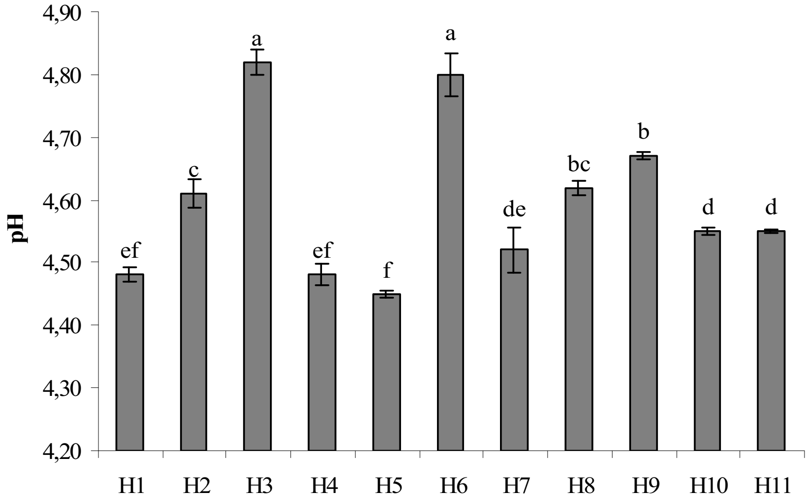

Fig. 2 pH of the different studied red hot pepper pastes. Data are means of three replicates ± standard error. Bars marked with the same letters are not significantly different (LSD test, $P < 0.05$).

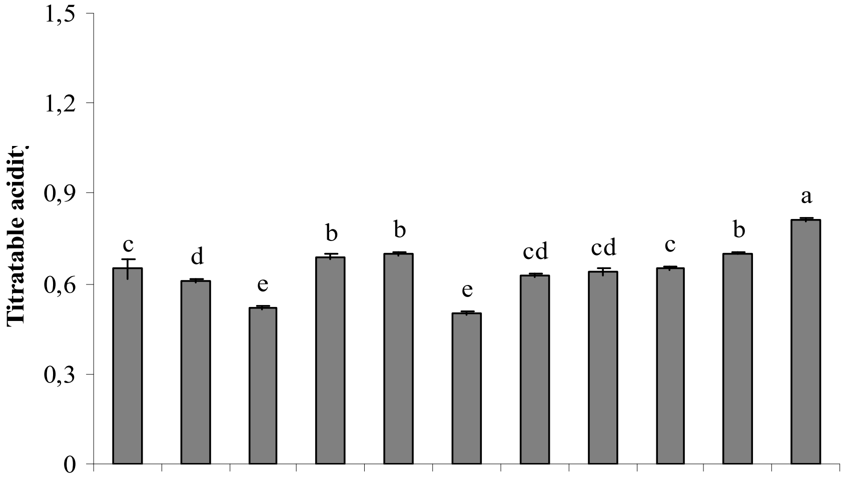

Fig. 3 Titratable acidity (citric acid %) of the different studied red hot pepper pastes. Data are means of three replicates ± standard error. Bars marked with the same letters are not significantly different (LSD test, $P < 0.05$).

ents (a^*/b^*) varied from 0.76 in H2 to 1.11 in H3. The ratio $(a^*/b^*)^2$ varied from 0.55 in H2 to 1.23 in H3. The ratio (a^*/b^*) increase with the increase of the red color in the studied (RHPP).

Besides these attributes we have also determined the amount of total carotenoids and lycopene in the different studied (RHPP). Total carotenoids and lycopene contents of the different studied (RHPP) are shown in **Figs. 4** and **5**, respectively. The obtained data showed that total carotenoids and lycopene content values varied significantly be-

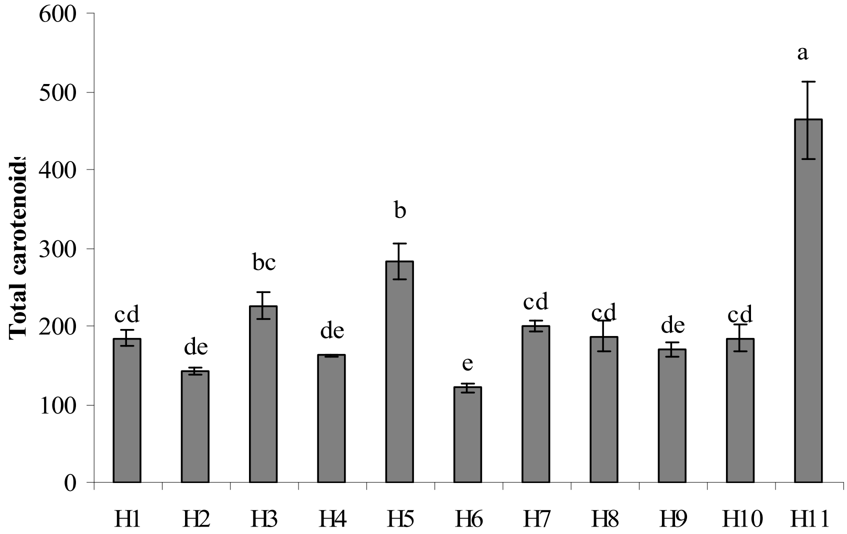

Fig. 4 Total carotenoids (mg β ca eq/kg fw) of the different studied red hot pepper pastes. Data are means of three replicates ± standard error. Bars marked with the same letters are not significantly different (LSD test, $P < 0.05$).

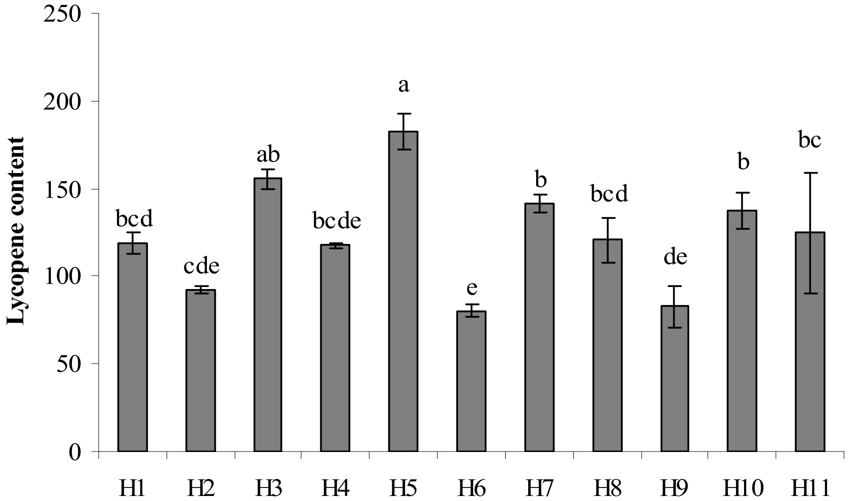

Fig. 5 Lycopene (mg /kg fw) content of the different studied red hot pepper pastes. Data are means of three replicates ± standard error. Bars marked with the same letters are not significantly different (LSD test, $P < 0.05$).

tween the studied (RHPP) ($P < 0.01$). Total carotenoids varied from 121.30 mg β-CaE/kg fw in H6 to 463.23 mg β-CaE/kg fw in H11. Variation from 1.2- to 3.8-fold compared to (H6) were obtained. At our knowledge, this is the first report on the carotenoid composition in different (RHPP) named 'Harissa' commonly consumed in Tunisia. Nevertheless, Olives Barba *et al.* (2006) reported that the total carotenoid in fresh red pepper ranged from 5 mg/kg fw in cv. 'Lamuyo' to 10 mg/kg fw in cv. 'Clavis'.

Although the red color in pepper fruit is mainly due to the presence of the red pigments capsanthin and capsorubin. Olives Barba *et al.* (2006) did not detect this red pigment in two red pepper cultivars using spectophotometric or HPLC methods. Navarro *et al.* (2006), studying the changes in the contents of antioxidant compounds in pepper fruits at different ripening stages as affected by salinity, detected the presence of this red pigment with an average of 322 mg/kg dry weight (dw). Ha *et al.* (2007) reported also that pepper fruits can accumulate many other types of carotenoids during the ripening process such as β-carotene and lycopene. For this reason we have also tested the presence of lycopene in the different studied (RHPP). In the present study, lycopene content ranged from 80.39 mg/kg fw in H6 to 182.62 mg/kg fw in H5. A variation of between 1.0- to 2.3-fold was detected among the studied (RHPP). At our knowledge this is the first report on the lycopene content in different (RHPP). The presence of lycopene in the fresh or in the processed product is of great importance since it is the most powerful natural antioxidant. Its antioxidant power is 3-fold higher than β-carotene.

Correlation study

Many authors have studied correlation between bioactive compounds and different physicochemical parameters in fruits and vegetable (Giovanelli *et al.* 1999; Arias *et al.* 2000; Brandt *et al.* 2006; Ilahy *et al.* 2009; Tlili *et al.* 2010). However, little of information is known about these types of correlations in (RHPP). Correlation coefficients among variables measured from different evaluated (RHPP) are listed in **Table 2**. For all studied (RHPP), lycopene was best correlated with the ratio (a^*/b^*) (R = 0.529 $P < 0.01$) and $(a^*/b^*)^2$ (R = 0.343 $P < 0.05$) indicating that the ratio

Table 2 Correlation coefficients and related significance among color index/coefficients and carotenoids/lycopene content of the different studied (RHPP).

Color indexes/ coeffiecients	Lycopene		Total carotenoids	
	Corr coeff	P	Corr coeff	P
L^*	-0.267	ns	-0.212	Ns
a^*	0.274	ns	-0.108	Ns
b^*	-0.270	ns	-0.245	Ns
(a^*/b^*)	0.529	<0.01	0.087	Ns
$(a^*/b^*)^2$	0.343	<0.05	0.061	Ns

ns, correlation not significant

(*a**/*b**) particularly can be used for the rapid estimation of the lycopene content and screening work in (RHPP) but not for accurate determinations. There was no significant correlation between (*a**), (*b**) or (*L**) and lycopene content. Similarly, total carotenoids were neither correlated with color indexes nor with the calculated coefficients.

CONCLUSIONS

This study has demonstrated the variability in the physicochemical attributes in different red hot pepper pastes consumed in Tunisia. We have found that although H11 was the richest source of total carotenoids, H5 was the richest source of lycopene. Even if the determined attributes are very important for both consumers and field industries, the determination of all the bioactive compounds and the antioxidant activity in such products is required in order to develop new marketing and convincing labels. Those labels are very important in order to attract the attention of the nowadays consumers.

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