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Amylose contents, rheological properties and gelatinization kinetics of yam (*Dioscorea alata*) and cassava (*Manihot utilissima*) starches

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Abstract

After defatting yam and cassava starches have amylose contents of 36.2 and 24.2%, respectively. Suspensions of these starches in water were analysed, in an oscillatory rheometer, using a heating rate of 4.0 °C min^{-1}, deformation of 1% and a frequency of 1 Hz, the initial temperatures of gelatinization being 71 and 62 °C for yam and cassava, respectively. A gelatinization study was also carried out by differential scanning calorimetry with different heating rates (2.5, 3.0, 4.0 and 5.0 °C min^{-1}), to give, by the Arrhenius equation, the activation Energy (E_a) of the process. Yam starch showed a more energetic gelatinization process of when compared to cassava starch and also had a lower rate constant (s^{-1}), indicating a relatively slow gelatinization process of at higher temperatures. Yam gels formed by autoclaving a suspension (50 g l^{-1}) showed after 24 h of refrigeration, a stronger structure than for a cassava gel.

Keywords: Yam; Cassava; Gels; Activation energy; Rate constant

1. Introduction

Starch is a reserve carbohydrate in the plant kingdom, that wordwide 70–80% of the calories consumed by humans, and is generally deposited in the form of minute granules or cells ranging from 1 to 100 μm or more in diameter (Buléon, Colonna, Planchot, & Ball, 1998; Whistler & BeMiller, 1997; Wurzburg, 1986; Zobel & Stephen, 1995).

Starch is a polymeric carbohydrate consisting of anhydroglucose units linked primarily through α-D-(1 → 4) glucosidic bonds. While the detailed fine structure has not been fully elucidated, it has been firmly established that starch is a heterogeneous material consisting of varying proportions of amylose and amylopectin (Buléon et al., 1998; Whistler & BeMiller, 1997; Wurzburg, 1986; Zobel & Stephen, 1995).

Amylose is essentially a linear polymer in which the anhydroglucose units are linked through α-D-(1 → 4) glucosidic bonds whereas amylopectin is a branched polymer with α-D-(1 → 4) glucosidic bonds, having periodic branches at the O-6 position (Buléon et al., 1998; Wurzburg, 1986).

Commercial starches are obtained from seeds (corn, waxy corn, high amylose corn, wheat and various rices) and from tubers and roots, particularly potato, sweet potato and cassava (Whistler & BeMiller, 1997). Other starches such as that of yam have less commercial applications, and publications on this starch are fewer in relation to those of corn starches. Hoover and Vasanthan (1994) studied the effect of heat-moisture treatment on the structure and physicochemical properties of cereal, legume, and tuber starches. They observed an apparent amylose content in yam starch of 27.1%, very similar to that of wheat starch and higher than that of oat and potato starches. Whistler and BeMiller (1997) have compared the general properties of some starch granules and pastes. Cassava or tapioca starches showed 17% of amylose, and the authors observe the formation of a translucent gel with high viscosity and a medium tendency to retrograde. Alves, Grossmann, and Silva (1999) and Mali, Grossmann, Garcia, Martino, and Zaritzky (2002) used yam starch to obtain films with

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glycerol. They used this starch due to its higher amylose content (30%), which gave rise to a film forming capacity as it is linear polymer. McPherson and Jane (1999) compared the starch of waxy potato with those of other root and tuber starches such as those of yam, normal potato and sweet potato. They observed that yam starch, have an apparent amylose content of 29.2% and that yam and sweet potato amylopectins had larger proportions (19.09 and 17.05%, respectively) of short branch chains (dp 6-12), when compared with those of normal and waxy potato amylopectins (13.07 and 14.75%, respectively).

Guanaratne and Hoover (2001) studied different starches from tuber and root. A comparative analysis of chemical compositions showed for those of yam and cassava amylose contents of 28.5 and 22.4%, respectively.

Starch gelatinization refers to the disruption of the molecular order within starch granules when they are heated in the presence of water. Evidence for the loss of an organized structure includes irreversible granule swelling, loss of birefringence and crystallinity. Gelatinization is an energy-absorbing process that can be followed by differential scanning calorimetry (DSC) (Whistler & BeMiller, 1997) and has been used to study starch (Bizot et al., 1997; Ghiasi, Honsey, & Varriano-Marston, 1982; Donovan, Lorenz, & Kulp, 1983; Le Lay & Delmas, 1998; Role & LeMeste, 1999; Yu & Christie, 2001).

To date, the few studies that have been carried out on the kinetics of gelatinization, have been on corn starch (Bhattacharya & Hanna 1987; Burros, Young, & Carroad, 1987; Kim & Wang, 1999) and potato starch (Pielichowski, Tomaski, & Sikora, 1998). We now investigate the composition, rheological properties, and kinetic analysis of gelatinization of yam (*Dioscorea alata*) and cassava (*Manihot utilissima*) starches, due the production of these plants in the Brazil, more specifically in economic terms in the State of Paraná.

2. Materials and methods

2.1. Plant material

Yam starch (*Dioscorea alata*), donated by Prof. Dra Maria Vitória E. Grossmann from Londrina State University was extracted and purified as described by Alves et al.

Table 1
Percentage chemical composition (g%) of yam and cassava starches

Starch	Carbohydrate[a]	Protein[b]	Moisture[c]	Ash[c]	Amylose[d]	Lipids[c]
Yam	88	0.1	8.8	0.09	36.0	1.1
Cassava	87.4	0.1	9.1	0.08	23.0	1.2

[a] Method of Dubois et al. (1956).
[b] Method of Hartree (1972).
[c] AOAC (1995).
[d] Method of Chrastil (1997).

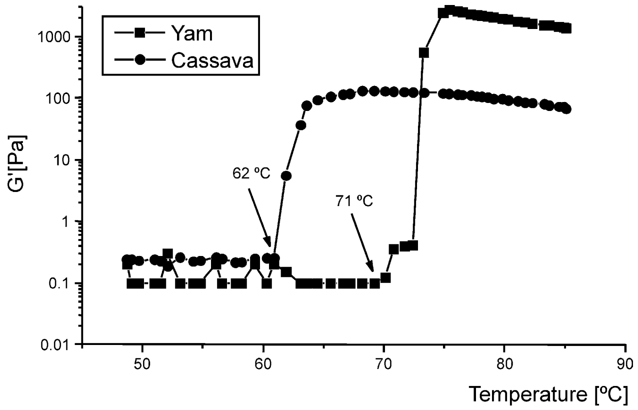

Fig. 1. G' as a function of the temperature at a heating rate of 4.0 °C min^{-1} at 50 g l^{-1} for suspension of yam and cassava starches, at a frequency of 1 Hz and deformation of 1%.

(1999). Cassava starch (*Manihot utilissima*) was obtained using the procedure of Willinger (1964) and was a gift of Prof. Dr José Domingos Fontana from UFPR.

2.2. Chemical analysis

Total carbohydrate was assayed by the phenol–H_2SO_4 method, with a necessary modification (Dubois, Gilles, Hamilton, Rebers, & Smith, 1956), protein by the procedure of Hartree (1972), ash, moisture and lipids were determined according to the standard AOAC (1995).

Deffating prior to preparation of samples for amylose determination was carried out by reflux extraction with ether for 5 h. The products were then dried at 100 °C.

Amylose contents were determined by the method of Chrastil (1987) with a modification, using amylose and waxy amylopectin (Sigma) as standards. Intermediate amylose proportions were obtained by mixing the amylose and amylopectin (100, 80, 70, 50, 40, 20, 0% of amylose). A straight line plot was used to determine the contents of amylose in the samples. The use of the multiplication factor of 45.8 for absorbance proposed by Chrastil to obtain

Table 2
Temperatures at the beginning (T_{onset}), end (T_{end}), and peak (T_m) of yam and cassava starch gelatinization at heating rates of 2.5, 3.0, 4.0 and 5.0 °C min^{-1}

Starch	Heating rates (°C min^{-1})	T_{onset} (°C)	T_{end} (°C)	T_m (°C)	ΔH (J g^{-1})
Yam	2.5	69.0	77.0	72.5	−11.5
	3	69.0	77.0	72.5	−11.5
	4	69.0	78.0	72.5	−12.0
	5	69.5	79.0	73.0	−11.5
Cassava	2.5	50.5	70.0	60.5	−8.5
	3	51.0	69.5	61.5	−7.0
	4	52.0	69.5	62.5	−6.5
	5	51.5	71.0	63.5	−6.5

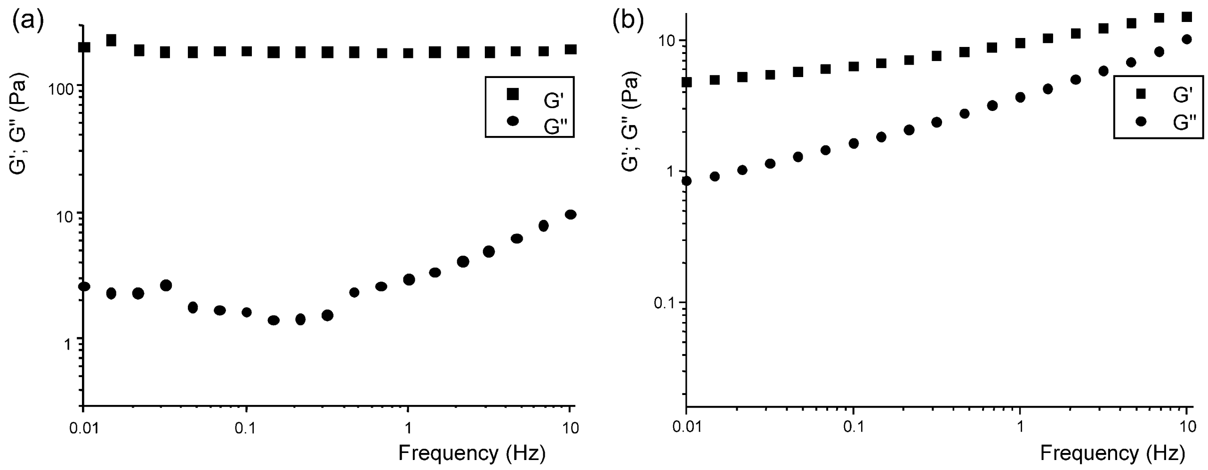

Fig. 2. Storage modulus (G'), loss modulus (G'') at 25 °C for yam (a) and cassava (b) starches pastes at 50 g l^{-1}.

the amylose content in g l^{-1} in the cuvet generated errors and was not used in this work.

2.3. Rheological analysis

2.3.1. Dynamical oscillatory

Gelatinization experiments were carried out using a suspension of 50 g l^{-1} starch in water, using a temperature range from 15 to 85 °C, heating rate of 4.0 °C min^{-1}, at a frequency of 1 Hz and a deformation of 1%.

Gels were also obtained at 50 g l^{-1} after autoclaving by 30 min and cooling at 5 °C for 24 h. All experiments were carried out in triplicate. The analysis was performed using an oscillatory Haake rheometer, model RS 75, sensor C 60/2° using a Peltier system to control the temperature. The stress used in the frequency sweep experiments (0.02–10 Hz) was 0.5 Pa. This value refers to the viscoelastic-linear region, where the gel structure was preserved. Cooling was carried out in the rheometer, using a layer of mineral oil to avoid evaporation.

2.4. Thermal analysis

2.4.1. DSC analysis

DSC analysis was performed using a Shimadzu DSC-50, with a sample weight of ~5 mg of starch and 10 mg of water. The heating rate was 2.5, 3.0, 4.0 and 5.0 °C min^{-1} in an inert atmosphere maintained with a nitrogen flux of 50 ml/min. The DSC calibration was performed with indium. The samples were weighed directly in the aluminium sample holder, and water was added with a Hamilton microsyringe. After sealing, the pan was left to equilibrate for 30 min, and weighed before and after the heating process to observe water loss during the heating cycle. As some of the pans did not support the temperature, pressure and loss of water, mainly at higher temperatures, these experiments were carried out in triplicate.

2.4.2. Kinetic analysis

The dependence of the rate constant on the temperature for gelatinization of starch samples was obtained using the Arrhenius equation (Eq. (1)). To determine the activation Energy (E_a), Ozawa (1965) and Pielichowski et al. (1998) proposed the plot of ln of the heating rates (2.5, 3.0, 4.0 and 5.0 °C min^{-1}), in place of the rate constant (K), as a function of the reciprocal of the absolute temperature at different gelatinization percentages, obtained by the slicing of the endothermic spectra and representing as α (%) for 0, 5, 10, 20, 30, 40, 50, 60, 80 and 100% of gelatinization. The angular fit of this plot gives the $-E_a/R$, and the linear fit the pre exponential factor (A), as shown in Eq. (1).

$$\ln K = \ln A - E_a/RT \qquad (1)$$

where:

K = rate constant (s^{-1})
A = pre exponential factor
E_a = activation energy (kJ mol^{-1})
R = Gas universal constant
T = absolute temperature (K)

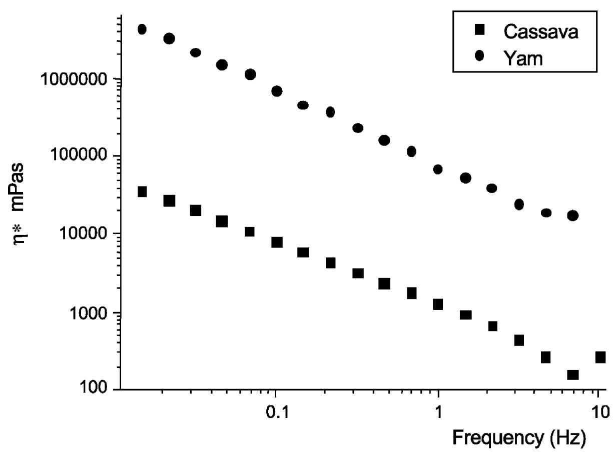

Fig. 3. Complex viscosity (η^*) at 25° for yam and cassava starches pastes at 50 g l^{-1}.

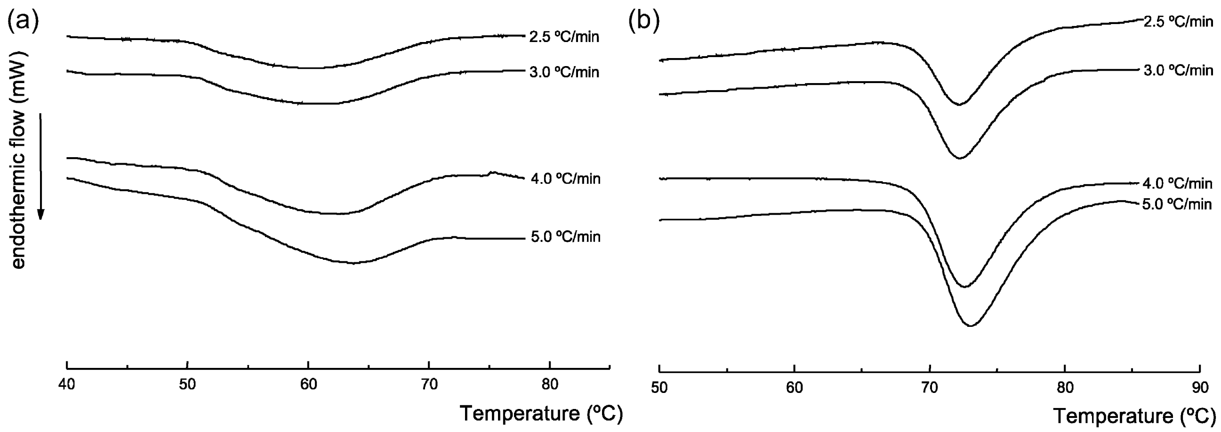

Fig. 4. DSC scans at 2.5–5.0 °C min^{-1} of cassava (a) and yam (b) starches (5 mg with 10 mg of water).

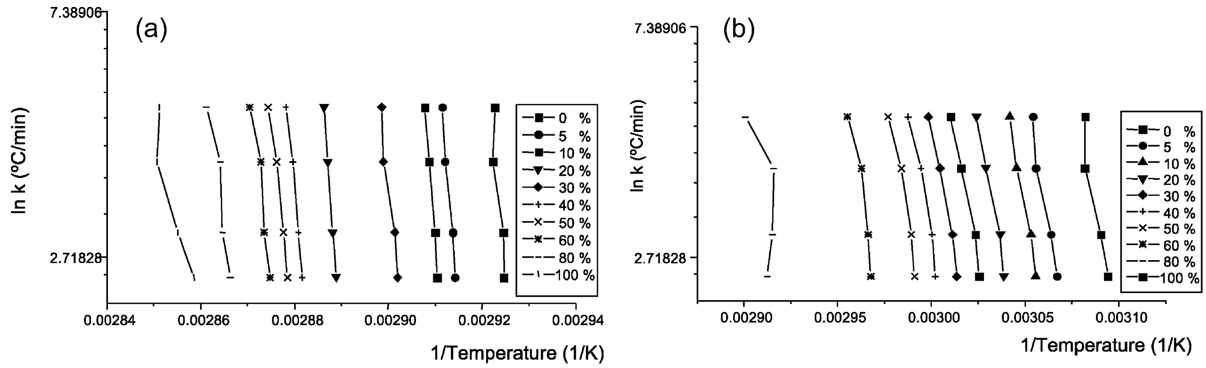

Fig. 5. ln k (°C min^{-1}) as a function of the inverse of the absolute temperature—$1/T$ (1 K^{-1}) to the yam (a) and cassava (b) starches (5 mg with 10 mg of water).

With the values of E_a and A, it is possible to obtain the rate constant, using constant temperatures of gelatinization of 65, 69, 71, 73 and 75 °C for yam and 50, 60, 65 and 70 °C for cassava starches. These temperatures refer to the beginning, middle and end of the gelatinization processes.

3. Results and discussion

3.1. Chemical analysis

The amylose content of yam starch is higher than that of cassava starch and also of common corn starch (Sigma) used here in a reference. The amylose contents of starch samples were determined by the method of Chrastil using an amylose and amylopectin standards, and the straight line obtained showed a correlation of 0.990. Using these modifications, after deffating, the values obtained for common corn Sigma (used here as reference), yam and cassava starches, 27.5, 36.2 and 23.0%, respectively. Table 1 summarize the chemical composition of the samples.

The amylose content in starches were different to that reported by other authors: 17% for cassava and 28% for corn (Whistler & BeMiller, 1997), 29% for yam (McPherson & Jane, 1999), 27% for yam (Hoover & Vasanthan, 1994), 28.5 and 19.8% for yam and cassava, respectively (Gunaratne & Hoover, 2001), and 30% in yam by Mali et al. (2002) and Alves et al. (1999). These differences might be explained by the different growing conditions, the method of lipid extraction and amylose determination (Mali et al., 2002).

3.2. Rheological analysis

Fig. 1 shows the gelatinization temperature of yam and cassava starches as determined by oscillatory

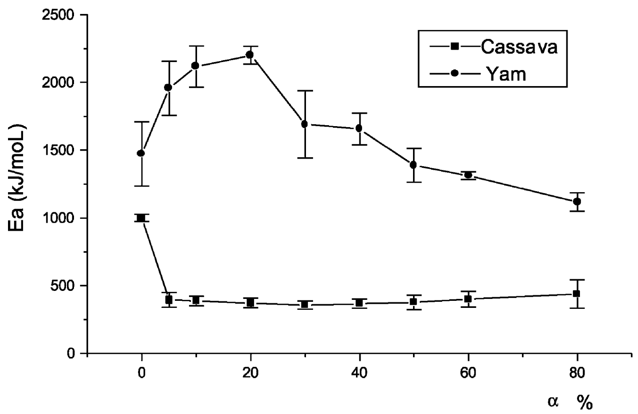

Fig. 6. Energy of activation (E_a) as a function of percentage gelatinization (α%) for yam and cassava starches.

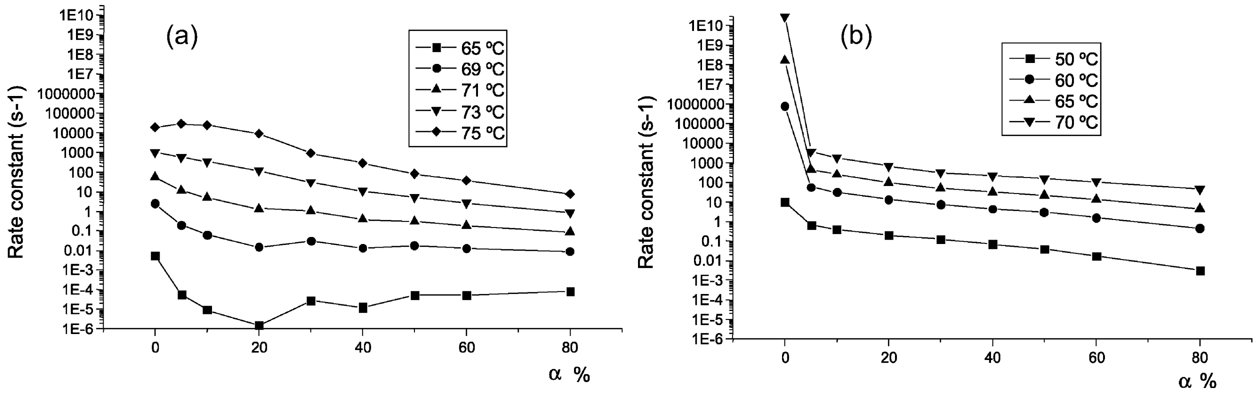

Fig. 7. Rate constant (s^{-1}) as a function of degree of gelatinization (α%) for yam (a) and cassava (b) starches.

rheometry, the initial temperatures being ~71 and ~62 °C, respectively. By DSC analysis, these were 69 and 52 °C. This disparity could be due to the difference in concentration. In the case of cassava, the process of gelatinization was a lower endothermic event, when analyzed by DSC (Table 2) and a spread gelatinization process (Fig. 4(a)). The yam starch had a better resolved process (Fig. 4(b)) and this probably generates a more accurate approximation in the DSC and rheological analyses.

In the dynamic rheological analysis, a viscoelastic behaviour was obtained over a frequency of 0.02–10 Hz. A linear G^* and deformation were less than 5% up to the stresses of 10 Pa for yam and 5 Pa for cassava starch (data not show). The currently used stress was 0.5 Pa.

The storage (G') and loss (G'') moduli after 24 h of refrigeration for yam and cassava starches at 50 g l^{-1} are shown in Fig. 2(a) and (b), where the formation of a true gel is shown, the G' value being three times greater than G''. The mechanical spectra in Fig. 3 shows that yam starch gives a high viscosity paste (up to three times), when compared with the cassava starch gel, at the same concentration. The gel formed by yam had a great tendency to suffer retrogradation and to become opaque. This behavior is due to the higher content of amylose in yam than in cassava starch. Translucency of the gel of cassava starch has been reported by Whistler and BeMiller (1997).

3.3. DSC and kinetic analysis

DSC curves of yam starch at different heating rates of 2.5, 3.0, 4.0 and 5.0 °C min^{-1} are presented in Fig. 4.

T_{onset}, T_{end} and T_m values of the gelatinization process are shown the Table 2. It can be observed that the maximum values and those at the beginning and end of the process are identical for all DSC curves, probably due the similarity of the heating rates.

From the gradient of Fig. 5, $-E_a/R$ was obtained where E_a is the activation energy of the gelatinization process and R is the gas universal constant.

Fig. 6 shows E_a (kJ mol^{-1}) as a function of the degree of conversion or degree of gelatinization (α%). These data show that an increase of energy occurs in 0–20% of gelatinization, and, that prior to this, the E_a values are smaller for yam, but practically constant for the cassava sample. The profile of yam starch is similar to that obtained by Pielichowski et al. (1998) in their study on potato starch gelatinization. However, the values of E_a were lower than owns, but the temperature range was higher in their investigation.

Using the value of E_a, shown in Fig. 6, it was possible to calculate the rate constant (s^{-1}), for different temperatures (65, 69, 71, 73 and 75 °C), as depicted in Fig. 7(a) and (b) for yam, and cassava starches, where temperatures of 50, 60, 65 and 70 °C were used. As an example, heating of starch at 60 °C, when compared with the heating at 75 °C, generates a decrease in the rate constant in the order of 10^{-13} s^{-1}. The higher values of the rate constant for cassava indicate a more rapid process of gelatinization when compared with yam starch.

4. Conclusion

A more defined process of gelatinization occurs with yam starch which generates a stronger gel, as well as a higher E_a of gelatinization when compared with that of cassava. This behaviour is in accordance with and dependent on the amylose content in the starch samples.

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