Synthesis of the Halal Fragrance Compound Menthyl $p$-Anisate from Fennel Oil

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Abstract. Menthyl $p$-anisate is an ester compound which can be used as chemical base of halal fragrance. Synthesis of menthyl $p$-anisate from Fennel Oil has been conducted. $p$-anisate acid was derivative of anethol from fennel oil that undergo oxidation process by KMnO$_4$ at $40^\circ$C for 2 hours. Esterification with menthol carried out at $40^\circ$C for 7 hours. Identification and determination of structure compound of the product was analysed by spectroscopic methods (FTIR and GC-MS). Organoleptic evaluation of the fragrance was carried out by 20 semi-trained panellists. The result showed that identification of menthyl $p$-anisate using FTIR indicated the presence of C-O ester at 1223.41 cm$^{-1}$ and 1180.44 cm$^{-1}$; and C = O carbonyl at 1689.64 cm$^{-1}$. However, methyl $p$-anisate was different from menthol which is shown by mass spectra with the absence of m/z 71 and m/z 57 peak. Organoleptic evaluation suggested that the menthyl $p$-anisate compound is in range of “fragrant” with score 4.90, “very sharp fragrant” with score 5.90, and acceptance in range of “preferred” with score 5.00. Thus, follow the conclusion that the compound exerted potent ability as chemical component in halal fragrant.

1. Introduction

The majority of perfumes on the market these days are synthetic and contain man made fragrance. The basic ingredients of making perfumes are derived from synthetic or natural ingredients. Perfume as a product is a fragrant composition formed of aroma-chemicals and or natural oils usually suspended in alcohol and water intended to be applied to the skin. One of the fragrance compound is the ester group from the reaction between alcohol and carboxylic acid [1]. The use of natural ingredients as fragrance compounds has been carried out by many researches. Iskandar and Prabawati [2] has been synthesized menthyl vanillate from vanillin as fragrance compounds. Vanillin also contains antioxidants $1,4$-Bis [(2 - Hydroxy - 3 - Methoxy - 5 - Formaldehyde - Phenyl) - Methyl] Piperazine which was successfully synthesized [3].

Natural ingredients that can be used as a fragrance compound other than vanillin are anetol which is the main component in fennel oil which is a class of essential oils. The sale value of fennel oil can be increased by derivatizing into ester derivatives. It can be used as an ingredient of halal fragrance components [4]. Wearing perfume is one of the sunnah from the Prophet Muhammad SAW. The term
alcoholic and non-alcoholic perfume caused a lot of debate in several people. Alcoholic perfume is haram because the level is high so it is intoxicating [5]. The alcohol law is regulated in MUI Fatwa number 11 of 2009 about Alcohol Law and number 12 of 2018 about Cosmetics Products Containing Alcohol / Ethanol. The use of alcohol / ethanol produced by the Khamr industry for food products, beverages, cosmetics, and drugs is haraam because the law is unclean. The use of alcohol / ethanol produced by non-chemical products (whether they are the result of chemical synthesis [from petrochemicals] or non-fermented industrial fermentation products for the production process of food products, beverages, cosmetics, and drugs is legally altered, if medically harmless [6].

Anetol which is the main component in fennel oil has another name p-propenilanisol, p-methoxy propenylbenzene or "anise champor" having the chemical formula C_{10}H_{12}O and molecular weight 148.20 g / mol. Taufikkurohmah [7] derivatized anetol into ethyl p-methoxycinnamic through the formation of p-anisaldehyde. Kusumaningsih et al. [8] synthesized ethyl p-anisate as a fragrance compound of anetol by oxidizing anetol to p-anisate acid and then doing esterification with ethanol. In this research, anetol derivatization was carried out to produce menthyl p-anisate compound which is expected to be used as a halal fragrance.

2. Methodology
The main ingredient is fennel oil from the essential oil group. The experiment began with the synthesis of p-anisic acid from fennel oil. p-anisic acid was analyzed by FTIR. The experiment was continued with menthyl p-anisate synthesis. The filtrate was weighed and then analyzed using FTIR and GC-MS. The last experiment was organoleptic analysis.

2.1. Equipment/Material
The equipment in this study were glassware, a set of reflux apparatus, beaker glass, hot plate, digital scale, FTIR spectrophotometer (Shimadzu Prestige 21), melting point test kit, ¹H-NMR (400 MHz) spectrophotometer and GC-MS (Shimadzu-QP2010S Rtx 5 MS). The materials used fennel oil, glacial acetic acid, polysorbate 80, dichloromethane, potassium permanganate, diethyl ether, sodium bisulfite, sodium sulfate anhydrous, sodium hydroxide, and ethanol.

2.2. Synthesis of p-anisate acid from fennel oils
The first step of synthesis of p-anisate acid were fennel oil 3,048 g (0.02 mol), distilled water 100 mL, glacial acetic acid 2 mL, sulfuric acid 50% 15 mL, polysorbate 80 15 mL and dichloromethane 100 mL put into three neck flasks 500 mL. The KMnO₄ crystal 9,798 g (0.062 mol) was added to the mixture and the temperature was kept no more than 30°C, then refluxed for 2 hours at 40°C. The solution was added H₂SO₄ 50% until pH 1-2. It cooled and added NaHSO₃ 3 g. The mixture was extracted with dichloromethane and dried with Na₂SO₄ anhydrous. The dichloromethane was evaporated and recrystallized using ethanol. Analysis of the structure of p-anisate acid was carried out by FTIR.

2.3. Synthesis of methyl p-anisate
Synthesis of methyl p-anisate was carried out after the synthesis of p-anisic acid from fennel oil1. The mixture of p-anisate acid 1 g (0.0065 mol), menthol 2,05 g (0.013 mol) and sulfuric acid 0.5 mL (0.009 mol) were put into three neck flask 250 mL containing diethyl ether 20 mL. The mixture was refluxed at 40°C for 7 hours. The mixture was cooled and then added with 10 mL of 10% NaHCO₃ solution. The organic phase was separated from the aqueous phase. It was added with anhydrous Na₂SO₄ then filtered and the remaining solvent was evaporated. The filtrate obtained was weighed and then analyzed using FTIR and GC-MS.

2.4. Organoleptic test
The Organoleptic test adopted the research of Winarto [9], to test several parameters such as the level of fragrance, sharpness, and preference for menthyl p-anisate compounds. Menthyl p-anisate
3. Results and Discussion

3.1. Synthesis of menthyl p-anisate

GC analysis of fennel oil showed the retention time of anetol at 27.70 minutes with 82.46% area. This result was accordance with Sastrohamidjodjo [10], that Anetol is the main component of fennel oil, about 80-90% of anetol was found in fennel oil. Synthesis of menthyl p-anisate begins with the synthesis of p-anisate acid. Synthesis of p-anisate acid by oxidizing fennel oil using calcium permanganate and catalyst polysorbate 80.

Synthesis of p-anisate acid was obtained as a white solid at 182\(^\circ\)C melting point. The results of FTIR data analysis was O-H stretching absorption from carboxylic acids that form dimers (hydrogen bonds), which appear at 3448.72 cm\(^{-1}\) wave numbers. Meanwhile the sharp uptake seen in 1681.93 cm\(^{-1}\) was the absorption of the carbonyl group. p-anisate acid was esterified using menthol with a sulfuric acid catalyst to produce menthyl p-anisate. The mechanism was shown in Figure 1.

![Figure 1. Mechanisms of menthyl p-anisate formation](image)

The menthyl p-anisate compound is a liquid, yellow and fragrant with 1.98 grams wave numbers. The results of FTIR analysis (Figure 2) showed that there was an absorption at 1689.64 cm\(^{-1}\) wave numbers which was the absorption of C = O carbonyl. It was lead the absorption at 1223.41 cm\(^{-1}\) and 1180.44 cm\(^{-1}\) wave numbers which is the absorption of C-O esters. The same results were also obtained in the research of Risnandar and Prabawati [11], the absorption of 1219 cm\(^{-1}\) and 1180 cm\(^{-1}\) wave numbers in the synthesis of menthyl vanillate compounds showed that the synthesized product had an esterification reaction with the loss of –OH absorption from the menthyl vanillate compound. The ester compound will produce sharp and strong of C-O absorption with 1300-1000 cm\(^{-1}\) wave numbers [12]. Weak

compounds was formulated into eu de cologne. A total of 20 respondents were trained to conduct organoleptic tests and fill out questionnaires containing assessments on a scale of 1-7 related to these 3 parameters. The rating scale 1 shows that it is not very fragrant / sharp / like while the rating scale 7 shows that it is very fragrant / sharp / like.
absorption at 1612.49 cm\(^{-1}\) wave number (Figure 2.) showed the presence of an aromatic C=C group from the benzene ring. The absorption at 2924.09 cm\(^{-1}\) and 2870.08 cm\(^{-1}\) wave numbers (Figure 2.) was the absorption of C (sp3) -H from the methyl group of the menthyl p-anisate composition. This absorption proves that the methyl group has been substituted into p-anisate acid compounds [11].

![Figure 2. FTIR spectrum of p-anisate acid and menthyl p-anisate](image)

Identification with GC-MS to determine product compounds and mass fragmentation. The results contained two compounds with 97.83% and 2.17% area. The retention time appeared at 17.45 and 20.54 minutes. The menthyl p-anisate compound was seen at retention time of 20.54 minutes. The compound produces a mass spectrum with a peak of \(m / z\) 138, 123, 109, 95, 81, 67, 55 and 43. The menthyl p-anisate compound appears at a longer retention time because it’s less polar than menthol. The mass spectra of the menthyl p-anisate compound did not show peaks \(m / z\) 71 and 57. According to Sastrohamidjodjo [10], peaks \(m / z\) 71 and 57 produced menthol fragments with hydroxyl groups. Peaks \(m / z\) 71 and 57 in the methyl p-anisate compound were not appeared because oxygen atoms come apart to form carboxylic acids. The mass spectra of the menthyl p-anisate compound can be seen in Figure 3.

![Figure 3. Mass spectra of menthyl p-anisate compounds](image)
The peak (m/z) 290 of menthyl \( p \)-anisate was not detected because the menthyl \( p \)-anisate compound was unstable. The same results obtained by Chasana et al. [1], they carried out the esterification reaction of the \( l \)-menthol compound with acetic acid anhydride to produce methyl acetate and \( l \)-menthol with propionic acid to produce methyl propionate. The GC-MS results from the two studies showed that there was no peak (m / z) of the ester compound that became the target molecule because the ester compound was unstable.

3.2. **Organoleptic test**

Menthyl \( p \)-anisate compounds derived from natural ingredients can be used as ingredients for halal fragrance. Anethol oxidation and esterification of fennel oil was carried out to obtain the menthyl \( p \)-anisate compound. The compound was formulated into eu de cologne using ethanol as a solvent. The law of mubah in Islam is that ethanol may not be mixed with other intoxicating substances (khamr or fruit fermentation with levels of more than 0.5%). Ethanol (alcohol) which is used as a perfume solvent, is ethanol which is not khamr and not intoxicating because perfume is inhaled [13].

![Organoleptic test of eu de cologne from menthyl \( p \)-anisate compound](image)

Figure 4. Organoleptic test of eu de cologne from menthyl \( p \)-anisate compound

The compound of menthyl \( p \)-anisate was formulated as eu de cologne. The results of organoleptic test (Figure 4) of eu de cologne from menthyl \( p \)-anisate compound from fennel oil obtained a scale of 4.5 (fragrant / sharp / like) - 6 (very fragrant / sharp / like). Panelist's evaluation of the level of fragrance of the menthyl \( p \)-anisate compound (scale of 4.90) was fragrant. The panelist's evaluation of the sharpness of the menthyl \( p \)-anisate compound (scale of 5.90) was very sharp. The panelist's evaluation of the level of preference for the menthyl \( p \)-anisate compound (scale of 5.00) was liked it.

4. **Conclusion**

The menthyl \( p \)-anisate compound can be formed through the oxidation reaction of anetol and the esterification with menthol. The results of organoleptic test from 20 panelist managed to get a range of scale 4 (slightly fragrant / sharp / like) - 6 (very fragrant / sharp / like). The eu de cologne product from the mentyl p-anisate compound can be used as a halal fragrance.

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