Synthesis of Vanillin from Trans-isoeugenol Using Electrooxidation Method with Platinum Gauze Electrode and Sodium Nitrate as Electrolyte

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Abstract

Vanillin is popular aromatic organic compound widely used as perfumes and flavouring material in the industries of foods, beverages and pharmaceuticals. Vanilin can be produced by natural and synthetic process. However, the production under natural process can not meet the high demand of vanillin. In Indonesia itself most of vanillin imported from China, whereas a lot of materials can be used in manufacture of vanillin, such as clove oil and numtag seeds. The objective of this research is to study the electrosynthesis of vanillin from *trans*-isoeugenol using electrooxidation method and platinum gauze electrode in sodium nitrate/methanol solution as electrolyte in order to short cut the time of electrosynthesis process and produce the high-purity product with a low cost. The required oxidation potential was determined using cyclic voltammetric method. The electrooxidation of *trans*-isoeugenol was carried out by varying the oxidation potential, the period of electrolysis, the addition of water and varying the concentration of *trans*-isoeugenol to obtain the optimum condition in the synthesis of vanillin. The electrolysis products were concentrated to obtained the solid crystals of vanillin which were characterized by Thin Layer Chromatography, Gas Chromatography Mass Spectrometry (GC-MS) and Fourier Transform Infra-red Spectroscopy. The analysis results showed that the optimum condition, was obtained a product with a fairly good purity of more than 20%, at the potential of 1.2 V in 60 minutes without water addition in 0.1 M *trans*-isoeugenol.

Keywords: Electrooxidation, electrolysis, trans-isoeugenol, vanillin, platinum gauze electrode

Introduction

Vanillin (4-hydroxy-3-methoxybenzaldehyde) is the primary component of the extract of vanilla bean(Lampman et al., 1976). It is contributes to about 2% (w/w) of the dry matter(Priefert, Rabenhorst, & Steinbuchel, 2001).Vanillin appears as crystaline powder with an intensely sweet vanilla odor. Commercially, the products of vanillin are divided into two types; namely, natural and synthetic(Walton, Mayer, & Narbad, 2003). Natural vanillinis relatively more expensive than vanillin synthetic(Binti & Muttalib, 2014). The high price of natural vanillin is mainly due to the limited availability of vanilla beans depending on climate-associate fluctuations of harvest yields (Priefert et al., 2001).Each year the market demand on vanillinkeeps increasing. Owing to theinscreasing demand of vanillin, there is a growing interest in producing vanillin from another materials.

Isoeugenol is a compound which used as mixture in fragrances, perfumes, skin care producs and also as starting material in the manufactures of synthetic vanillin (Kumar, Sharma, &Mishra, 2012). Isoeugenol can be produced from isomerization of eugenol and isolation from clove oil (Furuya, Kuroiwa, & Kino, 2017).

Nowadays various methods of producing synthetic vanillinwasdepeloved.Such as enzymatic reaction, biotransformation and biotechnology(Furukawa, Morita, Yoshida, & Nagasawa, 2003), yet, those methods is less efficient to produce synthetic vanillin with high concentretion. Moreover, the process is also relatively complex and costly. Therefore, in this researchthe electrochemical method is conducted by oxidizing *trans*-isoeugenol compound assested by platinum gauze electrode and sodium nitrate electrolyte in methanol solvent. This method is beneficial due to the simple process, cheap, need less materials and employee, also produce safe product with high purity.

Materials and Method

All chemical subtances used in synthesis of vanillin are analytical grade. The starting materials *trans*-isoeugenolwere gained from PT Indesso Aroma, Bogor, Jawa Barat, Indonesia.

The study of *trans*-isoeugenol electrochemical behavior was conducted by using cyclic voltammetry with one compartment system, consisting of platinum gauze as the working electrode, Pt spiral as supporting electrode and Ag/AgCl as the comparative electrode. *Trans*-isoeugenol solution 1 M and saturated solution of sodium nitrate in methanol were inserted in 3 different vessels. The cyclic voltammetric profile was observed in the potential range -0.75 V to 0.75 V with a scan rate of 0.1 V/s.

The electrolysis reactor consisted of two compartments made of glass vessels. The solution at the anode comprises asaturated solution of sodium nitrate electrolyte in methanol and 1 M of *trans*-isoeugenolin methanol in ratio 1: 3. The solution in the cathode consists of saturated solution of sodium nitrate electrolyte in methanol. The measurements were conducted in room temperature using Ag/AgCl as the reference electrode and platinum gauze as the working electrode. The spiral platinum was used as a supporting electrode placed on the cathode compartment. Electrolysis was carried out with overpotential variations of 0.9 V, 1.0 V, 1.2 V and 1.4 V respectively, time of electrolysis at 30, 60, 90, 120 and 150 minutes, variations in water addition and variation in the concentration of*trans*-isoeugenol. The samples of electrolysis result were characterized by FTIR and the productwas identified by using Gas Chromatography Mass Spectrometry (GC-MS).

Result and Discussion

The study of *trans*-isoeugenolelectrochemical with platinum gauzeelectrodesobtained an oxidation peak of 0.26 V (Figure 1). The study *trans*-isoeugenol electrochemical with scan rate variation showed that the relationship and linearity between oxidation peak currents with scan ratewas in accordance to the Randles-Sevick equation. Linearity showed that the transfer of the solution to the electrode was only influenced by the diffusion of the solution.

Three main spots in TLC chromatogram was observed and the result showed identical spot with standard vanillin. This is indicates the existence of vanillin compounds in the electrolysis sample. The FTIR analysis of electrolysis samples (Figure 2) showed that fungtional group signified of OH group around 3400 cm^{-1}, C-H aldehyde around 2800 cm^{-1} and C=C aromatic at 1600 cm^{-1} and it was a typical peak of vanillin compound. Identification of the product electrolysis of*trans*-isoeugenol was performed by GC-MS and the data is listed in Table 1. Five compounds were identified are vanillin,vanillic acid, methyl vanillate, dehydrodiisoeugenol, and intermediet compounds in electrolysis vanillin,

Dimer compound also formed from the electrolysis reaction(Sumi et al., 2012). Forming of dimer compound were influenced by several factors, including the potential used in the electrolysis system and time of electrolysis.This may cause the formed vanillin to undergo further oxidation reactions and form the dimer compound. Two factors above also lead the formation of radicals from trans-isoeugenol become uncontrolled, as result it will occure reaction competition between the radical and oxidation of trans-isoeugenol into vanillin and reducing vanillin yield during the electrolysis. The formation of dimers can occur when two reactants formed radical which then combined into larger compounds.

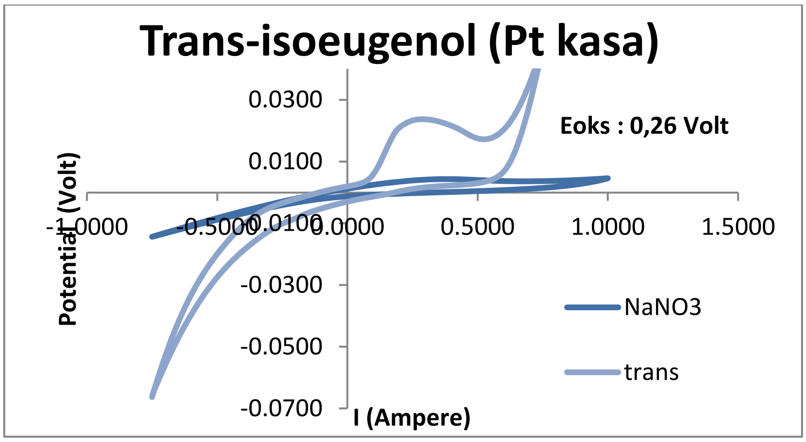


Fig. 1. Cyclivvoltamogram of trans-isoeugenol

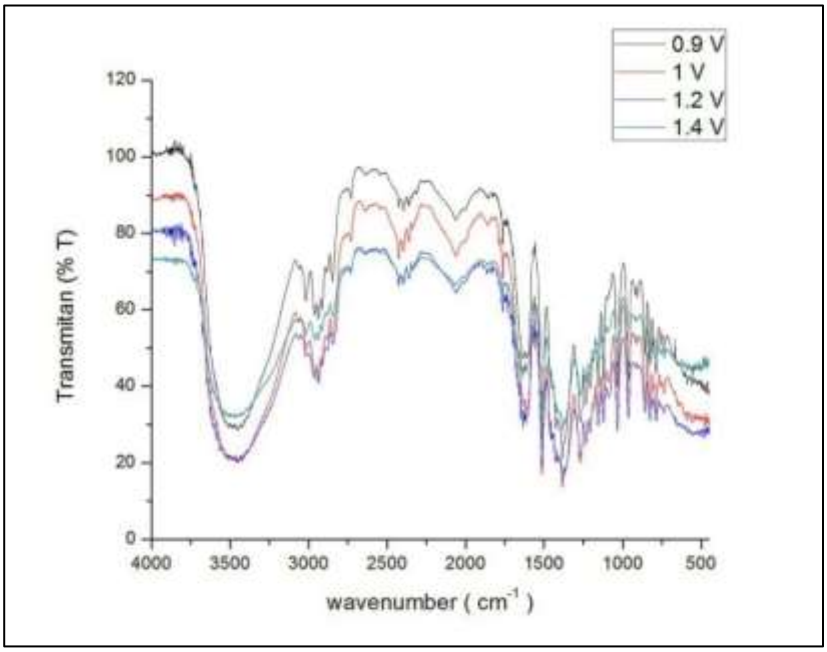


Fig. 2. FTIR spectra of electrolysis trans-isoeugenol

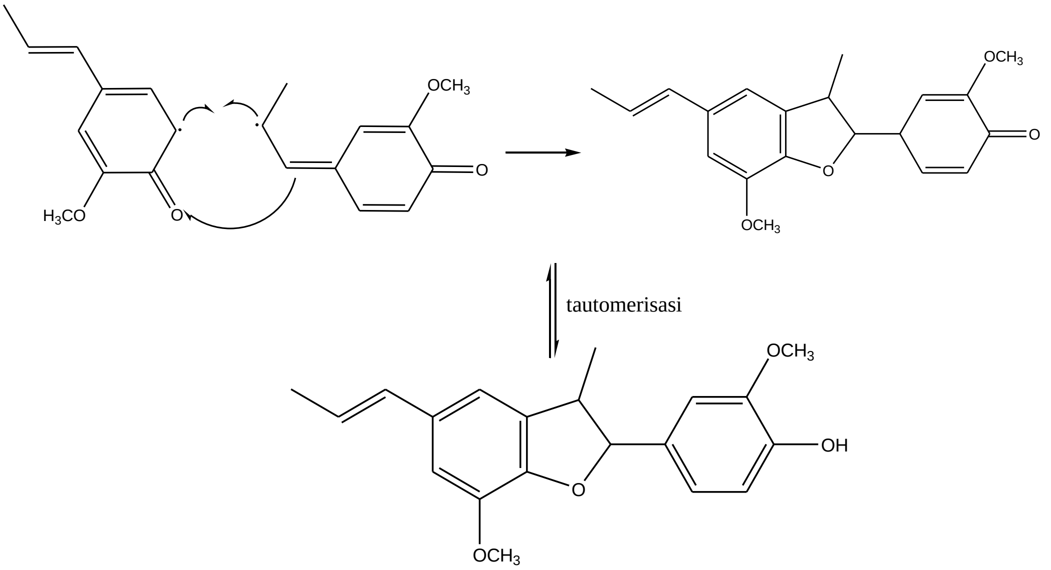
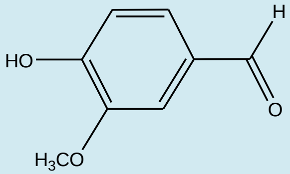
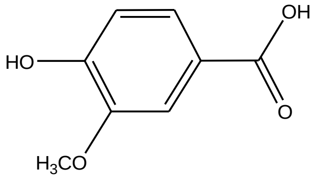
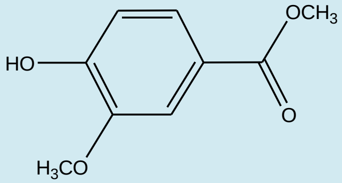
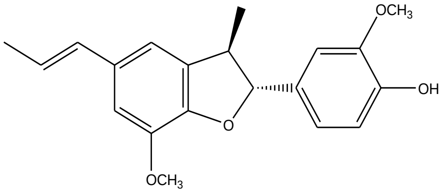


Fig. 3. Formation of dimer compound in electrolysis reaction (Sumi et al., 2012).

Table 1. GC-MS analysis of electrolysis trans-isoeugenol

No	Structure	Name
1		Vanillin (4-hydroxi-3-methoxybenzaldehyde)
2		AsamVanilat (4-hydroxi-3-methoxybenzoicacid)
3		Methyl Vanilate
4		Dehydrodiisoeugenol

Conclusion

Vanillin was successfully synthesized through electrochemical method using platinum gauze electrode and sodium nitrate/methanol as electrolyte. Formation of vanillin is identified by FTIR and confirmed by GC-MS. In the proposed mechanism, trans-isoeugenol undergoes oxidation of allyl group into diol and followed by oxidative cleavage into aldehyde. The optimum condition was obtained with varying the oxidation potential, time of electrolysis, amount of water and varying the concentration of trans-isoeugenol. The optimum condition in electrosynthesis vanillin was obtained a product with a fairly good purity of more than 20%, at the potential of 1.2 V in 60 minutes without water addition in 0.1 M *trans*-isoeugenol.

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