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Synthesis of Vanillyl Acetate through Fischer Esterification of Acetic Acid and Vanillyl Alcohol Product of Vanillyl Reduction

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ABSTRACT

The aims of this research are (1) synthesis of vanillyl alcohol compounds using sodium borohydride (NaBH4) and synthesis of vanillyl acetate compounds through Fischer esterification reaction between acetic acid and vanillyl alcohol from reduced product of vanillin, (2) characterization of vanillyl alcohol compounds and vanillyl acetate compounds using Thin Layer Chromatography (TLC), Fourier transform Infrared (FTIR) and Gas Chromatography Mass Spectroscopy (GS-MS). Vanillyl alcohol was obtained by reducing the aldehyde group of vanillin using sodium borohydride (NaBH4). Through the Fischer esterification reaction between the reduced compound of vanillin and acetic acid using H_2SO_4 as a catalyst, vanillyl acetate was characterized using TLC, FTIR, and GC-MS. The identification results using TLC showed the appearance of the functional group OH alcohol and CO alcohol in the area of 3442.22 cm^{-1} and 1153.99 cm^{-1} on the IR spectrum of vanillyl alcohol. Identification using GC-MS stated that vanillyl alcohol has a purity of 91.13% of 154 m/z value in the yield of 59.74%. The results of the esterification reaction form the brown solids with a yield of 63.98%. Meanwhile, the characterization results using TLC showed that the synthesis of vanillyl acetate has been formed by the appearance of the functional group C=O ester at a wave number of 1738.59 cm^{-1} and CO ester at 1274,2 cm^{-1} on the IR spectrum of vanillyl acetate.

Keyword: vanillyl acetate, reduction, esterification

1. INTRODUCTION

Vanillin or 4-hydroxy-3-methoxybenzaldehyde is an aromatic aldehyde compound that has the molecular formula $C_8H_8O_3$. Functional groups of Vanillin are methoxy, hydroxy, and aldehyde groups. The reduced aldehyde group in the vanillin compound will produce a new compound, namely vanillyl alcohol. To reducing the aldehyde group of vanillin, sodium borohydride ($NaBH_4$) can be used (Fowler, 1992). Sodium borohydride has the chemical formula $NaBH_4$. The reagent can be used in alcohol solvents or alkaline solvents in water (Clark, 2004). The use of $NaBH_4$ regent due to its unreactive nature with water so it is safer than lithium aluminum hydride with the chemical formula $LiAlH_4$ (Fessenden & Fessenden, 1998).

Vanillic alcohol compounds can be used in the formation of ester compounds (Budimarwanti, 2009). The synthesis of ester compounds is obtained through the Fischer esterification reaction. Esterification can be carried out using enzyme catalysts and inorganic acids (sulfuric acid or hydrochloric acid) with various alcohol variations (Ozgulsun, Karaosmanoglu & Tuter, 2000; Endo, Sanae & Kenshiro, 1997). Vanillyl alcohol compounds can be reacted with acetic acid through a Fischer esterification reaction with the help of a sulfuric acid as a catalyst (H_2SO_4) to produce a vanillyl acetate compound. The esterification process between carboxylic acids and alcohols using an acid catalyst has

been the subject of many researches. The esterification reaction has the advantage because the yield of the resulting yield is relatively large and the procedure is not too difficult. Acid esters have often been modified for food or other materials such as addictive substances, surfactants, and detergents. Most ester compounds have a fragrant aroma, but not all ester compounds have a fragrant aroma (Winarto, 2013).

The use of acetic acid in the community is better known as vinegar acid which has a CH_3COOH structure, it is belongs to the carboxylic acid group. The formula for acetic acid is often also written in the form CH_3-COOH, CH_3COOH, or CH_3CO_2H. It is generally used as a flavoring in food. In addition, acetic acid is also used in industrial fields such as preservatives, manufacture of medicines, dyes, plastics, manufacture of cellulose acetate fibers, and others (Sutresna, 2007).

2. RESEARCH METHOD

2.1 Vanillyl alcohol synthesis working procedure

The procedure was adopted from the previous research by Budimarwanti (2009). The reduction process was carried out by adding 2.997 grams of vanillin (0.0197 mol) and 20 mL of ethanol into a 250 mL three-neck flask equipped with a reflux. A total of 1.513 grams (0.04 mol) of $NaBH_4$ was added and stirred for 40 minutes at room temperature. After stirring, the mixture was acidified using 2.5 M HCl to reach the pH value 4.5. Then, the solution was filtered to produce residue and filtrate, followed by three times extraction process. using CH_2Cl_2. about 20 mL After that, the reaction product was put into a separatory funnel to separate the organic phase from the aqueous phase. The organic phase was dried using anhydrous Na_2SO_4, filtered, and evaporated, to analyzed by TLC, FTIR spectroscopy, and GC-MS spectroscopy.

2.2 Synthesis of vanillyl acetate procedure

The procedure was adopted from previous research by Winarto (2013). About 1.099 grams (0.0065 mol) of vanilyl alcohol, 20 mL of tetrahydrofuran (THF), and 0.324 gram of acetic acid (0.0054 mol). All materials were put into a 250 mL three-neck flask then equipped with a reflux. The magnetic stirrer was rotated at a consmagnetic in the constant speed of 300 rpm. After that, the H_2SO_4 98% was added for 5 hours at a temperature of 80^{o}C. The results from the reflux were filtered to obtain the residue and filtrate. After that, the filtrate was drying using anhydrous Na_2SO_4 then evaporated. The results then analyzed using TLC, FTIR spectroscopy, and GC-MS spectroscopy.

3. RESULTS AND DISCUSSION

3.1. Vanyllil alcohol synthesis

Reduction reaction using $NaBH_4$ as a reducing agent, produce a vanillic alcohol compound. The mole ratio between vanillin and $NaBH_4$ that used was 1: 4. Vanilyl alcohol obtained is a white solid. The compound resulting from the reduction reaction is determined by its melting point. Vanilyl alcohol has a melting point of 81-84^{o}C. Identification was continued using TLC to determine the progress of the reduction process by obtaining differences in stains and *Rf (Retardation factor)* values between vanillin and the reduced compounds. The eluents used in this research was dichloromethane, benzene, and acetic acid with a ratio of 12.5 : 05 : 0.25. The results of observations under a UV lamp showed that vanillin and reduction results has *Rf* value of 0.68 and 0.46. Based on the *Rf* results, the vanillin stain has an greater *Rf* value than the vanillin alcohol stain, so that the vanillin alcohol compound is polar. The results of the reduction of vanillin were then identified using FTIR to identify the functional groups of a compound. IR spectrum of vanillin and vanilyl alcohol in Figures 1 and 2.

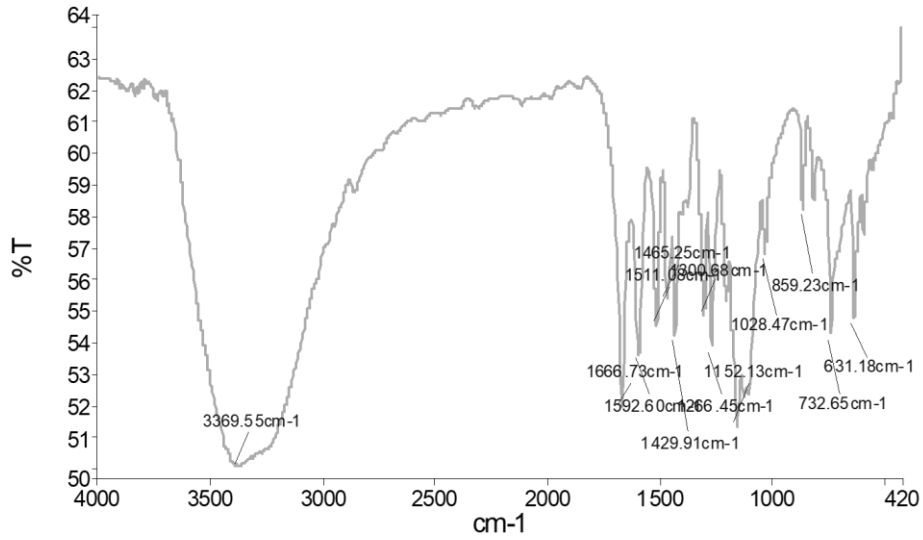

Figure 1. IR spectrum results of vanillin alcohol

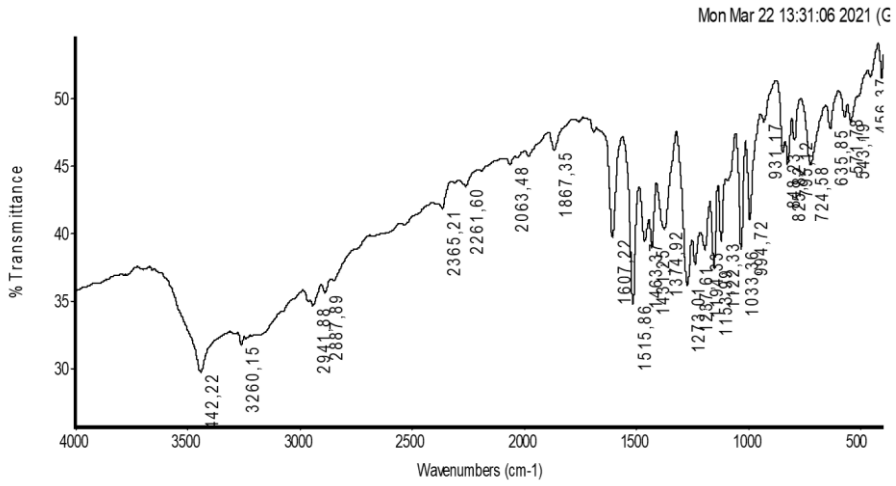

Figure 2. IR spectrum results of vanyllil alcohol

Based on the IR spectrum results, it shows that there are different functional groups absorption of vanillin and vanilyl alcohol compounds. It can be seen by the formation of the CO alcohol group on the vanilyl alcohol compound at a wavelength of 1153.99 cm^{-1}. In addition to the formation of a new group on the vanillic alcohol. It was also strengthened by a shift in the wave number of 1666.73 cm^{-1} which is a C=O aldehyde group, and a shift in the wave number of 2900-2700 cm^{-1} for CH aldehyde from the IR spectrum of vanillin which no longer appears on the IR spectrum of vanilla alcohol. Reduction already take place when the aldehyde functional group has been converted into a primary alcohol. The presence of primary alcohol indicated by the presence of free -OH absorption (alcohol) in the 3442.22 cm^{-1} of the vanilyl alcohol spectrum. There is a wide absorption in the 3260.15 cm^{-1} of the phenolic -OH absorption due to hydrogen bonding. The presence of primary alcohol is also supported by the presence of a methylene group (-CH_2-) at a wavelength of 1431.25 cm^{-1} in the IR spectrum of vanillyl alcohol. The results of the reduction of vanillin were followed by identification using GC-MS to determine the purity, molecular mass, and fragmentation of the compounds resulting from the reduction of vanillin. Vanilyl alcohol GC chromatogram can be seen in Figure 3 and the mass spectrum of vanilyl alcohol can be seen in Figure 4 and Figure 5 below.

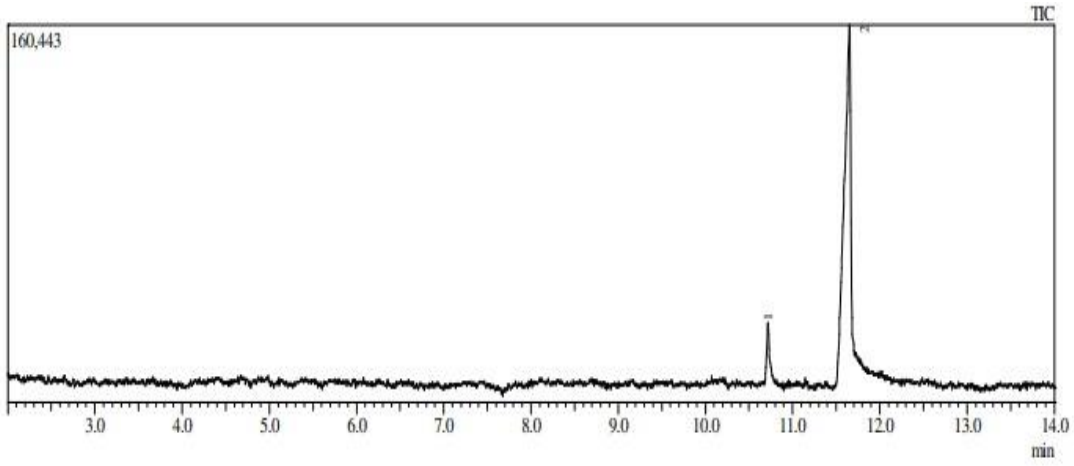

Figure 3. GC chromatogram of vanyllil alcohol

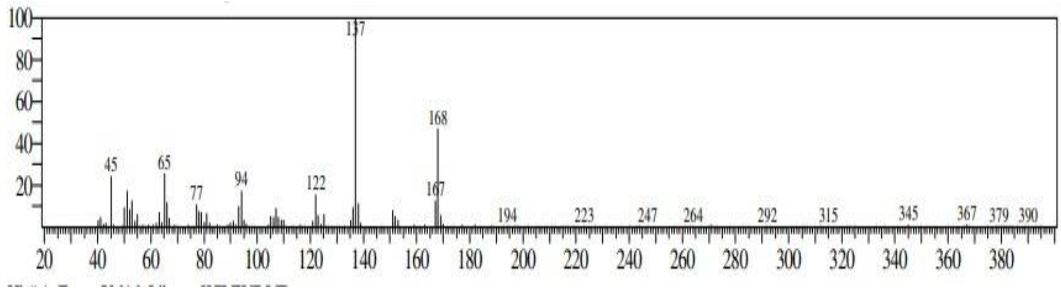

Figure 4. Mass spectrum of the 1st peak of vanilla alcohol with a retention time of 10,718

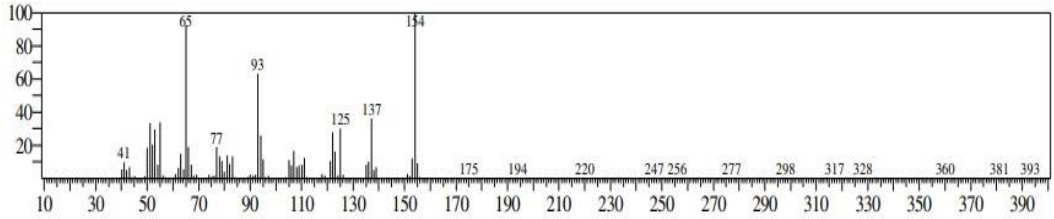

Figure 5. Mass spectrum of the 2nd peak of vanilyl alcohol with a retention time of 11,652 minutes

Based on the GC chromatogram in Figure 3, two peaks from the compound of reduction reaction were produced. The first peak show the percent area of 8.87% and retention time of 10.718 minutes with an *m*/*z* of 168. It means, the compound is 2-methoxy-4-(methoxymethyl)-phenol. While the second peak on the chromatogram shows a basic peak with an *m*/*z* of 154 with a retention time of 11.652 minutes. The *m*/*z* corresponds to the relative molecular mass of the vanilyl alcohol compound, which is 154. The vanilyl alcohol compound has a purity of 91.13%. This is supported by the fragmentation pattern of the vanillic alcohol compound in Figure 6. Based on theoretical calculations, the resulting vanilyl alcohol is 3.0369 grams (0.0197 mol). Meanwhile, in this study, the mass of the reduced was 1.991 grams, and the yield produced was 59.74%.

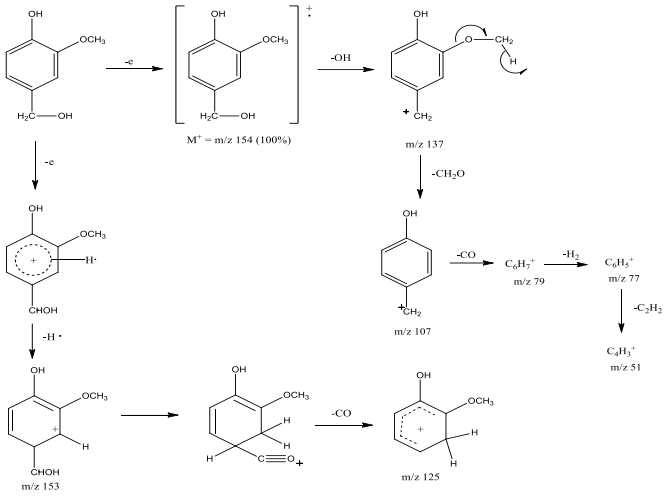

Figure 6. The fragmentation pattern of vanilyl alcohol

3.2. Synthesis vanyllil acetate

Synthesis of vanilyl acetate ester compounds was carried out through the Fischer esterification reaction process between acetic acid and the results of the reduction reaction of vanillin using H_2SO_4 98%. The mol ratio between acetic acid and vanillic alcohol is 1: 1,2. Vanilyl acetate obtained in the form of a brown solid about 0.7 grams. The esterification results were identified using TLC to determine the progress of the esterification process by obtaining the differences in stains and *Rf* between vanilyl alcohol and vanilyl acetate. The eluents used were dichloromethane, benzene and acetic acid with a ratio of 12.5 : 05 : 0.25. The following *Rf* value of vanillin, vanilyl alcohol, and vanilyl acetate compounds can be seen in Table 1.

Table 1. *Rf* value result

Sample	pH=4,5
Rf Vanilin	0,68
Rf Vanilil Alkohol	0,4
Rf Vanilil Asetat	0,48

Based on Table 1 it can be seen that there are three stains that have *Rf* value. The vanilyl acetate compound has *Rf* value compared to the *Rf* of the vanilyl alcohol compound. The larger the *Rf*, the less polar the compound. Based on the *Rf* value result, it was concluded that the order of the most polar compounds to the less polar compounds was vanilyl alcohol, vanilyl acetate, and vanillin, respectively. The esterification results then identified using FTIR to identify the functional groups of a vanilyl acetate compound. The IR spectrum of vanilyl acetate can be seen in Figure 7.

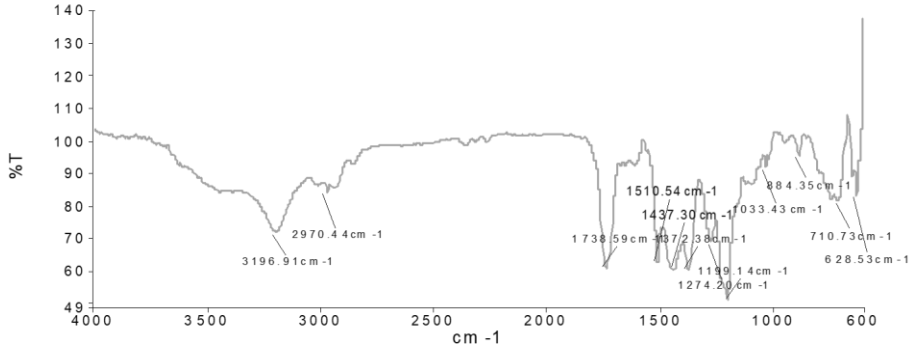

Figure 7. IR spectrum of vanilyl acetate

Based on the IR spectrum of vanilyl acetate, it shows that there are different functional group absorptions of the two compounds, vanilyl alcohol and vanilyl acetate. The difference is in the appearance of absorption of the C=O ester and CO ester groups on the vanilyl acetate compound. The absorption of the C=O ester group was at a wavelength of 1738.59 cm^{-1} followed by the appearance of the CO ester group at a wavelength of 1274.2 cm^{-1}. Esterification of vanilyl acetate compounds have been formed if the CO alcohol group in the vanillic alcohol no longer appears in the vanilyl acetate spectrum. Besides, being shown by the loss of the CO alcohol group, it was also strengthened by the loss of primary alcohol in the vanilyl acetate spectrum. The primary alcohol in question is the absorption of free OH (alcohol) and a methylene group (-CH_2-) in the vanilyl alcohol spectrum. The esterification results were followed by identification using GC-MS to determine the purity and molecular mass of the vanilyl acetate compound. The vanilyl acetate GC chromatogram can be seen in Figure 8 and the vanilyl acetate mass spectrum in Figure 9.

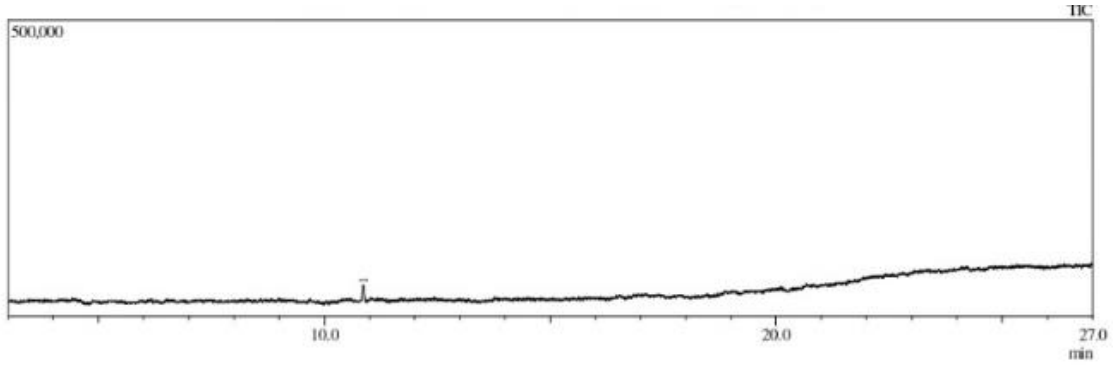

Figure 8. Vanilyl acetate GC chromatogram

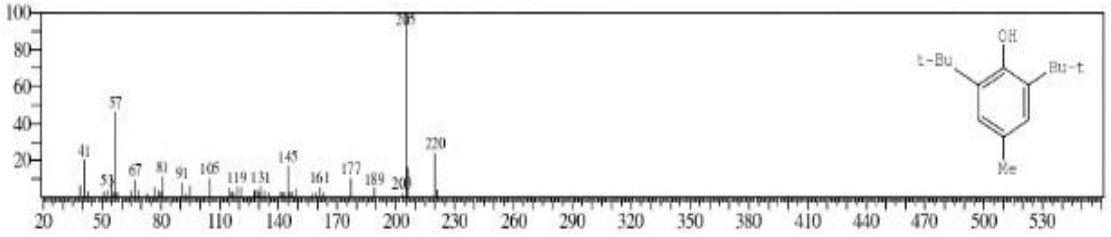

Figure 9. The mass spectrum of the vanilyl acetate peak with a retention time of 11,652 minutes

Based on the GC chromatogram in Figure 8, one peak resulted as a compound of esterification reaction. The first peak with a percent area of 100.00% with a retention time of 10,866 minutes. The compound has an *m*/zof 205 which is the relative molecular mass of the Phenol compound, 2,6-bis(1,1-dimethylethyl)-4-methyl-(CAS)4-Methyl-2,6-di-tert- butylphenol. The compound obtained in this test is not the expected ester compound. This is indicated by the *m*/*z* compound which does not correspond to the relative molecular mass of the vanilyl acetate compound, which is 196. The absence of a molecular ion peak from vanilyl acetate is due to the release of acetic acid molecules due to unstable vanilyl acetate. In addition, it can also be caused by the high boiling point of the vanilla acetate compound. The yield of vanilla acetate obtained was 63.98% based on theoretical calculations.

4. CONCLUSION

Vanilyl alcohol compounds can be obtained by reducing vanillin compounds using sodium borohydride ($NaBH_4$). Vanilyl alcohol obtained is in the form of a white solid which has a melting point of 81-84^{o}Cwith a yield of 59.74%. Vanilyl acetate compounds can be obtained through the Fischer

esterification reaction between acetic acid and vanilyl alcohol using a_2SO_4 98% concentratedVanilyl acetate obtained was in the form of a brown solid with a yield of 63.98%.

The results of the characterization of the vanillic alcohol compound showed that vanilyl alcohol had been formed, supported by the appearance of the absorption of the alcohol OH functional group in the 3443.22 cm^{-1}, the CO alcohol functional group in the 1153.99 cm^{-1}, bending -CH_2- in the 1431.25 cm^{-1}, and bend -CH_3 in the area of 1374.92 cm^{-1}. Based on identification using GC-MS, vanilyl alcohol has a purity of 91.13% with an *m/z* 154. The results of the characterization of the vanilyl acetate compound that a vanilyl acetate ester has been formed, this is supported by the appearance of the absorption of the C=O ester functional group at wave numbers 1738.59 cm^{-1} and CO ester at 1274.2 cm^{-1} in the IR spectrum of vanilyl acetate.

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