

Electrosynthesis of vanillin from isoeugenol using platinum electrode

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Abstract. Vanillin was synthesized from isoeugenol through electrochemical method in one compartment cell using platinum electrode. Cyclic voltammetry in 0.1 M TBAP in methanol and acetonitrile indicated the first oxidation potential at +0.21 and +0.16 V (vs. Ag/AgCl), respectively. Isoeugenol was proposed to undergo the oxidation accompanied by oxidative cleavage of alkene bond into aldehyde. Accordingly, the synthesis of vanillin was conducted using chronoamperometry technique. The electrosynthesis result was analyzed by HPLC and GC/MS. The optimum condition of the oxidation potential, solvent ratio, time of electrolysis and amount of water was investigated.

Keywords: electrosynthesis, vanillin, isoeugenol, oxidative cleavage

1. Introduction

Vanillin is one of main compound in vanilla. It is widely used as food and beverages flavoring, pharmaceutical substance, and fragrance [1]. The demand of vanillin was reported 15000 tons/year, where only 50 tons was produced naturally through extraction from vanilla beans. Natural vanillin was obtained from vanilla (*Vanilla planifolia* or *Vanilla fragrans*) through long process and needs a high cost, so its price ranges from \$2000/kg to \$4000/kg. Due to this reason, natural vanillin produces less than 1% from the market demand [2]. The demand of vanillin is catered by many industries producing synthetic vanillin, for example through catechol route which needs consecutive oxidation phase and the use of petroleum based phenol as the main source [3]. An alternative method is needed, especially using biomass derivative compound like isoeugenol, which is an essential oil compound, or lignin derivative compound.

Alternative methods of isoeugenol conversion into vanillin was reported, including synthesis using microorganism [4], cobalt porphyrin as heterogeneous catalyst through oxidative cleavage [5] and electrochemical synthesis from lignin compounds [6]. Synthesis using electrochemical method was the easiest way since the method minimizes the pollution, hazard, and toxicity risk [7]. In this work, electro oxidation of isoeugenol to form vanillin was performed using platinum electrode based on the report regarding electrooxidation of isoeugenol in methanol producing a fraction of vanillin [8]. The report indicated that by optimizing the potential and the reagent composition, a high percentage of vanillin can be produced by the method. Accordingly, the oxidation reaction was performed with different organic solvents, i.e. acetonitrile and methanol. The results showed that methanol is more suitable than acetonitrile to be applied as the solvent for isoeugenol conversion to vanillin. Furthermore, it was also found that water composition in the solvent is important to achieve a high percent yield of vanillin.



2. Materials and methods

2.1. Materials

Materials used in this work are mixture of cis/trans of isoeugenol (Wako), Vanillin (Wako), Tetrabutyl Ammonium Perchlorate (TBAP, Tokyo Chemical Industries), Methanol (Kanto Chemical Industries), Acetonitrile (Sigma-Aldrich), and Ultra High Purity Water (Merck Millipore).

2.2. Electrochemical study of isoeugenol and electrosynthesis of vanillin

Electrochemical study (CH Instrument, Inc.) was conducted using cyclic voltammetry in a self-fabricated one-cell compartment with three electrodes system. Pt foil (dia. 0.58 cm) was used as the working electrode, Pt spiral as the counter electrode, and Ag/AgCl system (ALS Co., Ltd) as the reference electrode. The electrochemical equipment was cleaned using sonicator for 5 min by water and isopropanol. Then, 2.5 mL of 0.1 M isoeugenol and 0.1 M TBAP in methanol or acetonitrile solvent and 1 mL of water were added into the compartment.

Electrosynthesis method was conducted using the same electrochemical cell based on the cyclic voltammetry results at +0.1 and +0.2 V for 30 and 60 min under 500 rpm stirring. Various volumes of water were used for the reagent.

2.3. Analysis of electrosynthesis product using HPLC and GC/MS

Electrosynthesis product was analyzed using HPLC (LC-20AD Prominence, Shimadzu) with C-18 column (YMC-Triart C-18). A binary gradient pump system with 0.1% formic acid (25%) and acetonitrile (75%) was used as mobile phase with UV detector at 280 nm. GC/MS (Agilent Technologies) was controlled by an increasing temperature from 70°C with 20°C/min rate to maximum temperature of 325°C.

3. Results and discussion

3.1. Electrochemical behavior of isoeugenol at Pt electrode

Cyclic voltammograms (CVs) of isoeugenol at Pt electrode in 0.1 M TBAP in methanol and acetonitrile are shown in figure 1a and 1b, respectively. An oxidation potential at +0.21 V can be observed in methanol solvent, whereas it was at +0.16 V in acetonitrile. The difference of polarity from solvent was responsible for the shift of the oxidation potential. Since acetonitrile is more polar than methanol, the faster mass transfer with respect of metallic electrode surface can lead to the lower oxidation potential. The mass transfer at this condition is assumed to be under diffusion controlled only. An investigation with various scan rates was found to provide linear current responses to the square of the scan rates (data not shown).

3.2. Analysis of product using HPLC and GC/MS

Table 1 displays the analysis products using HPLC and GC/MS. Optimum condition at Pt electrode was obtained at potential +0.41 V in methanol solvent for 30 min with percent conversion up to 4.11% (162.74 mg/L). Although the cyclic voltammogram shows the onset of isoeugenol oxidation at +0.2 V (figure 1a). Table 2 shows that a higher potential or higher energy than +0.2 V was required to convert isoeugenol to vanillin. However, it was also observed that when the longer time applied to the system, the conversion percentage will be decreased because vanillin can be further oxidized to produce the dimerization. In acetonitrile solvent, the conversion of vanillin was less than in methanol. The possible reason is due to the different polarity between methanol and acetonitrile. Electrochemical reaction of isoeugenol needs water to produce hydroxyl radicals. On the contrary, isoeugenol is not completely

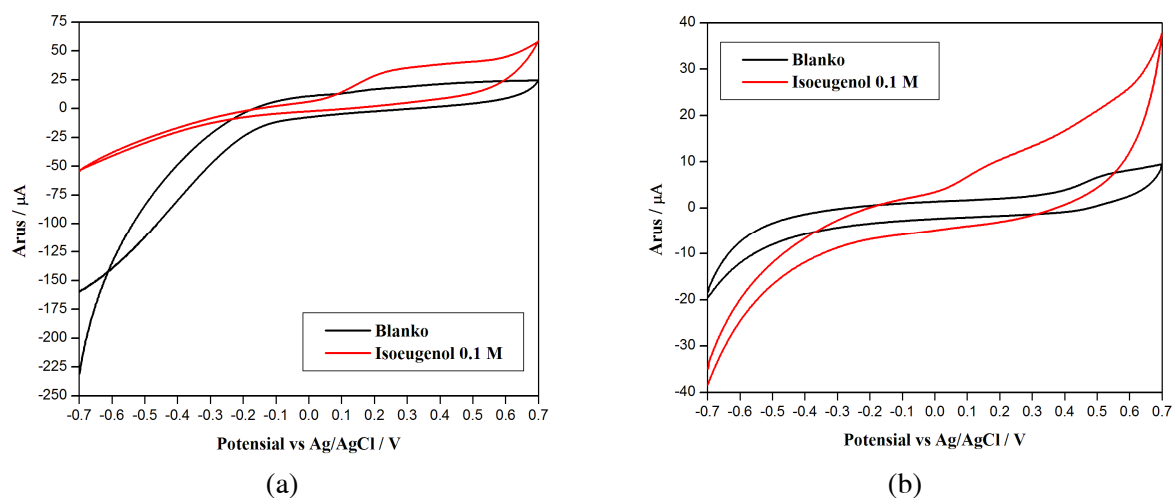


Figure 1. Cyclic voltammograms of 0.1 M isoeugenol in 0.1 M TBAP at Pt electrode in (a) methanol and (b) acetonitrile solvent.

Table 1. HPLC analysis of the electrosynthesis products

Solvent	Potential (V)	Time(minute)	Isoeugenol reacted (%)	Vanillin conversion (%)	Amount of vanillin (mg/L)
Methanol	0.21	30	31.82	0.47	12.01
		60	35.85	0.32	9.12
	0.31	30	33.47	0.48	12.91
		60	35.45	0.33	9.25
	0.41	30	49.51	4.11	162.74
		60	53.14	3.30	140.39
Acetonitrile	0.16	30	22.02	0.44	7.73
		60	48.66	0.15	5.89
	0.26	30	40.00	0.25	7.91
		60	66.11	0.10	5.11
	0.36	30	57.63	0.11	5.07
		60	67.80	0.10	5.03

dissolved in polar solvent. Therefore, the reaction in polar solvent will be limited. Since acetonitrile is more polar than methanol, it is reasonable if the conversion of isoeugenol in acetonitrile was lower than that in methanol.

The vanillin conversion decreases as the water volume increases from 0 mL to 0.5 mL, it might be due to the hydroxyl radicals generated by water oxidation to form other products. The optimum addition of water was 1 mL. The vanillin product decreases at the water content of 1.5 mL, probably due to the change of isoeugenol solubility as it was reported that the electrochemically oxidative cleavage is strongly influenced by water content [9]. High water content also causes the formation of more intermediate species [10]. Moreover, the vanillin which has formed can react with residual water and lead to further oxidation.

Table 3 shows that compound 1 to 5 can be formed from oxidation of alkene group with respect of water, hydroxyl radical, or methoxy radical, while compound 6 can be formed with 2 radicals from isoeugenol which lead to dimerization product, i.e. licarin A. Based on the structure, it was clearly shown that compounds 1 to 5 can be formed through the backbone radicals of isoeugenol, while the compound no. 6 was formed due to the dimerization of the isoeugenol backbone. The result confirmed to the previous report by Sumi *et al.* [8].

Table 2. Variation of water addition.

System	Water Volume (mL)	Isoeugenol Reacted (%)	Vanillin Conversion (%)	Amount of Vanillin (mg/L)
Pt-methanol-0.41 V-30 min	0	18.8	1.10	16.56
	0.5	42.43	0.53	18.13
	1	49.51	4.11	162.74
	1.5	54.35	0.40	17.21

Table 3. Compound formed at vanillin electrosynthesis characterized by GC/MS.

No	Structure	Name	Fragmentation (m/z)
1		Vanillin (4-hydroxy-3-methoxybenzaldehyde)	151, 109, 81, 53, 29
2		Methyl vanillate (methyl 4-hydroxy-3-methoxybenzoate)	182, 151, 123, 80, 52
3		1-(4-hydroxy-3-methoxyphenyl) acetone	180, 137, 94, 43
4		Methyl (3,4-dimethoxyphenyl) hydroxy acetate	226, 195, 167, 151, 137, 109
5		2-methoxy-4-(1'-methoxypropyl) phenol	196, 167, 151, 137, 57
6		Licarin A – 98%	326, 202

3.3. Proposed mechanism of reaction

Isoeugenol reaction into vanillin is one example of oxidative cleavage from C=C bond into C-C followed by the cleavage into aldehyde or carboxylic group. This reaction takes place at electrode surface with

rearrangement in the medium. There are two proposed reaction mechanisms in this oxidative cleavage, which are oxidation at the vinyl (figure 2) [9] alkene and the phenol groups (figure 3) [11].

The first step of the oxidation at the alkene group is the formation of radical cation, when one electron is taken from pi bond at the vinyl group. Then, the nucleophilic attack of water occurs, followed by loss of proton to form neutral benzylic radical intermediate. The second step is the oxidation followed by the second nucleophilic attack to form diol intermediate. After diol formation, the oxidation of one OH from the diol group forms radical cation, followed by the cleavage of C-C sigma bond and the loss of proton. The final step is the rearrangement to form aldehyde group. Oxidation through this mechanism needs two equivalents of water and four electrons as well as loss of four protons.

The oxidation at phenol group starts from the formation of radicals, which is able to resonate (figure 4) [12]. As the consequence, the loss of electrons from phenol groups occurs. After the formation of the fourth resonance intermediate, the next step is the attack of hydroxyl radicals formed through water oxidation at the electrode surface. Then, the arrangement of OH group will form the epoxide by losing 1 proton. In the presence of water and proton, the epoxide ring can be opened to form diol. The next step is the cleavage of C-C sigma bond and formation of aldehyde as in the first proposed reaction mechanism.

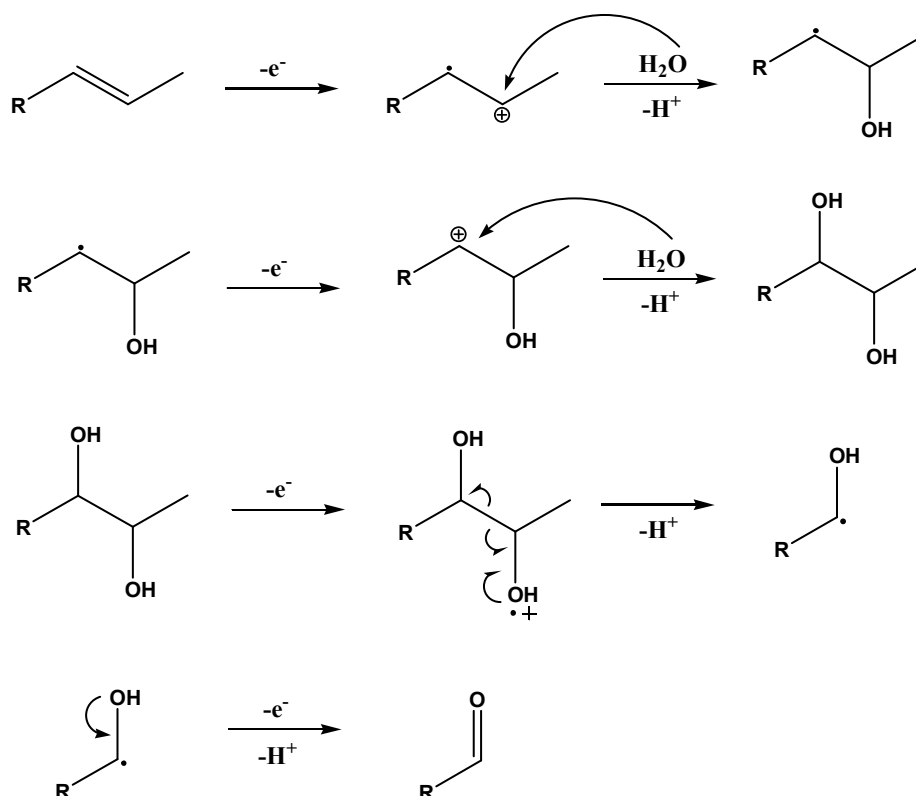


Figure 2. Mechanism of vanillin electrosynthesis through vinyl group.

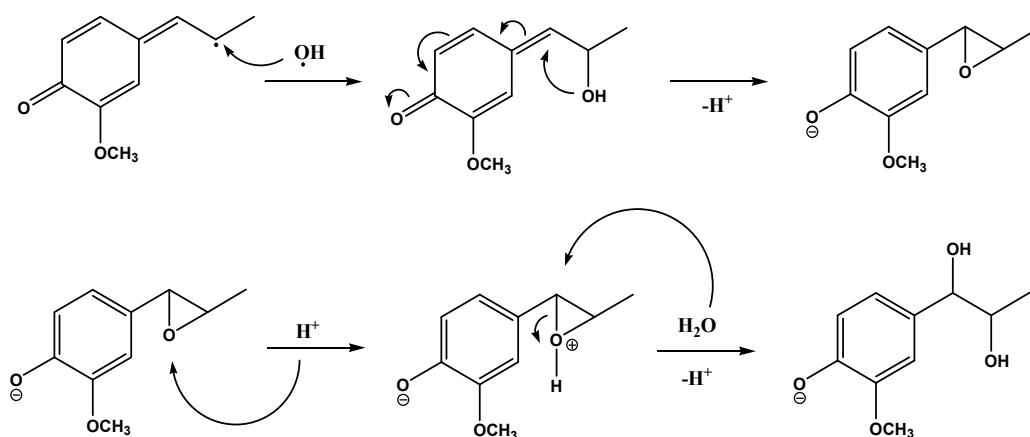


Figure 3. Mechanism of vanillin electrosynthesis via phenol group.

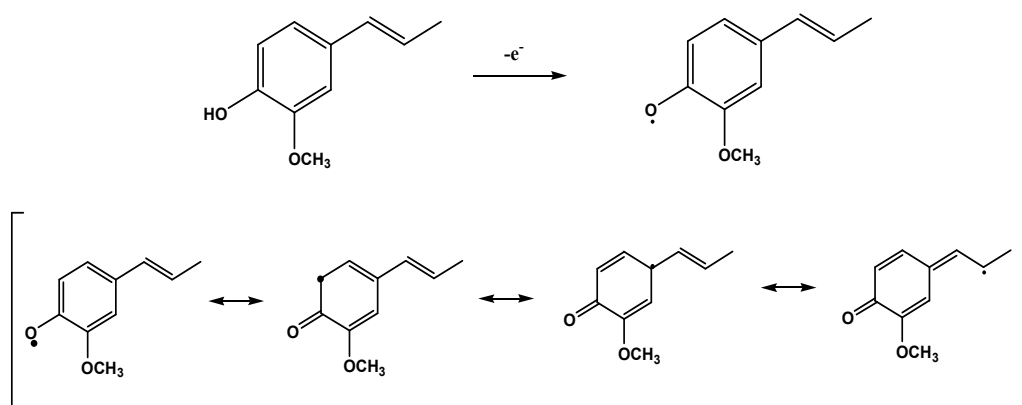


Figure 4. The resonance of radical isoeugenol.

4. Conclusions

Electrosynthesis of vanillin from eugenol has been successfully performed using Pt electrode. Optimum condition of the electrosynthesis were obtained at a potential of 0.41 V for 30 min in methanol solvent. Influence of the feedstock water was found to affect the oxidation process with 1 mL of water as the optimum condition. A conversion up to 4.11% (162.74 mg/L) could be achieved. The reaction mechanism was proposed through the oxidation of the C=C bond and the phenol group.

References

- [1] Walton N J, Mayer M J and Narbad A 2003 *Phytochemistry* **63**(5) 505-15
- [2] Priefert H, Rabenhorst J and Steinbuchel A 2001 *Appl. Microbiol. Biotechnol.* **56** 296-314
- [3] Metivier P 2001 *Method for preparing a 4-Hydroxybenzaldehyde and derivatives* United States Patent 6184421 B1 February 6
- [4] Rana R, Mathur A, Jain C K, Sharma S K and Mathur G 2013 *Intl. J. Biotechnol. Bioeng. Res.* **4** 227-34
- [5] Adilina I B, Hara T, Ichikuni N and Shimazu S 2012 *J. Molecular Catal. A: Chemical* **361-362** 72-9
- [6] Reichert E, Wintringer R, Volmer D A and Hempelmann R 2012 *Physical Chemistry Chemical Physics* **14**(15) 5214
- [7] Shibano S, Ivandini T A, Terashima C, Nakata K and Einaga Y 2014 *Chem. Lett.* **43** 1292-3
- [8] Sumi T, Saitoh T, Natsui K, Yamamoto T, Atobe M, Einaga Y and Nishiyama S 2012 *Angew. Chem. Int. Ed.* **51** 1-5

- [9] Wu X, Davis A P and Fry A J 2007 *Organic Letters* **9**(26) 5633-6
- [10] Lee J H Q, Tay B K, Ganguly R and Webster R D 2015 *Electrochim. Acta* **184** 392-402
- [11] Smith J G 2011 *Organic chemistry* (New York: McGraw Hill Education) p 323, pp 343-6
- [12] Smith J G 2011 *Organic chemistry* (New York: McGraw Hill Education) pp 575-6