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SONOCHEMICAL SYNTHESIS OF ETHYL CINNAMATE

Yuliana Purwaningsih*, Mighfar Syukur, and Ungsari Rizki Eka Purwanto

Departmen Pharmacy, Semarang Pharmaceutical College
Jl. Letjend Sarwo Edhie Wibowo KM 1, Plamongansari, Semarang 50192, Central Java, Indonesia

* Correspondence: phone : (024) 6706147; email: y14purwaningsih@gmail.com

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ABSTRACT

This research aimed to determine the yield of ethyl cinnamate synthesized by the sonochemical method and its potency as a sunscreen agent. Ethyl cinnamate was synthesized from cinnamic acid and ethanol with concentrated sulfuric acid as catalysts assisted by ultrasonic waves. The Identification of compounds was carried out by infrared spectrophotometry and gas chromatography-mass spectroscopy. Synthesis of ethyl cinnamate resulted in the form of clear yellow liquid with a fragrant aroma of a cinnamon ester with a 96.61% yield. Identification by an infrared spectrophotometer showed many functional groups of ethyl cinnamate. Identification by GC-MS was given a relative abundance of 98.96%. The product of synthesis had SPF number 4.769 at 10 ppm used Mansur Equation. Based on this research, it concluded that it has potential as a sunscreen agent. The sonochemical method provides an excellent yield of ethyl cinnamate.

***Keywords**: ethyl cinnamate, sonochemistry, sunscreen, synthesis, ultrasound irradiation*

INTRODUCTION

Three categories ultraviolet radiation dependent on wavelengths are known as short wavelengths UVC (200-280 nm), medium wavelengths UVB (280-320 nm), and long wavelengths UVA (320-400 nm) [1, 2, 3]. production, synthesis of vitamin D and melanin pigment [1]. Overexposure of the ultraviolet radiation causing any damages in the skin like sunburns, hyperpigmentation, photo-aging and skin cancer [1, 2]. Dermatologists recommended sunscreen with has higher SPF to minimize effects caused by UV radiation [3,4]. Sunscreens are used to protect against harmful UV radiation from the sun based on its ability to absorb, reflect or scatter the sun's rays [2].

There are two types of sunscreens; organic and inorganic [6,7]. Popular choices for inorganic sunscreens are Titanium dioxide (TiO_2) and Zinc oxide (ZnO). Organic sunscreens normally have aromatic compounds consist of a carbonyl group such as para-aminobenzoic acid (PABA), cinnamates, salicylates, octocrylene, and benzophenone [2,3]. Organic sunscreens protect the skin by absorbing the radiation, protecting against erythema and skin wrinkling, and reflect UV radiation [3]. Synthetic ethyl cinnamate is widely used in the food industry, especially for beverages and baked goods. Application of ethyl cinnamate in the cosmetic and pharmaceutical industry is also significant due to the characteristic flavor and fragrance, as well as high boiling point and stability [4]. Ethyl cinnamate can be used as flavor fixative agent in the perfume industry [4].

Ethyl cinnamate can be synthesized using different methods: esterification of corresponding cinnamic acids with alcohols, Wittig reaction, Reformatsky reaction, Heck reaction, as well as other methods [4]. Classical methods and microwave methods were used for synthesis of this compound in the industry [5]. Sonochemistry has been chosen for synthesis in the last years. A large number of many synthesis organic use of this technique. This technique is more convenient and easily controlled than traditional methods [10,11]. Synthesis organic using ultrasound irradiation offers reduction on-time reaction, simplicity of operation, cleaner reaction, easy and highly yields [6], eco-friendly because minimize waste and reduce energy [13,14,15].

Synthesis of ethyl cinnamate using the classical method is carried out for a long time [9], and synthesis of ethyl cinnamate using sonochemistry has never been done. Based on this point of view, this research was to develop a simple sonochemical approach to ethyl cinnamate synthesis. The aim of this research was to determine the yield of ethyl cinnamate synthesis using the sonochemical method and potency of ethyl cinnamate as a sunscreen agent.

METHODS

1. Instrumentation

Sonication was performed in the Bransonic CPX1800H-E type. The IR spectra were recorded on Agilent Technologies Cary 630 FTIR in Semarang Pharmaceutical College. The GC-MS spectra were obtained in LPPT UGM. Spectrophotometer Shimadzu double beam for sunscreen assay.

2. Material

Cinnamic acid was purchased from Sigma-Aldrich, ethanol from Mallinckrodt Chemicals, ether, sodium bicarbonate, magnesium sulphate, concentrated sulphuric acid was pro analysis.

3. Synthesis of ethyl cinnamate

A Mixture of cinnamic acid (0.03 mol), 25 mL ethanol, and sulfuric acid (1 mL) were taken in a conical flask. The flask was kept in sonicator and set the time 40 minutes and 60°C. The mixture was evaporated under pressure to reduce ethanol. The residue was added $NaHCO_3$ saturated until pH 8-10 and extracted with ether. The phase of ether was added $MgSO_4$ anhydrate and evaporated with an evaporator vacuum to give pure ester. The product was characterized by FT-IR and GC-MS.

4. Sunscreen activity of ethyl cinnamate

The ability of the product to protect UV light was assayed by spectrophotometer UV. The concentration of the product was made by 10 ppm and assayed at 290-320 nm with every 5 nm increment used spectrophotometer UV. The ability of sunscreen was expressed as Sun Protection Factor (SPF) and determined by Mansur equation [15,17].

RESULTS AND DISCUSSION

A green synthesis for ethyl cinnamate was developed by esterification Fischer used the ultrasonic probe in excellent yields. Cinnamic acid reaction with ethanol used sulphuric acid as a catalyst in an ultrasonic bath at 40 minutes (Figure 1).

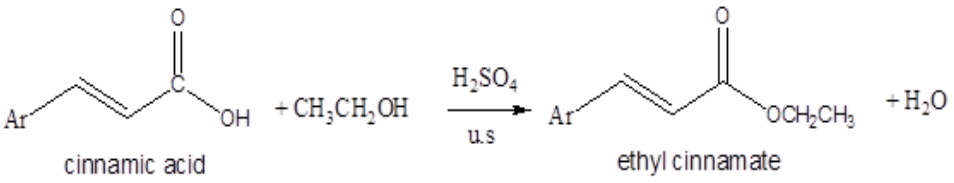

Figure 1. Esterification reaction to produce ethyl cinnamate

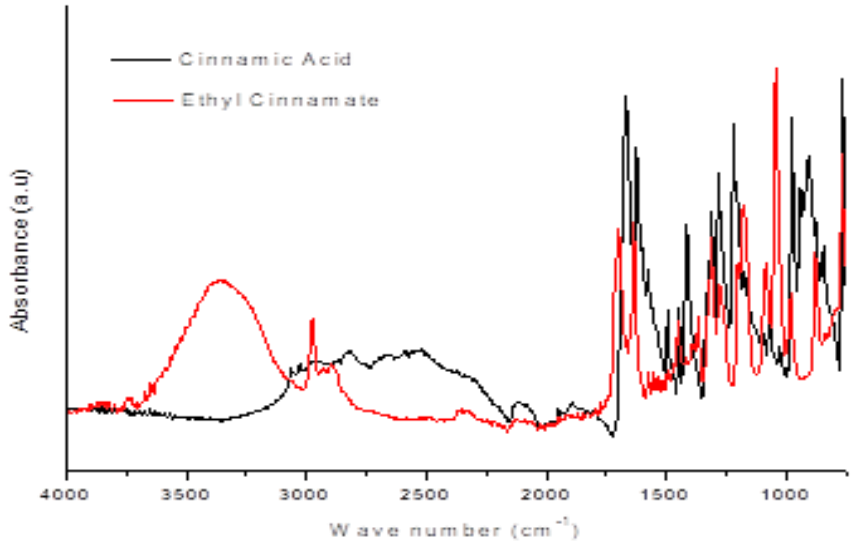

Figure 2. FT-IR spectrum of ethyl cinnamate

The product was given liquid yellow transparent. Identification by an infrared spectrophotometer showed many functional groups (Figure 2). The functional group of this product indicated that cinnamic acid was changed to ethyl cinnamate because the hydroxyl of carboxylic acid wasn't apparent. The appearance ethyl group showed the spectra at the number 2974 cm^{-1} indicated the presence of the -CH group and strengthened at the peak of 1450 cm^{-1} indicated the vibration of bending -CH. A peak of 1700 cm^{-1} represented of a carbonyl group, it was supported by 1162 cm^{-1} that indicated the presence of a C-O ester group. Uptake with a peak of 1636 cm^{-1} indicated an aromatic benzene group conjugated with alkene [7]. Based on that spectrum, the product contained ethanol was showed wave number at 3334 cm^{-1}. The Data of GC-MS (Figure 3) showed that ethyl cinnamate appeared at retention time 21.89-22.72 minutes with a relative abundance of 98.96%. Based on this data the ethyl cinnamate was able to synthesis from cinnamic acid under an ultrasonic wave with a yield of 96.61%. It could be interpreted that the sonochemical method was better than classical methods. The Sonochemical method could reduce their reaction time [9,11,17,18].

A molecule had vibrational motion when the ultrasound probe was transmitted through a medium. In this condition, the structure of molecules was compressed and stretched due to a time-varying pressure so the distance among the molecules varies as

the molecules oscillate around their mean position [12]. When the intensity of ultrasound in a liquid was increased, the intramolecular forces were not able to hold the molecular structure intact and then it separated, and a cavity was formed [8]. The cavity caused physical and chemical effects for a molecule. The cavitation supplied energy for chemical reaction [9].

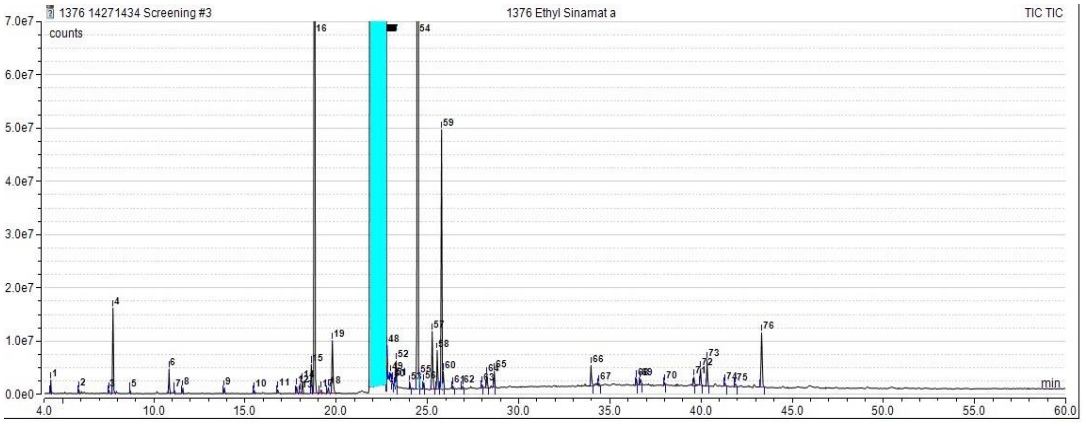

Figure 3. GC-MS of product synthesis

Analysis of MS ethyl cinnamate was showed in Figure 4 and Figure 5. The spectra indicated of the product caused by mass spectra was 176.1 as the molecular weight of ethyl cinnamate. It was strengthened by the spectra of the compound with m/z 131 as the base peak [7].

Figure 4. Mass spectra of ethyl cinnamate

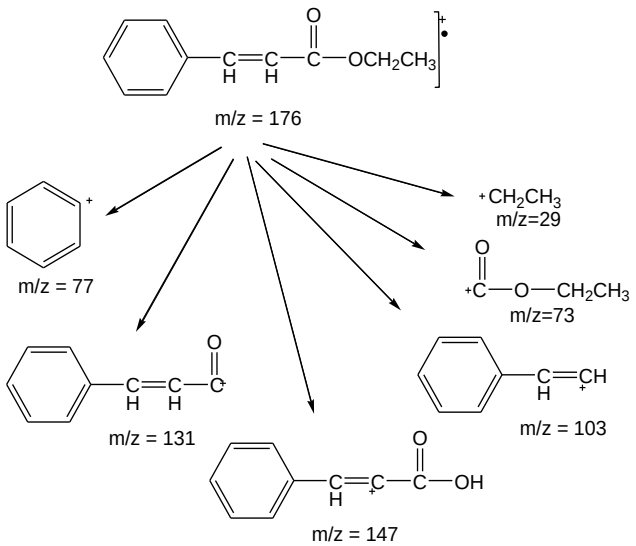

Figure 5. Fragmentation pathway of ethyl cinnamate

Activity as Sunscreen Agent

The activity of ethyl cinnamic as sunscreen agent was assayed by spectrophotometer ultraviolet due to the Mansur equation (1) [10].

$$SPF = CF \times \sum_{290}^{320} EE\ (\lambda) \times I\ (\lambda)\ Abs\ (\lambda) \quad (1)$$

where CF = correction factor 10, EE (λ) = erythematogenic effect of radiation wavelength (λ), I (λ) = sunlight intensity at a wavelength (λ), and Abs (λ) = spectrophotometric determination of absorbance of the formulation in solution at a wavelength (λ).

The SPF of the product of synthesis used this equation was 4.769 and cinnamic acid was 3.457 at 10 ppm (on ethanol solution). It was mean that at 10 ppm, ethyl cinnamate more effective than cinnamic acid as a sunscreen caused ethyl cinnamate blocked UV B by 75% - 83% effectively [11].

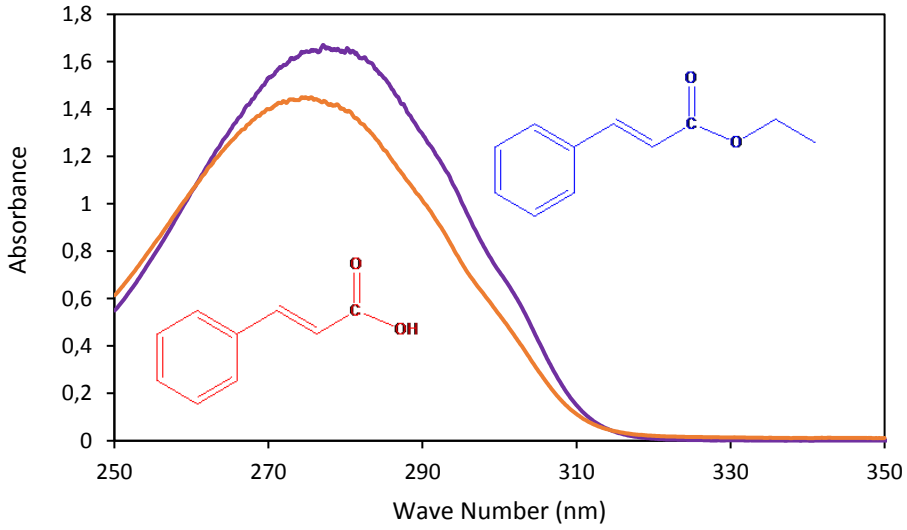

Figure 6. UV absorption spectrum of equimolar ethyl cinnamate and cinnamic acid (ethanol solution)

UV spectroscopy stimulates appreciation of why an ester cinnamate is chosen as a sunscreen component rather than the precursor cinnamic acid [16]. Ethyl cinnamate can absorb UVB radiation more effectively than cinnamic acid (Figure 6) [10]. Ethyl cinnamate has a highly conjugated compound to absorb radiation at 290-320 nm wavelength [10]. Derivative of cinnamic acid is the best candidate to filter of UVB irradiation [3].

CONCLUSION

Ethyl Cinnamate was able to be synthesized from cinnamic acid and ethanol with concentrated sulphuric acid as a catalyst using ultrasound waves with yield 96.61%. The SPF number of ethyl cinnamate at 10 ppm was 4.769 so it can be concluded that ethyl cinnamate was able to act as a sunscreen. Sonochemistry can help the synthesis reaction of ethyl cinnamate become more efficient, and faster than classical methods with excellent yield.

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