Cocoa butter symmetrical monounsaturated triacylglycerols: separation by solvent fractionation and application as crystallization modifier

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Abstract Symmetrical monounsaturated triacylglycerols—also known as SUS (saturated unsaturated saturated triacylglycerols)—are the main triacylglycerols present in cocoa butter (CB), exhibiting decisive influence in the tempering process conditions and sensorial characteristics in chocolate products. CBs with lower amounts of SUS do not crystallize adequately in chocolate processing, generating a low quality product with higher susceptibility to fat bloom formation. In this context, fractions with higher contents of SUS triacylglycerols were obtained by solvent fractionation of cocoa butter, under four operating conditions varying crystallization temperatures (17, 18, 20 and 22 °C) and sample/acetone solvent ratios (1:7 and 1:5, in w/v). After solvent evaporation, CB fractions were evaluated in terms of triacylglycerol profile, solid fat content and melting point. The solvent fractionation performed at 17 °C with a 1:7 ratio of cocoa butter:acetone favored the separation of a higher concentrated SUS stearin (denominated as S17) with 7.1% increment in SUS triacylglycerols, mainly StOSt—1-stearyl-2-oleoyl-stearin (26.9%) and POSt—1-palmitoyl-2-oleoyl-stearin (45.0%). Additionally, S17 was added to pure cocoa butter at three different proportions of CB:S17 (95:5, 90:10 and 80:20, in w/w) and

the blend was evaluated by isothermal crystallization (at 17.5 °C) and consistency (at 10, 15 and 20 °C). Compared to the pure cocoa butter, at 10 °C, the blend with 20% stearin (80:20) showed an increment of 67% in the consistency and considerable higher crystallization rates at 17.5 °C were found, confirming the potential contribution of the SUS triacylglycerols as crystallization modifiers of CB.

Keywords Cocoa butter · Symmetrical monounsaturated triacylglycerols · Solvent fractionation · Acetone fractionation · Lipid crystallization

Introduction

Cocoa butter (CB) is formed by a mixture of several triacylglycerol types, and depending on the variety, origin, seasonality and also handling techniques for obtaining organic CB, its triacylglycerol (TAG) composition can vary significantly, as generally occurs to natural vegetable fats and oils. Usually, the fatty acid profile of CB is mainly composed of oleic (O), stearic (St) and palmitic (P) acids in ranges of, approximately, 32.5–36.5, 33.0–37.5 and 24.0–28.0%, respectively. POP (1-palmitoyl-2-oleoyl-palmitin), StOSt (1-stearyl-2-oleoyl-stearin) and POSt (1-palmitoyl-2-oleoyl-stearin) are the main TAGs determined for CB, preferably with oleic acid esterified in the *sn*-2 position of the glycerol molecule, forming symmetrical monounsaturated triacylglycerols (SUS, from saturated unsaturated saturated). These specific symmetrical TAGs represent approximately 79 to 89% of cocoa butter composition and exhibit unique crystal packing characteristics, affecting greatly the material crystallization behaviour. Therefore, due to its TAG composition, cocoa butter

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displays specific physical characteristics as, for example, sharp melting point near mouth temperature and bright surface, when subjected to a precise and controlled crystallization process (Yamada et al. 2005; Awad and Marangoni 2006; Beckett 2008; Zarringhalami et al. 2010; Jahurul et al. 2013; Vieira et al. 2015).

Compared to CB produced in other countries as Malaysia, Sri Lanka and Nigeria, the SUS composition of the Brazilian CB is generally considered low with values of, approximately, 36, 25 and 18% in POST, StOST and POP, respectively. According to Foubert et al. (2004), the Brazilian cocoa butter generally contains specifically less StOST triacylglycerol amounts and, therefore, exhibits softer consistency compared to other cocoa butter origins. Besides this critical characteristic, the amount of SUU (saturated unsaturated triacylglycerols) of the Brazilian CB is generally higher than the CB from other geographical origins, aiding the formation of a decreased thermal resistance crystal structure. Therefore, when combining these composition characteristics, these CBs can exhibit inadequate crystallization behaviour for chocolate production, favouring the appearance of some structural defects as fat bloom formation, loss of surface gloss and delayed melting behaviour at mouth temperatures (Lipp and Anklam 1998). In order to avoid the appearance of these defects in the final product and the probable rejection by the consumers, the application of a CB with softer consistency usually requires that a blend with a harder CB or other fats be previously implemented (Ribeiro et al. 2012).

One possible alternative for standardizing cocoa butter quality for chocolate production is the fractionation of the softer cocoa butter in order to obtain a concentrated fraction in high-melting point TAGs—specially the symmetrical monounsaturated ones—for being implemented as a harder CB material. Thus, the initial softer CB can be blended with the separated CB stearin in order to conform suitable industrial standard requirements.

Usually fats can be fractionated without or with solvent addition, depending on the triacylglycerol composition of the lipid system and the desired final fraction characteristics. After fat fractionation, two fractions with different melting behaviours are obtained and commonly named stearin and olein, respectively, for the higher and low melting point lipid materials. The dry fractionation requires a rigid control of the cooling rate for crystals formation and is generally applied for fats systems containing TAGs with sufficiently different melting point range, allowing their separation only by the temperature control. Due to CB triacylglycerol tight composition, it is necessary the addition of a solvent for the dissolution of the TAG mixtures and promote their crystallization and separation in high purity fractions. Hexane and acetone are the most common

solvents used in wet fractionation and they exhibit different benefits for the separation process. For instance, hexane evinces higher solubility towards lipid systems than acetone, and therefore, can be applied at lower amounts. On the other hand, acetone presents higher selectivity to different TAG types, allowing higher amounts of symmetrical monounsaturated triacylglycerols to crystallize in the cooling process (Kellens et al. 2007; Illingworth 2002; Hashimoto et al. 2001).

Besides its application in standardizing cocoa butter composition, the use of a high-melting point CB fraction was reported to aid the inhibition of fat bloom in chocolate products (Weyland 1992; Lonchamp and Hartel 2004) and also as a CB fraction (obtained by acetone fractionation at 0 °C of a 9% solution) for studying the polymorphic behaviour in blends of pure CB and olive oil (Lovegren et al. 1976). Although these disclosures have already reported about cocoa butter fractionation, neither the applied fractionation conditions as solvent and process temperatures were acknowledged nor a more suitable temperature and sample/ratio were investigated.

In this context, the main objective of the current work is to present a detailed examination on possible crystallization temperatures and sample concentration after dilution in acetone to allow a suitable fractionation process for the separation of a high concentrated SUS CB fraction. Furthermore, the evaluation in terms of consistency and isothermal crystallization behaviour after the addition to pure cocoa butter of the high-melting point CB fraction at different concentrations (95:5, 90:10 and 80:20, in w/w of pure CB and CB stearin) was determined in order to increase the understanding of the action of symmetrical monounsaturated triacylglycerols as main responsible for the proper crystal network formation in cocoa butter for chocolate production.

Materials and methods

Materials

Deodorized cocoa butter (CB) was provided by Cargill Agrícola S.A. (Brazil) with the main fatty acids composition: palmitic, stearic and oleic acids as 25.6, 34.6 and 34.6%, respectively. Acetone (HPLC grade) was purchased at Mallinckrodt Baker, Inc. (USA).

Solvent fractionation of cocoa butter

Four different experiments were performed varying the fractionation (crystallization) temperature and the sample/solvent ratio, in order to separate a cocoa butter stearin with high concentration of symmetrical monounsaturated

Table 1 Operating conditions of the cocoa butter (CB) solvent fractionation procedures and the respective stearin and olein identification

Experiment	CB:acetone ratio (weight/volume)	Crystallization temperature (°C)	Stearin identification	Olein identification
#1	1:5 (50 g/250 mL)	18	S18	O18
#2	1:5 (50 g/250 mL)	20	S20	O20
#3	1:5 (50 g/250 mL)	22	S22	O22
#4	1:7 (50 g/350 mL)	17	S17	O17

triacylglycerols (SUS). For each experiment, 50 g of melted cocoa butter and 250 or 350 mL of acetone were transfer to a 500 mL-closed vessel (Marconi, Brazil) with a thermal jacket compartment connected to a thermostatic bath (Lauda, Germany), stabilized at the crystallization temperature of 17, 18, 20 or 22 °C. The operating conditions for each fractionation experiment are described in Table 1. The processing variables—crystallization temperature and volume of acetone added in each test—were previously selected by preliminary tests. The crystallization process was performed under pneumatically stirring of approximately 20 rpm, with a stirring paddle (diameter: 7.5 cm) consisting of two flaps with a central orifice of 1.0 cm diameter in each side, for improving sample homogenization. The blend of cocoa butter and solvent was kept at the crystallization temperature during 24 h to promote the formation and growth of lipid crystals. The particles formed were removed by simple filtration, using filter paper (with a mean pore diameter of 14 µm) in a room with controlled temperature of, approximately, 20 °C to prevent melting of the crystals. Solvent entrapped in the fractions was later removed by a rotary evaporator (Buchi, Switzerland), followed by application of nitrogen gas to enable complete acetone desorption. The stearin and olein fractions of cocoa butter were stored at room temperature for further evaluation. In the complementary material, Scheme 1 (Online Resource 1) displays apparatus photos and the fractionation processing performed.

Blends preparation

Cocoa butter stearin—obtained as mentioned in Section “Solvent fractionation of cocoa butter”, and pure cocoa butter were completely melted at 60 °C, in order to eliminate all previous crystalline forms. Blends were obtained by adding the melted CB and CB stearin at three different proportions: 95:5, 90:10 and 80:20 (in w/w), respectively, and then subjected to constant stirring at 60 °C, during 10 min to ensure complete homogenization. After incorporation of the lipid materials, the blends were cooled and stored at room temperature (approximately 20 °C) in closed amber glass bottles.

Methods

Fatty acid composition

Gas Chromatograph (GC) system Agilent 6850 Series (USA) equipped with a capillary column was used to obtain fatty acid composition of the cocoa butter, as described by the AOCS Method Ce 2-66 (AOCS 2009). The fatty acid methyl esters were separated according to Hartman and Lago (1973), using a 60 m length DB-23 Agilent capillary column (USA) (50% cyanopropyl-methylpolysiloxane) with internal diameter of 0.25 mm and coated with a 0.25 µm film. Qualitative composition was determined by comparing peak retention times with the respective standards for fatty acids. Samples were analyzed in duplicate and the values reported are means of two injections.

Triacylglycerol composition

Triacylglycerol composition was determined in triplicate by the capillary GC CGC Agilent 6850 Series GC System (USA), with a DB-17 HT Agilent capillary column (USA) (50%-phenyl-methylpolysiloxane) 15 m in length and 0.25 mm of internal diameter, coated by a 0.15 µm film. The operating conditions were: 1:100 split injection ratio; initial column temperature of 250 °C, heated up to 350 °C at 5 °C/min; helium as stripping gas at 1.0 mL/min; injector temperature of 360 °C; detector temperature of 375 °C; 1.0 µL injection volume and 10 mg/mL in tetrahydrofuran of sample concentration. Triacylglycerols were identified by comparing retention time with standard samples and were quantified by relative peak area evaluation (Antoniosi Filho et al. 1995).

Solid fat content and melting point

Solid fat content (SFC) was obtained using a nuclear magnetic resonance (NMR) spectrometer Bruker pc 120 Minispec (Germany), as described at AOCS direct method Cd 16b-93 (2009). The samples were first melted at 60 °C for 15 min, chilled at 0 °C for 90 min, kept at 26 °C for

40 h and at 0 °C for 90 min in a high precision dry bath (TCON 2000, Duratech, USA). After this preparation, the samples were held at each measuring temperatures (10, 20, 25, 30, 35 and 40 °C) for 60 min prior to SFC measurements. The results were expressed as the mean of two determinations. Melting point range was determined from the temperature range corresponding to a SFC of approximately 4%, as reported on Ribeiro et al. (2009).

Consistency

Consistency was determined in a texture analyzer TA-XT Plus (Stable Micro Systems, UK). Prior to the determination, the samples were heated to 60 °C for complete melting of the fat crystals, conditioned in 50 mL-plastic beakers, cooled to 5 °C during 24 h, and then conditioned for 24 h at each of the measurement temperatures (10, 15 and 20 °C). The probes applied were Plexiglas® cones with non-truncated tip angle of 40° and 45°, selected according to the test temperature. The analysis operation conditions were: penetration depth of 10 mm and probe velocity of 2 mm/s. The compression force was obtained in gram force (g_F) and converted to yield value (YV), as described by Haighton (1959), in the following Eq. (1):

$$YV = \frac{K \cdot W}{p^{1.6}} \quad (1)$$

where YV is yield value, in g_F/cm^2 ; K is a constant dependent on the cone angle (for 40° and 45°, K = 5840 and 4700, respectively); W is compression force, in g_F ; p is penetration depth, in units of 0.1 mm. The samples were analyzed in quadruplicate and the results were expressed as the means of the replicates.

Isothermal crystallization

Solid fat content as a function of crystallization time was automatically monitored by NMR (Bruker pc120 Minispec, Germany) at intervals of 1 min, under isothermal temperature of 17.5 °C, until stabilization of SFC values. Prior to the evaluation, the samples were melted at 60 °C for 15 min to ensure destruction of all crystalline forms, and maintained at 50 °C for 1 h in a high precision dry bath (TCON 2000, Duratech, USA). The results were expressed as the mean of two determinations.

Statistical analysis

Yield value (g_F/cm^2) was statistically evaluated by one-way analysis of variance (ANOVA) using STATISTICA V.8 (StatSoft Inc., USA). Tukey's post hoc test was applied

for statistical comparison among the means with a significance level of 5% ($p < 0.05$).

Results and discussion

Separation of cocoa butter stearin through solvent fractionation

In order to obtain a concentrated fraction in SUS triacylglycerols from cocoa butter, four fractionation experiments were carried out in the presence of acetone and under specific crystallization temperature, as shown in Table 1. After fractionation, two distinct fractions were obtained and termed as olein (O) and stearin (S) for the low and high melting point fractions, respectively.

Figure 1 displays the composition in symmetric monounsaturated triacylglycerols—StOSt, POSt and POP—of pure cocoa butter (CB), cocoa butter stearins (S17, S18, S20 and S22) and oleins (O17, O18, O20 and O22), obtained at the respective fractionation temperatures of 17, 18, 20 and 22 °C. A more detailed TAG composition of CB and CB fractions is presented in Table 1 of the complementary material (Online Resource 1).

Before fractionation, the cocoa butter presented a total of 83% of SUS triacylglycerols, comprising 20, 23 and 40% of POP, StOSt and POSt, respectively. According to Shukla (2005), depending on the CB origins, the SUS content can vary between 71 and 87%, usually with the lowest value found for the Brazilian CB and the highest, for the Malaysian one. As the SUS triacylglycerol composition implies directly in the hardness characteristics of CB samples due to their unique crystal packing behavior, the Brazilian CB is commonly classified as the softest and the Malaysian CB, in the other hand, as the hardest type. The CB evaluated in the present study contained approximately 83% of SUS, a SUS value higher than expected for a Brazilian material, probably because it was produced by blending different cocoa butter samples. The use of cocoa butter blends from different origins in order to modify their crystallization and consistency behavior is a common industrial practice in Brazil, mainly for chocolate production (Timms 2003).

After fractionation, POP was preferable found in the olein fractions in all the experiments performed due to its lower melting point compared to POSt and StOSt triacylglycerols. The highest contents of POP were determined for O17, O18 and O20, with approximately 10% of POP increment compared to pure CB.

On the other hand, POSt and StOSt were preferable found in the stearin fractions at the applied crystallization temperatures. The highest increases of POSt and StOSt contents were determined, respectively, for stearin S17 and S20 with 5 and 6% of increments compared to pure CB.

Fig. 1 Composition (in %) of symmetric monounsaturated triacylglycerols—StOSt, POSt and POP—of pure cocoa butter (CB), cocoa butter stearins (S17, S18, S20 and S22) and oleins (O17, O18, O20 and O22) at respective fractionation temperatures of 17, 18, 20 and 22 °C

Some studies based on crystal polymorphs of cocoa butter and pure triacylglycerols revealed that StOSt is prone to initiate the β -crystallization, which is the desired crystal form in chocolate products (Schenck and Peschar 2004, Foubert et al. 2004, Hachiya et al. 1989). As reported by Shukla (2005), the Brazilian CB contains approximately 23.8% of StOSt, whilst the Malaysian CB presents 31% of this specific TAG. Therefore, stearin S20, containing about 29% of StOSt, can be applied as a starting material and subjected to additional fractionation steps as a possible source of StOSt triacylglycerols.

Considering the total amount of symmetric monounsaturated triacylglycerols in the fractions obtained after each fractionation process, S17 presented the highest content of SUS with a total of 90%, i.e., 7% higher than the original CB SUS content. Correspondingly, the olein O17 obtained in the same experiment conditions showed the lowest SUS content (63%). The contrasting SUS composition of S17 and O17 ratified the efficiency of TAG separation of the fractionation experiment carried out at 17 °C and a sample/solvent ratio of 1:7. Oppositely, the operating conditions used to obtain S22 and O22 corresponded to the less effective CB separation, demonstrated by their similar SUS TAG composition.

According to Hashimoto et al. (2001), acetone tends to selectively crystallize higher amounts of symmetric monounsaturated triacylglycerols than the nonsymmetrical ones, making it suitable for the specific separation of a higher SUS concentrated fraction compared to other traditional lipid solvents applied as, for instance, hexane. Therefore, besides the appropriate crystallization

temperature of 17 °C, the efficient separation of a concentrated fraction in SUS triacylglycerols in stearin S17 is also due to the more effective dispersion/dissolution and SUS selectivity provided by the higher addition of acetone applied in this specific fractionation process.

As a complement to the chemical composition, the efficient separation of CB in two lipid fractions (stearin and olein) can also be validated by evaluating the physical characteristics of the two distinct materials obtained. Figure 2 shows the solid fat content as a function of measurement temperatures for pure cocoa butter (CB), cocoa butter stearins (S) and oleins (O).

An overall inspection of the solid curves (Fig. 2), confirms that S17 and O17 were the fractions that presented major differences in solid fat contents at the same equilibrium temperatures compared to the other pairs of CB fractions (S18/O18, S20/O20 and S22/O22). The stearin fraction S17 presented the highest amount of symmetric monounsaturated triacylglycerols (90%), as described previously in the TAG composition results, and also showed increased solid fat contents at all measured temperatures, confirming the efficiency of the fractionation process carried out at 17 °C and with a CB/acetone ratio of 1:7. The S17, for instance, exhibited 82% of solid fat content at 20 °C (17% higher than pure CB at the same temperature), whilst O17 presented only 1%, i.e., it liquefied.

On the other hand, the fractionation process performed at 22 °C did not achieve distinct stearin (S22) and olein (O22) fractions, due to the higher crystallization temperature.

Fig. 2 Solid fat content (in %) as a function of temperature (°C) of pure cocoa butter (CB), cocoa butter stearins (S) and oleins (O)

The melting temperature of cocoa butter and fractions was considered as the value corresponding to 4% of solid fat content. According to Shukla (2005), cocoa butter can display melting temperatures between 32 and 35 °C, depending on its triacylglycerol composition. Additionally, it is desirable that the melting temperature of cocoa butter and chocolate products be less than 36 °C in order to melt at the mouth temperature.

Observing the solid curves in Fig. 2, cocoa butter and all the stearins presented melting temperature of approximately 34 °C, whilst the oleins O17, O18, O20 and O22 presented, respectively, lower melting temperatures of 19, 19, 27 and 33 °C.

The similar melting temperature of the stearins compared to the pure cocoa butter allows their application in chocolate products, at least considering their ability of melting at corporal temperature.

As expected, the oleins showed lower melting temperatures, pointing out, however, that O22 presented a melting point closer to its correlated stearin (S22), confirming once more the inefficiency under these experiment conditions. On the other hand, S17 and O17 showed again a very dissimilar melting characteristic and, therefore, a highly efficient separation of their fractionation procedure, corroborating with previous results.

Lovegren et al. (1976) reported the polymorphic behaviour using differential scanning calorimetry evaluation of cocoa butter, cocoa butter stearin and olein added to olive oil at different concentrations (10, 20, 30 and 50%). The cocoa butter fractions were obtained by a fractionation process at 0 °C of a 9% solution of cocoa butter in acetone.

As also observed in the present research, the composition of the high-melting fraction of cocoa butter was concentrated in POST, StOST and POP. However, probably due to the rather low fractionation temperature and the high cocoa butter:solvent ratio used, they reported a melting point of 38 °C for the CB stearin, an increment of 3 °C compared to the one of pure cocoa butter. The higher melting temperature of the CB stearin will favour the formation of a more thermally resistant crystal structures, but can also lead to waxy sensorial defect.

Application of high concentrated SUS stearin to modify crystallization and consistency behaviors of cocoa butter

After the evaluation of the triacylglycerol composition and crystallization of the fractions presented in the previous section, the stearin S17—with 90% of SUS TAG content—

Table 2 Composition (in %) of symmetric monounsaturated triacylglycerols (TAG)—POP, POST and StOST—of pure cocoa butter (CB), cocoa butter stearin (S17) and blends of CB:S17 in the proportions of 95:5, 90:10 and 80:20 (w/w)

TAG (%)	CB	CB:S17 95:5	CB:S17 90:10	CB:S17 80:20	S17
POP	19.6	19.5	19.3	19.1	17.0
POST	40.3	40.5	40.7	41.2	44.7
StOST	22.7	23.0	23.2	23.8	28.0
Total	82.6	83.0	83.2	84.1	89.7

Fig. 3 Yield value (in g_F/cm^2) of pure cocoa butter (CB), CB stearin (S17) and 95:5, 90:10 and 80:20 (w/w) blends of CB:S17 measured at 10, 15 and 20 °C. Same letters for the same temperature indicate that there are no significant differences between the means evaluated by Tukey's test ($p < 0.05$)

Fig. 4 Crystallization isotherm at 17.5 °C (% of solid fat content vs. time in min) of pure cocoa butter (CB), CB stearin (S17) and blends of CB:S17 in the proportions of 95:5, 90:10 and 80:20 (w/w)

obtained at 17 °C and with a CB/acetone ratio of 1:7 was considered for modifying the lipid structure characteristics of cocoa butter, at three proportions of CB and S17, respectively 95:5, 90:10 and 80:20, in w/w.

The symmetric monounsaturated triacylglycerols (POP, POST and StOst) composition of these blends are shown at Table 2.

The presence of higher levels of SUS triacylglycerols favors the increment of thermal resistance of lipid materials and, consequently, increases its hardness characteristics. In order to assess the effects in the consistency behavior of the modified CB added with S17, samples were evaluated in

terms of their yield value (YV) in g_F/cm^2 at three different measurement temperatures (10, 15 and 20 °C) and the results are shown in Fig. 3.

The yield values of S17 presented almost three times the values determined for pure CB at 10 °C, with an increment of approximately 53,700 g_F/cm^2 . At the same measured temperature, samples 90:10 and 80:20 (CB:S17) displayed YV of approximately 58,000 g_F/cm^2 , whilst the pure CB presented 34,000 g_F/cm^2 . Sample 95:5 (CB:S17) did not show significant modification of the YV at the three temperatures applied with values comparable to the sample with no S17 addition.

Crystallization isotherms of CB, S17 and blends measured at 17.5 °C are exhibited in Fig. 4. The blends of CB and S17 showed similar initial crystallization behavior. After 50 min at the setting temperature, however, the 80:20 sample (CB:S17) displayed slightly higher solid content than the other blends. During this same period, CB presented lower solid levels compared to the other samples, specially compared with pure stearin and the 80:20 (CB:S17) blend.

The results showed that about 10% addition of cocoa butter stearin in pure cocoa butter is able to significantly alter the crystallization behavior and consistency of CB. Therefore, the use of a stearin fraction concentrated in symmetrical monounsaturated triacylglycerol can be an important issue to enhance the thermal resistance and consistency hardness of confectionary fats. Besides, the presence of higher amounts of StOSt triacylglycerols can also strengthen the development of β crystals in the tempering process—desirable in the chocolate production—and also inhibit the formation of fat bloom during chocolate storage.

Conclusion

A lipid fraction with 89.7% of symmetrical monounsaturated triacylglycerols (SUS), comprised mainly by POSt, StOSt and POP, was separated by solvent fractionation of cocoa butter at 17 °C with a CB/acetone ratio of 1:7 (in w/v). This fraction concentrated in SUS can be applied to modify the crystallization and consistency behavior of softer cocoa butter and further in the development of higher thermally resistant chocolate products, facilitating tempering process and inhibiting fat bloom formation over storage period.

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