Synthesis of oleic acid based esters as potential basestock for biolubricant production

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Abstract

Ester derivatives of 9, 10-dihydroxystearic acid were prepared and characterized. The processes involved were epoxidation of oleic acid, opening of the oxirane ring, and esterification. The structures of the products were confirmed by FTIR, ^{1}H- and ^{13}C-NMR. The low-temperature properties of each product were characterized using the pour point test. Other physical properties, such as flash point and viscosity, were also determined. The results show that desirable low temperature properties were obtained for triester **7**, with a pour point value of –25 °C. It was discovered that increasing the chain length of the mid-chain ester and the branching at the end-chain ester had a positive influence on low-temperature properties of the triesters. These products could plausibly be used as biobased industrial materials in biolubricants, surfactants, or fuels.

Key Words: Oleic acid based esters, pour point, biolubricants

1. Introduction

The need to utilize biobased resources is of considerable importance due to high cost of petroleum feedstock. Furthermore, due to strict government regulations and increasing public concern for a pollution-free environment, there has been a constant demand for environmentally friendly biolubricants (Adhvaryu et al., 2000; Adhvaryu and Erhan, 2002). Most lubricants originate from petroleum stock, which is toxic to the environment and difficult to dispose of. Vegetable oils with high oleic content are considered potential candidates to substitute conventional mineral oil-based lubricating oils and synthetic esters (Adhvaryu et al., 2005).

Of particular interest is the synthesis of branched oleochemicals, which are being studied in the lubricant (Altın et al., 2001), surfactant (Carlsson, 2009), and fuel additive (Caro et al., 1997) industries. The use of renewable feedstocks, such as vegetable oils, to obtain industrial products is of increasing importance. Vegetable oils are a viable and renewable source of environmentally favorable oils (Adhvaryu et al., 2004).

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The development of new, efficient, and environmentally benign pathways, which can lead to new value added products, is still an area with high potential (Aramaki and Khalid, 2004; Campanella et al., 2010). This strategy can decrease our dependence on non-renewable, and therefore limited, resources such as mineral oil. Vegetable oils as biolubricants are preferred because they are biodegradable and nontoxic, unlike conventional mineral-based oils. Vegetable oils have different properties than mineral oils due to different chemical structures. They have very low volatility due to the higher molecular weight of the triacylglycerol molecule and a narrow range of viscosity changes with temperature. Superior anticorrosion properties of vegetable oils result from their high affinity for metal surfaces (Metzger, 2009). Vegetable oils are classified as non-flammable liquids because they have high flash point values of over 300 $^{\circ}$C. Polar ester groups are able to adhere to metal surfaces, and, therefore, possess good boundary lubrication properties. In addition, vegetable oils have high solubilizing power for polar contaminants and additive molecules. On the other hand, vegetable oils show poor oxidative stability, primarily due to the presence of bisallylic protons, and they are highly susceptible to free radical attack and subsequently undergo oxidative degradation to form polar oxy compounds (Fox and Stachowiak, 2007). Furthermore, low-temperature studies have shown that most vegetable oils exhibit cloudiness, precipitation, poor flow properties, and solidification at -10 $^{\circ}$C, upon long-term exposure to cold temperatures. These characteristics are disadvantages of vegetable oils, in sharp contrast to mineral oil-based fluids (Salimon and Salih, 2009).

Chemical modification of vegetable oils is an attractive way to solve these problems and to obtain valuable commercial products from renewable raw materials (Knothe and Carlson, 1998; Chi, 1999; Knothe, et al., 2000). The introduction of branched or bulky moieties into the structure of esters of various acids can enhance properties (for example, fluidity range) required for numerous practical applications such as biolubricants and cosmetics. On the other hand, some compounds with bulky moieties did not significantly influence the cloud point of vegetable oil methyl esters, which would be required to improve the cold-flow properties of those esters when used as alternative biolubricants (Knothe, 2001).

One useful reaction for the chemical modification of oleochemicals is epoxidation. Epoxidation methods for transforming olefinic and oleochemical compounds have been known for many years (Findley et al., 1945; Schmits and Wallace, 1954), and the process has been studied (Scala and Wool, 2002) and patented (Crocco et al., 1992). Epoxidations, are generally performed using organic peracids formed in situ via the attack of H_2O_2 on a carboxylic acid in aqueous solution. Epoxidation of fatty acids derived from vegetable oils is an important, yet less studied, approach to producing value added materials.

In this paper, we report the synthesis of novel α-hydroxy esters and tri-esters from 9, 10-epoxystearates, utilizing both head group manipulation and branching strategies to impart favorable low-temperature behavior to these lipid-based materials. Addition of behenic acid to the oxirane moiety of epoxidized oleic acid at elevated temperature (100 $^{\circ}$C) is the key step (Figure) in a 4-step sequence that includes epoxidatin, oxirane ring opening and esterification. The structures of all synthesized compounds were confirmed by FTIR, ^{1}H-, and ^{13}C-NMR analysis with subsequent evaluation of the products (**3-7**) for low temperature operability using pour point (PP) determinations. This study may aid in the continued development of biobased materials for use as alternatives to petroleum products in industry and elsewhere.

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2. Materials and methods

2.1. Materials

Formic acid (88%) was obtained from Fisher Scientific (Pittsburgh, PA, USA) and oleic acid (92%) from ChemaR (Poland). All other chemicals and reagents were obtained from Aldrich Chemical (Milwaukee, WI, USA). All materials were used without further purification. All organic extracts were dried using anhydrous magnesium sulfate (Aldrich Chemical).
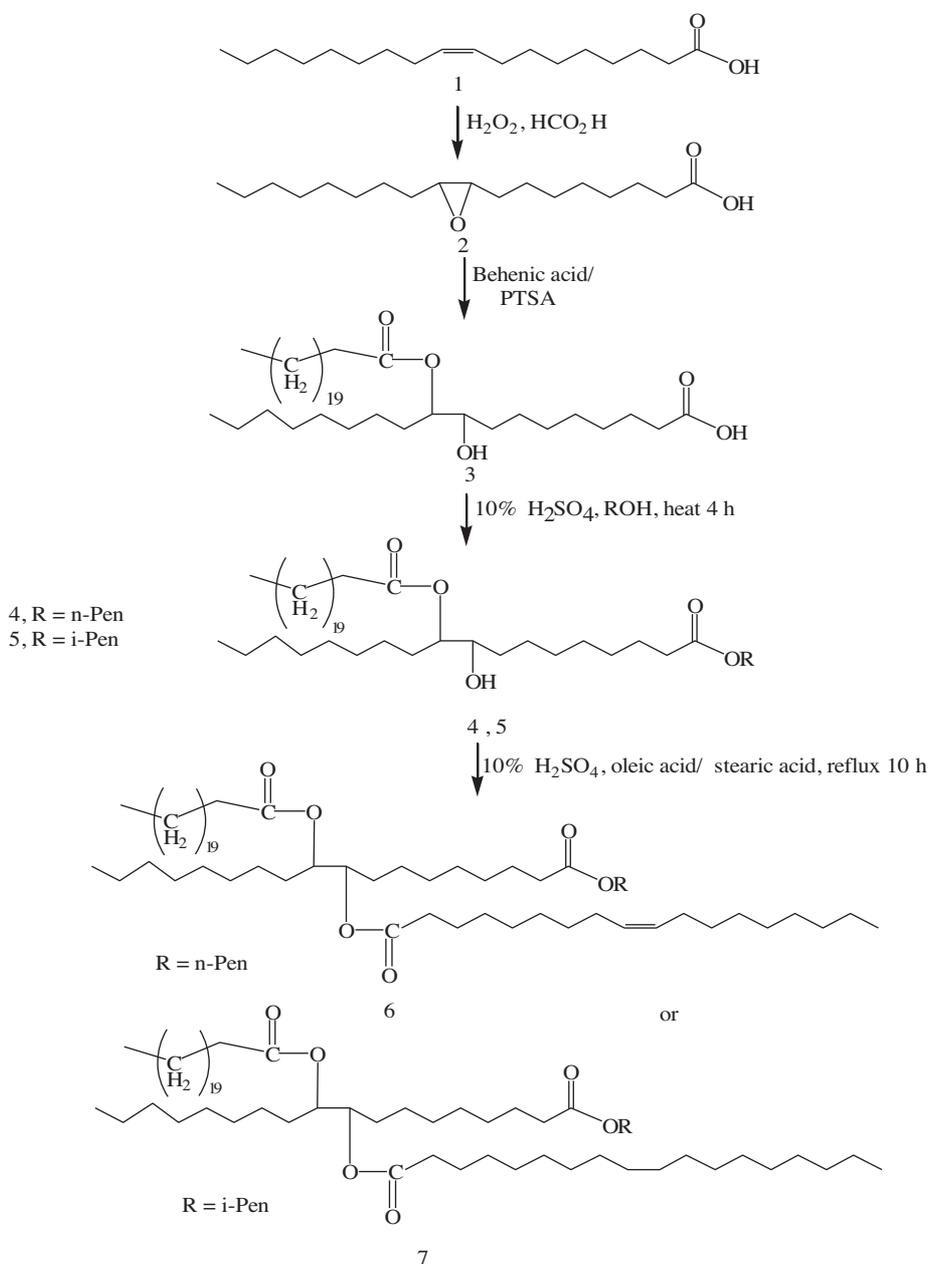

Figure. Synthesis of triesters from oleic acid.

2.2. Characterization

The ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL JNM-ECP 400 spectrometer (400 MHz ^{1}H/100 MHz ^{13}C) using DMSO-d$_6$ as a solvent in all experiments. Fourier transform infrared (FTIR) spectra were recorded on a Perkin Elmer GX FTIR Spectrophotometer (USA).

2.3. Low temperature operability

The PP is defined as the lowest temperature at which the sample still pours from a tilted jar. This method is routinely used to determine the low temperature flow properties of fluids. PP values were measured according to the ASTM D5949 method (ASTM Standard D5949) using a Phase Technology Analyzer, Model PSA-70 S (Hammersmith Gate, Richmond, B.C., Canada). Each sample was run in triplicate and average values rounded to the nearest whole degree are reported in the Table. For a greater degree of accuracy, PP measurements were done with a resolution of 1 °C instead of the specified 3 °C increment. Generally, materials with lower PP exhibit improved fluidity at low temperatures than those with higher PP (Table).

Table. Pour point, flash point, viscosity values, and percentage yield of the prepared products.

Compound	R	Yield (%)	PP^c	FP^d	DV^e
2	-	70	-	132	-
3	-	62	-	202	65
4	n-Pen^a	50	-20	187	78
5	i-Pen^b	75	-22	297	88
6	n-Pen	65	-24	265	105
7	i-Pen	77	-25	245	113

^{a}n-Pen = n-pentyl
^{b}i-Pen = iso-pentyl
^{c}PP = pour point; Means n = 3, SE ± 1 °C
^{d}FP = flash point, Means n = 2, SE ± 1 °C
^{e}DV = dynamic viscosity

2.4. Flash point values

The flash (FP) is defined as the minimum temperature at which the liquid produces a sufficient concentration of vapor above it that it forms an ignitable mixture with air. The lower the FP is, the greater the fire hazard. FP determination was run according to the American National Standard Method using a Tag Closed Tester (ASTM D 56-79) (ASTM Standard D 56-79). Each sample was run in duplicate and the average values rounded to the nearest whole degree are reported in the Table.

2.5. Dynamic viscosity measurements

The dynamic viscosity at 25 °C was measured on a calibrated Brookfield Viscometer equipped with a spindle (size 4) at a speed of 100 rpm. Viscosity was described in centipoise (cp) with millipascal-second (mPa s) units (Table).

2.6. Epoxidation oleic acid

Hydrogen peroxide (30% in H_2O, 8.0 mL) was added to a stirred solution of oleic acid (92%, **1**, 10 g) in formic acid (88%, 9.0 mL) at 4 °C (ice bath) and the combined reaction was allowed to proceed at room temperature with vigorous stirring (900 rpm) until the formation of a white, powdery solid was observed in the reaction vessel (about 2-5 h). The solid was collected via vacuum filtration, washed with H_2O (chilled, 3 × 10 mL), and placed for 12 h under high vacuum. The product was further dried by a Kugelrohr vacuum and the resulting precipitate collected and recrystallized from ethanol to give 9,10-epoxystearic acid **2** as a colorless, powdery-solid. ^{1}H-NMR (400 MHz, DMSO-d$_6$): δ 11.3 (1H, O–**H**), 2.9 (1H, -**C**H(O)CH-), 2.3 (2H, -**CH**$_2$CO$_2$H), 1.8-1.6 (2H, -**CH**$_2$CH$_2$CO$_2$H), 1.5-1.3 (4H, -**CH**$_2$CH(O)CHC**H**$_2$-), 1.1-0.8 (20H, -**CH**$_2$-), 0.6 (3H, -C**H**$_3$); ^{13}C-NMR (100 MHz, DMSO-d$_6$): δ 178 (-**C**O$_2$H), 33 (-**CH**$_2$CO$_2$H), 30 (-**C**H(O)CH-), 15 (-**C**H$_3$). FT-IR (neat): 2924 and 2850 cm^{-1} (sharp CH$_2$ stretch), 1743 (sharp carbonyl stretch), 1462 (CH$_2$ bending vibrations), 1422 (O-H bending), 1370 (CH$_3$ symmetrical bending vibrations), 1290 (acid C-O stretch), 721 (CH$_2$ rocking vibrations), 1146 (ether C-O-C symmetrical stretch), 894 (C-C asymmetrical ring stretch), 825 ("12 micron band") (Sliverstien et al., 2005) and a small peak at 3413 (O–H stretch).

2.7. Synthesis of monoester

Epoxidized oleic acid (**2**, 6 g) and 5 g of *p*-toluenesulfonic acid (PTSA) were dissolved in toluene in a 250-mL 3-neck flask equipped with a cooler, a dropping funnel, and a thermometer. The mixture was maintained at 5 °C. Behenic acid (6 g) was added over 1.5 h, keeping the reaction mixture temperature between 70 and 80 °C. The reaction mixture was subsequently heated at 90-100 °C for 3 h. After reaction's completion, the heating was discontinued and the mixture was left to stand overnight at ambient room temperature. The mixture was then washed with water and the organic layer was dried over anhydrous magnesium sulfate. The solvent was removed using a vacuum evaporator to provide ring opening product **3**. ^{1}H-NMR (400 MHz, DMSO-d$_6$): δ 11.4 (1H, O–**H**), 3.7 (1H, -CH(O**H**)), 3.5 (1H, -**C**H(OH)), 3.2 (1H, -**C**H(OCOC$_{21}$H$_{43}$)), 2.6 (2H, -**CH**$_2$CO$_2$H), 2.4-2.2 (2H, -**CH**$_2$CH$_2$CO$_2$H), 1.9-1.7 (2H, -**CH**$_2$CH(OH)-), 1.5-1.4 (2H, -**CH**$_2$CH)OCOR), 1.2-0.7 (40H, -**CH**$_2$-), 0.9 (6H, -C**H**$_3$ × 2); ^{13}C-NMR (100 MHz, DMSO-d$_6$): δ 176 (-**C**O$_2$H), 174 (-**O**COR), 80 (-**C**H(OH)-), 72 (-**C**H(OCOC$_{21}$H$_{43}$)), 36 (-**CH**$_2$CH(OCOC$_{21}$H$_{43}$)), 15 (-**C**H$_3$). FT-IR (neat): 3486 cm^{-1} (O–H stretch), 2922 and 2850 (sharp CH$_2$ stretches), 1730 (sharp carbonyl stretch), 1463 (CH$_2$ bending vibrations), 1372 (CH$_3$ symmetrical bending vibration), 1248, 1177, and 1109 (ester C-O stretch), 721 (CH$_2$ rocking vibrations).

2.8. Synthesis of diesters

Sulfuric acid (10% H_2SO_4) was added to a solution of 9(10)-hydroxy-10(9)-behnyloxystearic acid (**3**, 1.0 g) in either 3.35 mL *n*-pentanol or 3.35 mL *iso*-pentanol. The suspension was heated with stirring at 60 °C for 4 h. Hexanes (5 mL) was then added, and the solution was washed with NaHCO$_3$ (sat. aq., 1 × 0.5 mL) and brine (2 × 1 mL), dried over anhydrous magnesium sulfate, filtered, concentrated in vacuo, and placed under high vacuum for 6 h to yield the desired compounds of (**4**) or (**5**) respectively. ^{1}H-NMR (400 MHz, DMSO-d$_6$): δ 11.5 (1H, O–**H**), 3.9-3.7 (1H, -CH$_2$**C**H(CH$_3$)$_2$), 3.4 (1H, -**C**H(OCOC$_{21}$H$_{43}$)), 2.5 (2H, -**CH**$_2$CO$_2$-), 1.9-2.1 (2H, -**CH**$_2$CH$_2$OCO-), 1.6-1.4 (2H, -**CH**$_2$CH$_2$CO$_2$-), 1.3-1.1 (2H, -**CH**$_2$CH(OH)-), 1.0-0.7 (60H, -**CH**$_2$-), 0.9-0.8 (2H, -**CH**$_2$CH(CO$_2$C$_{21}$H$_{43}$)-), 1.1 (9H, -C**H**$_3$× 3); ^{13}C-NMR (100 MHz, DMSO-d$_6$): δ 175, 174 (2C,

-CO_2-), 76, 72 (2C, -C-O-), 36 (1C, -CH_2CO_2R), 15 (-CH_3). Additional signals in the ^{1}H- and ^{13}C-NMR spectra vary with the different ester groups. FT-IR (neat): 3420 cm^{-1} (O–H stretch), 2924, 2856 (sharp CH_2 stretch), 1737 (sharp carbonyl stretch), 1460 (CH_2 bending vibrations), 1370 (CH_3 symmetrical bending vibration), 1247, 1173, 1105 (ester C-O stretch), 721 (CH_2 rocking vibrations).

2.9. Synthesis of triesters

Either oleic acid (5 g) or stearic acid (5 g) was added to a solution of alkyl 9(10)-hydroxy-10(9)-behnyloxystearate (4 or 5, 5 g) and sulfuric acid (10% H_2SO_4) in a 2-neck round-bottomed flask equipped with a magnetic stir bar at room temperature; then the reaction mixture was refluxed with stirring for 10 h. After the reaction was transferred to a separatory funnel, the lower aqueous phase was removed, and hexane (20 mL) was added to the upper oily phase. The organic phase was then washed with NaHCO$_3$ (sat. aq., 2 × 5 mL) and brine (2 × 5 mL), dried over anhydrous magnesium sulfate, filtered, concentrated in vacuo, and placed under high vacuum for 6 h to provide the triesters (6 and 7) as clear oils, which were stored over molecular sieves to mitigate potential hydrolysis. ^{1}H-NMR (400 MHz, DMSO-d$_6$): δ 5.6-5.4 (2H, -$CH=CH$-), 4.4-4.6 (1H, -$CH_2CH(CH_3)_2$), 3.4 (CH(OCO-oleyl(strearyl))), 2.4-2.2 (2H, -CH_2CO_2-), 1.6-1.4 (2H, -$CH_2CH_2CO_2$-), 1.2-1.1 (2H, -$CH_2CH(CO_2C_{21}H_{43})$-), 0.8-0.6 (12H, -CH_3 × 4); ^{13}C-NMR (100 MHz, DMSO-d$_6$): δ 176-172 (3C, -CO_2-), 77-74 (3C, -C-O), 37 (1C, -CH_2CO_2R), 16 (-CH_3). Additional signals in the ^{1}H- and ^{13}C-NMR spectra vary with the different ester groups. FT-IR (neat): 2941, 2824 (sharp CH_2 stretches), 1737 (sharp carbonyl stretch), 1462 (CH_2 bending vibrations), 1370 (CH_3 symmetrical bending vibration), 1244, 1174, 1106 (ester C-O stretch), 721 (CH_2 rocking vibrations).

3. Results and discussion

3.1. Synthesis

In our earlier studies on the synthesis of diesters (Salimon and Salih, 2010) we described the treatment of epoxidized ricinoleic acid with appropriate fatty acids in the presence of catalytic p-toluenesulfonic acid (PTSA) to yield various ring opened products. The process was followed by the esterification of carboxylic acid group with isobutanol to afford diester products. In the present work, we describe the synthesis of the ester derivatives 3-7 through epoxidation of oleic acid, oxiran ring opening to afford compound 3, esterification of carboxylic acid hydroxyl group with n-pentanol and iso-pentanol to give diesters 4 and 5, and finally esterification of the resulting α-hydroxy group in diesters 4 and 5 with oleic and to give triesters 6 and 7.

In this study, the end-chain esters (R= n-pentyl, iso-pentyl) were employed for comparison between linear (R= n-pentyl, 4) and branched (R= iso-pentyl, 5) esters with respect to low temperature properties. Additionally, to study the effect of mid-chain substituents, unsaturated acid 6 (oleic acid) and saturated acid 7 (stearic acid) were studied to reveal their low-temperature properties. The addition of behenic acid to oxirane 2 to afford monoester 3 by ring opening esterification (Campanella and Baltanás, 2007) was accomplished at elevated temperature (100 °C), and this step of the reaction required a catalyst due to the large, bulky structure of behenic acid. The use of a catalyst is necessary to avoid either an extended reaction time or failure to react.

When behenic acid was added to oxirane moiety in the manner described above, monoesters were produced. The additional mid-chain ester group serves as a point of branching along an otherwise linear fatty

acid backbone. Behenic acid was selected such that a long mid-chain substituent would allow for the study of branch size on the low temperature properties discussed below. No efforts to distinguish the regiochemistry (**3**; 9-hydroxy-10-behnyloxystearic acid versus the equally likely 10-hydroxy-9-behnyloxystearic acid regio-isomers) or the stereochemistry (R or S at C9 and C10) of the monoester were made, due to the laborious chromatography required and the economics involved when potentially taken to larger commercial scales. If such materials are eventually adopted for commercial use, then production costs relating to synthesis and purification are of paramount importance. Therefore, the mono-, di-, and triesters prepared here were tested for low-temperature behavior without further purification.

3.2. Low temperature operability

The ability of a substance to remain liquid at low temperatures is an important attribute for a number of industrial materials, such as lubricants, surfactants, and fuels. Therefore, mono-, di-, and triesters **3**-**7** were screened for cold-flow performance through determination of their PPs. An improvement in the cold-flow behavior of triesters **6** and **7** (Table) was obtained over that of alkyl 9(10)-hydroxy-10(9)-behnyloxystearate precursors **4** and **5**. Actually there are 2 reasons for this behavior. The first reason is that in the triester compounds the lack of a hydroxyl group means there are no hydrogen bonds, which could cause the molecules to stack together. Secondly, as mid-chain ester substituents increase in size, a corresponding improvement in low-temperature behavior was observed. We hypothesize that this behavior is due to the greater ability of these substituents to more effectively disrupt crystal formation at reduced temperatures. For example, comparing di- and triesters (**4** and **6**) (Figure), we noted an improvement in PP when there are fewer hydroxyl groups in the molecule and an increase the number of mid-chain substituents (PP = –20 °C, **4** and PP = –24 °C, **6**). A similar trend was exhibited when comparing **5** to **7**; increasing the number of substituents in the mid-chain group prevents individual molecules from coming close for easy stacking and breaks the symmetry of the molecules. This behavior results in the formation of microcrystalline structures rather than macro-structures. At lower temperatures, such microcrystalline structures can easily tumble and glide over one another, resulting in better fluidity of the total matrix. Furthermore, the nature of the end-chain ester group also plays a role in the cold-flow behavior of di- and triesters; branching in the end-chain ester lowers the PP (Salimon and Salih, 2010). We can see this trend when we compare PP of **4** to **5** and **6** to **7**, which also helps favor microcrystalline structures rather than macro-structures. On the other hand, the medium to high viscosity of the synthesized compounds was due to their bulky structures.

4. Conclusion

Based on the results obtained, the presence of long chains alkyl groups in the middle of the molecules has a strong influence on the cold-flow properties by disrupting of the arrangement of the molecules into an orderly pattern and lowering the temperature at which crystallization occurs. Furthermore, the nature of the end-chain ester group also plays a role in the cold-flow behavior of the synthesized compounds. Triesters **7** and **8** exhibited the most favorable cold-flow characteristics, as determined by PP. Of the triesters, compound **7** yielded the best performance, with PP of –25 °C. For the mono-, di-, and triesters the viscosity increases, whereas the PP decreases. This behavior is due to the increasing in the chain length of the branching agents.

Acknowledgments

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