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Synthesis Octyl *P*-Methoxycinnamate as Sunblock by Transesterification Reaction with the Starting Material Ethyl *P*- Methoxycinnamate

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Abstract

Synthesis octyl *p*-methoxycinnamate substance as sunblock, has been done by transesterification reaction. The starting material of the reaction was ethyl *p*-methoxycinnamate isolated from *Kaempferia galanga* L.The transesterification reaction was carried out by reacting ethyl *p*-methoxycinnamate with octanol. The product was identified by UV-VIS, Infra Red and Mass Spectroscopy. The result of measurements on erythemic %T at various concentrations demonstrate that octyl p-methoxycinnamate is applicable as a sunblock compound.

Keywords: octyl *p*-methoxycinnamate, transesterification, ethyl *p*-methoxycinnamate, sunblock

INTRODUCTION

Sunscreen compound octyl *p*-methoxycinnamate can be synthesized from ethyl *p*-methoxycinnamate by esterification reaction, either directly or through intermediate compounds. Direct esterification between a carboxylic acid with an alcohol (Fessenden & Fessenden, 1989). Direct esterification reaction has been used in the synthesis of octyl *p*-methoxycinnamate of ethyl *p*-methoxycinnamate, after previously ethyl *p*-methoxycinnamate hydrolyzed into *p*-methoxycinnamic acid. This reaction produces octyl *p*-methoxycinnamate as much as 71.40% (Hidajati, 1997).

Other esterification reaction through intermediate compounds is a reaction that occurs between an acid halide with an alcohol (Fessenden and Fessenden, 1989). This method requires a longer reaction stage.

In addition to esterification, the another synthesis of an ester known as transesterification, i.e. the ester formation reaction of another ester (Mc Murry J., 2008). Ethyl *p*-methoxy cinnamate compound is an ester, which allows the use of methods of transesterification in the synthesis of octyl *p*-methoxycinnamate in one step reaction.

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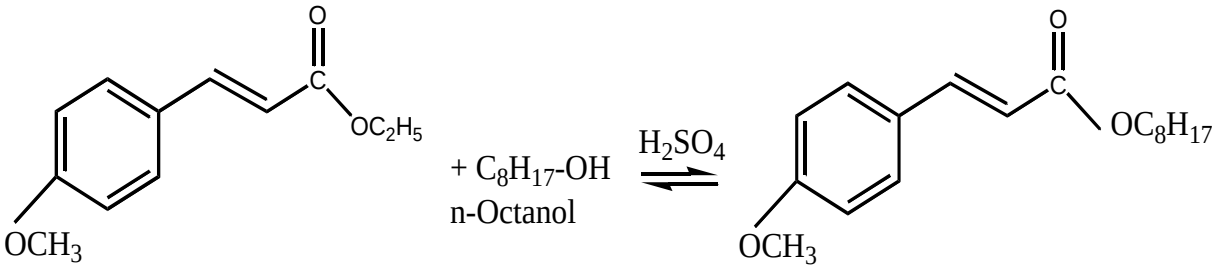

Ethyl p-methoxycinnamate

Octyl *p*-methoxycinnamate

Figure 1. Steps of the Synthesis of Octyl *p*-Methoxycinnamate

In consideration of the reaction path that is shorter, so hopefully obtain more results, hence in this study we used the method of transesterification.

MATERIALS AND METHODS

Isolation of ethyl *p*-methoxycinnamate of rhizome *kencur* (*Kaempferia galanga* L.)

Rhizome powder *kencur* (*Kaempferia galanga* L.) was percolated with 96% ethanol for ± 24 hours. Solvent of the percolate was evaporated with *Rotary vacuum evaporator*, and then cooled to obtain crystals of ethyl p-methoxycinnamate. The crystals was washed with methanol and recrystallized with methanol-water (Hidajati, 1997).

Synthesis of octyl *p*-methoxycinnamate

Into a round bottom flask put 500 mg of ethyl *p*-methoxycinnamate, 10 ml octanol and 0.5 ml of sulfuric acid, shake until the crystal dissolve.. The mixture was refluk for 7.5 hours with the temperature 150 ^oC. To remove any residual reagents, the mixture were distilled fraction in vacuum. The residue was extracted with hexane. The extract obtained is purified by column chromatography. Stationary phase used was silica gel G60 F_{254} and used n-hexane: ethyl acetate: acetone (65:15:5) as eluent.

Identification structure of ethyl *p*-methoxycinnamate and octyl *p*-methoxycinnamate

Identification of ethyl *p*-methoxycinnamate was done by determination of melting point using a *Electrothermal Melting Point Apparatus*; Thin Layer Chromatography with stationary phase silica gel G60 F_{254} and 3 kinds of mobile phase, respectively = hexane: ethyl acetate: acetone (65: 15: 5) , hexane: chloroform: acetic acid (5:4:1), hexane: ethyl acetate (4: 1), with ultraviolet light as the detection; infrared spectrophotometer, UV spectrophotometer, mass spectrometer.

Determination of % T erythema and %T pigmentation

Created a solution of octyl *p*-methoxycinnamate in methanol with various concentrations (5, 10, 15, 20, 25, 30, 35, 40 ppm), and then measuredita transmition at a wavelength of 292 to 372 nm with intervals of 5 nm using UV-VIS spectrophotometer. Were determined with Cumpelik method the size % T erythema and %T pigmentation (Dinunzio, 1990; Cumpelik, 1972; Kreps, 1972).

RESULTS AND DISCUSSION

In this research, 2 (two) steps of research is the isolation of ethyl *p*-methoxycinnamate from rhizome *kencur* and transesterifikasi reaction octanol and ethyl *p*-methoxycinnamate. Isolation of ethyl *p*-methoxycinnamate of rhizome *kencur* done by percolation using ethanol 96%. The resulting crystals purified by recrystallization using a solvent mixture of methanol-water, to obtain white needle crystals which have a melting range 47–48 °C, whereas according to literature from melting range of 48–48.5 °C (Tanjung,1997). From this isolation is obtained ethyl *p*-methoxycinnamate 1.25% of the dry weight of rhizome *kencur* (*Kaempferia galanga* L.), in the form of needle crystals, white and odorless.

Transesterification reaction of octyl *p*-methoxycinnamate with early material gives ethyl *p*-methoxycinnamate percent yield was 87.40%, solid, cream-colored with a melting point of 28.5 °C.

The purity by TLC using silica gel $G_{60}F_{254}$ stationary phase and stain showing used UV light. Rf value TLC results of octyl *p*-methoxycinnamate and ethyl *p*-methoxycinnamate can be seen in Table I.

Table I. Rf value TLC results of octyl *p*-methoxycinnamate and ethyl *p*-methoxy-cinnamate with used UV light as detection

Eluent	Value R_f	
	ethyl *p*-methoxycinnamate	Octyl *p*-methoxycinnamate
hexane : ethyl acetate : acetone (65:15:5)	0,66	0,76
hexane : $CHCl_3$: glacial acetic acid (5:4:1)	0,90	0,92
hexane : ethyl acetate (4:1)	0,73	0,84

Identification of isolates by UV-Vis spectrophotometer to give the peak wavelength of maximum absorbance at 225 nm and 307 nm, in accordance with earlier research that ethyl *p*-methoxycinnamate to provide maximum absorption peak at wave 225 and 307 nm (Tanjung, 1997). Identification using an infrared spectrophotometer showed the existence of clusters C = O ester at a wavelength of 1707 cm^{-1}; ester CO group at 1168 cm^{-1} and 1253 cm^{-1} for bound aromatic ether groups. Identification by mass spetroscopy shows molecular weight 206. The compound was identical as ethyl *p*-methoxycinnamate.

Table. II. Characterization of UV spectra, IR and MS compound ethyl *p*-methoxy-Cinnamate

UV Spectrum; λ maximum (nm) In methanol solvent	225 and 307
IR Spectrum; λ (cm^{-1}) In KBr pellet	1707 (C=O ester); 1168 (-C-O- ether); 1253 (CH_3O- aromatis)
Mass Spectrum (m/e)	78 ($C_6H_5^+ + H^+$); 133(M - $COO\text{-}C_2H_5)^+$; 161 (M - $OC_2H_5)^+$; 179 (M - $C_2H_4)^+$; 206 $(M)^+$

Identification of compounds synthesized using UV-VIS spectrophotometer to give the peak wavelength of maximum absorbance at 225 nm and 309 nm. In the literature mentioned that in order to be used as a sunscreen compound must meet the criteria as a sunscreen compound that has a maximum wavelength between 270-360 nm-1 (group cinnamate) (Shaath, 1986). Identification with an infrared spectrophotometer data obtained wave number at 1712 cm^{-1} for group C = O ester, 1168 cm^{-1} for CO ester and 1251 cm^{-1} for bound aromatic ethers. Identification of a mass spectrometer shows compounds synthesized has a relative molecular mass (Mr) of 290. (Kemp.W., 1979; Silverstein RM, 1986). The compound was identical as octyl *p*-methoxycinnamate.

Table III. Characterization of UV spectra, IR and MS compound octyl p-methoxycinnamate

UV Spectrum; λ maximum (nm) In methanol solvent	225 and 309
IR Spectrum; λ (cm^{-1}) In KBr pellet	1712 (C=O ester); 1168 (-C-O- ether); 1251 (CH_3O- aromatis)
Mass Spectrum (m/e)	77 ($C_6H_5^+ + H^+$); 133(M - $COO\text{-}Octyl)^+$; 161 (M - $O\text{-}Octyl)^+$; 178 (M - $CH_2{=}CH\text{-}C_6H_{13})^+$; 290 $(M)^+$

Transesterification reaction is a reversible reaction. To prevent the reaction shifted to the left in order to get maximum results by using excess alcohol or eliminate the side product (Fessenden, 1992; Morrison and Boyd, 1989). In this research, to prevent the reaction shifts to the left of excessive alcohol use (about twenty-six times the number of moles required). The excess of alcohol was removed by vacuum fractional distillation.

Distillation fraction is intended to remove excess alcohol boiling point difference with the compounds synthesized are very small (n-octanol boiling point 178-180 °C). While the vacuum performed for synthesized compounds are not damaged or broken down due to high heat. With a vacuum at a pressure of 9 mm Hg, then the n-octanol was separate with a relatively low boiling point of 48-52 °C.

Removal of excess n-octanol quite difficult, because of difficulties in removal of excess alcohol in the transesterification method is less efficient than the method of esterification step (esterification via acylation reaction) using alcohol with molecular ratio of 1:1 (Vogel, 1986). The result of the determination of %T erythema and %T pigmentation octyl p-methoxy-cinnamate can be seen in Table IV.

Table IV. The result of the determination of %T erythema and %T pigmentation octyl p-methoxycinnamate

Concentration (ppm)	%T erytema	%T pigmentation
5	71,05	90,76
10	50,54	83,34
15	44,21	82,72
20	30,98	77,09
25	19,36	72,49
30	16,74	62,58
35	11,15	63,45
40	9,19	64,57
50	4,01	57,65
60	2,60	54,36
70	1,27	62,34

Table V. Clasification of compounds sunscreen octyl *p*-methoxycinnamate

Concentration octyl p-methoxycinnamate (ppm)	Classification product	Literature	
		%T Erytema	% T Pigmentation
> 70	Total blocks	< 1 %	3-40%
50 - 70	Extra protection	1-6%	42-86%
35 – 40	Suntan fixed	6-12%	45-86%
< 35	Tanning rapidly	10-18%	45-86%

Classification of compounds sunscreen octyl *p*-methoxycinnamate based on % T erythema and % T pigmentation can be seen in Table V. The calculation of the coefficient extingsi octyl p-methoxycinnamate molar yield of 15 544. Based on the % T erythema and % T pigmentation sunscreen compounds can be grouped into a total block, extra protection, suntan tanning equipment and fast (Kreps, 1972).

From the value of % T erythema and % T pigmentation, octyl p-methoxycinnamate can function as a sunscreen compound with the classification type of extra protection at a concentration of 50-70 ppm, the type of suntan fixed at a concentration of 35-40 ppm and the type of tanning rapidly at concentrations <35 ppm and at concentrations > 70 ppm as total blocks.

CONCLUSIONS

The ethyl acetate extract of *Aspergillus brevipes* RK06 showed growth inhibition against *Klebsiella pneumonia, Pseudomonas aeruginosa,* and *Staphylococcus aureus*. Based on the assays, the extract showed a potential citotoxity and both low antioxidant and hemolytic activities.

1. Synthesis of compounds sunscreen octyl p-methoxycinnamate can be done through a transesterification reaction between n-octanol with ethyl p-methoxycinnamate with hail percent amounting to 87.40%.
2. From the value of % T erythema and % pigmentation, octyl p-methoxycinnamate can function as a sunscreen compound with the classification type of extra protection at a concentration of 50-70 ppm, the type of suntan fixed at a concentration of 35-40 ppm and the type of tanning rapidly at concentrations <35 ppm and at concentrations > 70 ppm as a total block.

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