

The Effect of Methyl and Chloro Substituent Compounds in Amida Derivatives Synthesis from *p*-Metoxycinnamic Acid with Microwaves Irradiation

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ABSTRACT

Background: The difference in the nature of these aromatic amine substituents, i.e. methyl and chloro will affect the N atom of aniline as a nucleophile to attack the carbonyl C atom in the *p*-methoxycinnamoyl chloride in the synthesis two amides derivate of *p*-methoxycinnamic acid, namely *N*-(*p*-methylphenyl)-*p*-methoxycinnamide and *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide. **Aim:** to obtain the *N*-(*p*-methylphenyl)-*p*-methoxycinnamide and the *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide compound from *p*-methoxycinnamic acid using the microwave irradiation method as source of energy. Beside that, it also to determine the effect of the presence of methyl and chloro substituents in *para* position of aromatic amines in the yields of reactions. **Method:** The reactions were carried out by microwave irradiation at three powers, i.e 120 watts, 200 watts, 280 watts. After separation and purification steps, the products were identified by spectrometric methods. **Result:** At power of 200 watts for reaction time of 7.5 minutes, the yield of *N*-(*p*-methylphenyl)-*p*-methoxycinnamide is larger than *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide. The percentage of the product synthesis of *N*-(*p*-methylphenyl)-*p*-methoxycinnamide was 51.84% and the percentage of *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide was to 47.20%. **Conclusion:** The effect of substituent methyl is increase the percentage yield of *N*-(*p*-methylphenyl)-*p*-methoxycinnamide compound than that substituent chloro of *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide compound under the same reaction conditions. Based on the identification of the structure of the synthesized compound using a UV spectrophotometer, infrared spectrophotometers and ¹H-NMR spectrometer it can be concluded that the synthesized compounds are *N*-(*p*-methylphenyl)-*p*-methoxycinnamide and *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide.

Keywords: microwave, *N*-(*p*-methylphenyl)-*p*-methoxycinnamide, *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide

Introduction

Amides are compounds that have trivalent nitrogen in the carbonyl group. Amide is a weak base with pK_b 15-16. Amide synthesis can be obtained by reacting amines and carboxylic acid derivatives. This amide formation reaction is a nucleophilic acyl substitution reaction. This substitution is a nucleophile substitution in an acyl carbon. Acid halides are the most reactive carboxylic acid derivatives, because halides are good leaving groups. Most acyl halide reactions occur through nucleophilic substitution. Therefore, in forming *N*-(*p*-methylphenyl)-*p*-methoxycinnamide and *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide, we need *p*-methoxycinnamic acid (PMCA) as starting material which is then converted to the form of acyl halide and being reacted with *p*-methyl aniline (Figure 1) and *p*-chloroaniline (Figure 2). The methyl substituent in the aromatic amide has the property of an electron booster while the chloro substituent in the aromatic amine is an electron attractor (Pertwi, 2016).

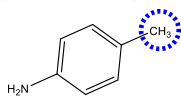


Figure 1. *p*-methyl aniline

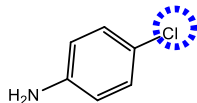


Figure 2. *p*-chloroaniline

The different properties of these aromatic amine substituents will affect the N atom which acts as a nucleophile that will attack the C carbonyl atom on the acyl

halide of PMCA. In this study, it is expected to get information about the effect of the presence of substituents on aromatic amides on the percentage of synthesis. This study also conducted the reaction of *p*-methoxycinnamoyl chloride with *p*-chloroaniline and produced *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide. Chloro-groups are electron-withdrawal group so that the aromatic amide group will influence the reactivity of the compound (Nurcahyaningtyas, 2017).

The synthesis of the two compounds was carried out in a tetrahydrofuran solvent and with a triethylamine catalyst. The structure of tetrahydrofuran has a C-H bond that can mix with organic compounds and has an O atom that can bind to a water compound so that it can mix with water. The nature of tetrahydrofuran is the reason for the solvents used in this study. Triethylamine is a weak base and commonly used to make esters and amides. This reaction will produce hydrochloric acid which will then react with triethylamine and produce triethylammonium chloride salt. The existence of the formation of the triethylamain salt can remove hydrochloric acid from the reaction solution so that the reaction runs smoothly (Costa, 2016).

This study used microwaves to carried the organic reaction. The use of microwaves is based on the efficient heating of the material by the microwave dielectricheating effect. Therefore, the use of microwaves depends on the ability of certain materials (solvents or reagents) to absorb microwave energy and convert it to heat. The electrical

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component of the electromagnetic field that causes heat is obtained from two main mechanisms: dipolar polarization and ionic conduction. The interaction of electric field components with a matrix is called a dipolar polarization mechanism so that substances that can produce heat when irradiated with a microwave oven. The purpose of this study is to obtain *N*-(*p*-methylphenyl)-*p*-methoxycinamide and *N*-(*p*-chlorophenyl)-*p*-methoxycinamide from PMCA using the microwave irradiation method, and also to determine the effect of the presence of methyl and chloro substituents in aromatic amines (Polshettiwar&Varma, 2008; Kappe, 2004).

Material and Methods

In this study, the method used to react these compounds is microwave irradiation. The mechanisms that occur in microwaves are dipole polarization and ion induction (Kappe, 2004). Therefore, we used polar compounds in this experiment. This method was chosen because it allows synthesis to be carried out more efficient. The results of the synthesis are almost productive with microwave irradiation of 120 watts, 200 watts, 280 watts and the reaction time is quite short (Mourat, 2007). In this study, we conducted amides synthesis by microwave irradiation and compared to the percent yield of *N*-(*p*-methylphenyl)-*p*-methoxycinamide and *N*-(*p*-chlorophenyl)-*p*-methoxycinamide. The purity test by thin layer chromatography (TLC) and point melting. Structure identification analysis of the synthesized compounds with FT-IR, NMR spectrometer and also UV-VIS spectrophotometer analysis.

Results and discussions

Synthesis of *N*-(*p*-methylphenyl)-*m*-methoxycinamide in Various Microwave Conditions

Synthesis of *N*-(*p*-methylphenyl)-*p*-methoxycinamide, was following the method below then the best conditions was selected which produced the biggest yield and then being applied to the synthesis of the second amide compound (Table 1).

Table 1 Percentage of yield in various microwave reaction conditions

Power	Time	Percentage of synthesis results
120 watts	3 mins	60 %
200 watts	7.5 mins	63 %
280 watts	3.5 mins	62 %

Crystal of *N*-(*p*-methylphenyl)-*p*-methoxycinamide

Based on the synthesis of the selected conditions at 200 watts of microwave power and reaction time of 7.5 minutes, a percentage of yield of *N*-(*p*-methylphenyl)-*p*-methoxycinamide compound as shown in Table 1, we produced *N*-(*p*-methylphenyl)-*p*-methoxycinamide as clear brownies crystals as shown in Fig. 3.



Figure 3. Crystal of *N*-(*p*-methylphenyl)-*p*-methoxycinamide

Purity Test with TLC method

The purity of the compound is indicated by the presence of a single stain which had a different Rf value than the starting materials, PMCA and *p*-methyl aniline. Based on the results of the purity test, it showed that *N*-(*p*-methylphenyl)-*p*-methoxycinamide had a single spot with different Rf value than the starting materials. This showed that the synthesized compound obtained was pure.

Table 2 Data from the Test of the purity of the synthesized compound using TLC

Solvent	Material	Number of stains	Rf	Rf (average)
<i>n</i> -Hexane: Ethyl acetate (1: 1)	<i>p</i> -Methoxycinamic acid	1	0.40	0.40
	<i>p</i> -Methyl aniline	1	0.80	0.80
	<i>N</i> -(<i>p</i> -methylphenyl)- <i>p</i> -methoxycinamide repl. I	1	0.61	0.61
	repl. II	1	0.61	
repl. III	1	0.61		
Chloroform: Ethyl Acetate (5: 1)	<i>p</i> -Methoxycinamic acid	1	0.31	0.31
	<i>p</i> -Methyl aniline	1	0.91	0.91
	<i>N</i> -(<i>p</i> -methylphenyl)- <i>p</i> -methoxycinamide repl. I	1	0.83	0.83
	repl. II	1	0.83	
repl. III	1	0.83		
Chloroform: Acetone (19: 1)	<i>p</i> -Methoxycinamic acid	1	0.37	0.37
	<i>p</i> -Methyl aniline	1	0.91	0.91
	<i>N</i> -(<i>p</i> -methylphenyl)- <i>p</i> -methoxycinamide repl. I	1	0.86	0.86
	repl. II	1	0.86	
repl. III	1	0.86		

Melting Point Purity Test

The purity test was performed by the melting point examination of *N*-(*p*-methylphenyl)-*p*-methoxycinamide and replicated under the same conditions (Table 3).

Table 3 Purity test using melting point

Replication	Melting Point (°C)
1	156.0 °C
2	156.0 °C
3	158.0 °C
Average	156.67 °C

Structure Identification with Ultraviolet Spectrophotometer

N-(*p*-methylphenyl)-*p*-methoxycinamide had a maximum wavelength that is different from PMCA so that this showed that the synthesized compound was different compound from the initial compound (Table 4).

Table 4 Maximum wavelength of compound

Compound	Maximum wavelength
PMCA	285.0
<i>N</i> -(<i>p</i> -Methylphenyl)- <i>m</i> -methoxycinamide	313.5

Structure Identification with Infrared Spectrophotometer

Identification of the structure of *N*-(*p*-methylphenyl)-*p*-methoxycinamide with an infrared spectrophotometer. The synthesized compound is an amide group carboxylate derivative, had specific absorption at certain wave numbers. Based on the interpretation results of infrared spectra, the

synthesized compound was identical to *N*-(*p*-methylphenyl)-*p*-methoxycinamide.



Figure 5. Powder form of *N*-(*p*-chlorophenyl)-*p*-methoxycinamide

Table 5 Wave numbers of synthesized compounds

Theoretical wave number	Wave numbers of synthesized compounds (cm ⁻³)	Functional groups
3200-3600	3270	N-H
1515-1570	1525	N-H
3000-3100	3031	C-H
1430-1650	1619	C=C
1600-1900	1689	C=O
1075-1400	1249	C-O

Structure Identification with ¹H-NMR spectroscopy

Identification of the structure using ¹H-NMR spectroscopy was carried out for the purpose of knowing the number of protons, types of protons and protons in their environment. Table 6 below shows the analysis spectra of ¹H-NMR of *N*-(*p*-methylphenyl)-*p*-methoxycinamide in CDCl₃ solvent.

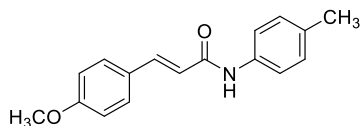


Figure 4. the structure of *N*-(*p*-methylphenyl)-*p*-methoxycinamide

From Table 6, it shows the sum of the proton of the synthesized compound is 16, one proton of NH amide didn't occur. The amide moiety of this compound appears at IR spectra (Table 5). Based on the results, it was concluded is *N*-(*p*-methylphenyl)-*p*-methoxycinamide (Figure 4).

Table 6 Interpretation of ¹H-NMR spectra of compound *N*-(*p*-methylphenyl)-*p*-methoxycinamide

Chemical shift (ppm)	Multiplicity	Proton	The location of the proton	Coupling constant (J=Hz)
2.31	Singlet	3H	Ar-CH ₃	-
3.82	Singlet	3H	CH ₃ -O	-
7.68	Doublet	1H	C-CH=CH-CO	15.2
6.42	Doublet	1H	CH=CH-CO	15.2
7.42-7.49	multipl et	5H	N-H Ar-H	-
6.84	Doublet	2H	H-Ar	8
6.84	Doublet doublet	1H	Ar-H	4 & 4

Synthesis of *N*-(*p*-chlorophenyl)-*p*-methoxycinamide

Synthesis of *N*-(*p*-chlorophenyl)-*p*-methoxycinamide was carried out under selected conditions which had been carried out previously on the synthesis of *N*-(*p*-methylphenyl)-*p*-methoxycinamide. The selected microwave conditions for the synthesis of *N*-(*p*-chlorophenyl)-*p*-methoxycinamide were 200 watts for 7.5 minutes, with percentage yield of the compound *N*-(*p*-chlorophenyl)-*p*-methoxycinamide is 47%.

The synthesized product was obtained as white crystals/powders as shown in Fig. 5.

Purity Test with Thin Layer Chromatography (TLC)

Based on the results of the purity test showed that *N*-(*p*-chlorophenyl)-*p*-methoxycinamide had a single spot with different R_f value than the starting material, PMCA and *p*-methyl aniline. This showed that the synthesized compound was pure.

Table 7 Data from the Test of the purity of the synthesized compound using TLC

Solvent	Material	Number of stains	R _f	R _f (average)
Hexane: Ethyl acetate (1: 1)	<i>p</i> -Methoxycinamic acid	1	0.40	0.40
	<i>p</i> -chloro aniline	1	0.68	0.68
	<i>N</i> -(<i>p</i> -chlorophenyl) - <i>p</i> -methoxycinamide	repl. I repl. II repl. III	1 1 1	0.67 0.66 0.66
Chloroform: Ethyl Acetate (5: 1)	<i>p</i> -Methoxycinamic acid	1	0.31	0.31
	<i>p</i> -chloro aniline	1	0.73	0.73
	<i>N</i> -(<i>p</i> -chlorophenyl) - <i>p</i> -methoxycinamide	repl. I repl. II repl. III	1 1 1	0.84 0.84 0.84
Chloroform: Acetone (19: 1)	<i>p</i> -Methoxycinamic acid	1	0.34	0.34
	<i>p</i> -chloro aniline	1	0.80	0.80
	<i>N</i> -(<i>p</i> -chlorophenyl) - <i>p</i> -methoxycinamide	repl. I repl. II repl. III	1 1 1	0.86 0.86 0.86

Purity Test with Melting Point

The melting point evaluation of *N*-(*p*-chlorophenyl)-*p*-methoxycinamide was performed triplicate under the same conditions (Table 8).

Table 8 Purity Test with Melting Point

Replication	Melting Point (°C)
1	179 °C
2	180 °C
3	179 °C
Average	179.3 °C

Structure Identification with Ultraviolet Spectrophotometer

N-(*p*-chlorophenyl)-*p*-methoxycinamide had a maximum wavelength that was different from PMCA. It showed that the synthesized compound is different from the initial compound.

Table 9 Maximum Wavelength of Compounds

Compound	Maximum wavelength
PMCA	285.0
<i>N</i> -(<i>p</i> -chlorophenyl)- <i>m</i> -methoxycinamide	296.0

Structure Identification with Infrared Spectrophotometer

Based on the results of the infrared spectra interpretation, it can be seen that the synthesized compound is identical to the *N*-(*p*-chlorophenyl)-*p*-methoxycinamide.

Table 10 Synthesized wave number

Theoretical wave number	Wave numbers of synthesized compounds (cm ⁻³)	Functional groups
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3200-3600	3476	N-H
1570-1515	1525	N-H
3000-3100	3053	C-H
1430-1650	1617	C=C
1600-1900	1671	C=O
1075-1400	1252	C-O
785-540	782	C-Cl

Structure Identification with ¹H-NMR spectroscopy

The ¹H-NMR spectra of compounds synthesized by *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide in CDCl₃ solvent had shown in Table 11.

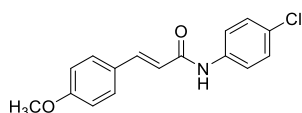


Figure 6. the structure of *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide

From table 11, it showed that the sum of proton in *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide was 14. In the chemical shift 2.33 ppm, there was a peak of impurities that should not be present so that in this synthesis further purification is needed.

Table 11 Interpretation of spectra ¹H-NMR compound *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide

Chemical shift (ppm)	Multiplicity	Proton	The location of the proton	Coupling constant (J=Hz)
3.84	Singlet	3H	CH ₃ -O	-
6.40	Doublet	1H	C-CH=CH-CO	16.0
7.68	Doublet	1H	C-CH=CH-CO	16.0
7.32	singlet	1H	-N-H	-
7.45-7.50	multiplet	4H	H-Ar	-
7.13	doublet	2H	H-Ar	8.0
6.87-6.92	Doublet	2H	H-Ar	2.0
	doublet			&8.0

Since amine group is a nucleophile, so made it easier to attack C-carbonyl in *p*-methoxycinnamoyl chloride. The increased activity of N atom also caused the organic reactions conducted faster. The chloro group in the aniline at *para* position was an electron-pulling group because it has a higher electronegativity than the N group. Based on this property, the electron of the N group will be drawn towards Cl so that the reactivity of the N group in attacking C-carbonyl atoms is lower. This caused the formation of *N*-(*p*-methylphenyl)-*p*-methoxycinnamide was more easily to be formed and the percentage of yield was greater than *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide (Puspasari, 2011).

The purity test results with TLC were said to be pure if each compound obtained a single spot and had a different R_f than the starting material. *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide performed a single spot and had the R_f value which was different from PMCA.

Based on the melting point test, *N*-(*p*-methylphenyl)-*p*-methoxycinnamide had the melting point of 156 °C and *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide had the melting point of 179 °C.

From UV spectra, this occurred a shift towards greater or referred to as bathochromic. The use of ethanol solvents could affect the wavelength shift where transition occurred. The effect of the N group on aniline affected the shift of the maximum wavelength towards a longer direction (Muswanto, 2019).

From infrared spectrophotometer data, *N*-(*p*-methylphenyl)-*p*-methoxycinnamide showed the NH group of secondary amide indicated by wave number at 3270 cm⁻¹ for stretching mode and for stretching mode found at 1525 cm⁻¹. Amide band (C = O) was shown the stretching absorption at 1684 cm⁻¹ and the CO bond at 1249 cm⁻¹. The results of infrared spectra interpretation was identical to *N*-(*p*-methylphenyl)-*p*-methoxycinnamide (Rachman, *et al*, 2018). The agreement of *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide was shown by the presence of stretching amide band at 1652 cm⁻¹. The C-O bond was located at 1252 cm⁻¹. The bounch mode N-H group was found at 1542 cm⁻¹ and the stretching mode at 3467 cm⁻¹. Based on these data, the infrared spectra actually belonged to *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide. The two amide synthesized compounds differed at wave number of 785-540 cm⁻¹. There was a bond between C-Cl only appearing in the synthesis of *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide (Barus, 2009).

From ¹H-NMR data, *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide had three protons (O-CH₃) bound to the aromatic ring which gave a chemical shift at 3.84 ppm with singlet multiplicity. The eight proton aromatic was occurred at 6.87-7.50 ppm. The two vinyl proton was showed at 6.40 & 7.68 ppm, with *J*_{ab} = 16Hz, in *trans* form isomer. Proton of NH amide showed as singlet peak at 7.32 ppm. Those data correspond with the structure of *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide.

The three protons of *N*-(*p*-methylphenyl)-*p*-methoxycinnamide (O-CH₃) gave a chemical shift of 3.82 ppm as singlet and three protons of -CH₃ as singlet peak at 2.31ppm. The two vinyl protons of these compounds provided chemical shifts of 6.42 and 7.68 ppm each as doublets with coupling constant of 16 Hertz. The structure of *N*-(*p*-methylphenyl)-*p*-methoxycinnamide had two aromatic rings. The aromatic ring had a number of protons of 8H. Both of these aromatic rings had substituents in the form of *para*, thus providing a chemical shift of 6.42-7.49 ppm. One proton of NH amide didn't occur in ¹H-NMR spectra, but it can be proved through IR spectra. From the spectroscopic data, it was concluded the structure was *N*-(*p*-methylphenyl)-*p*-methoxycinnamide.

Conclusion

From this study, it can be concluded that *N*-(*p*-methylphenyl)-*p*-methoxycinnamide and *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide could be synthesized from PMCA using microwave irradiation. The effect of methyl and chloro substituents made the percentage yield of *N*-(*p*-methylphenyl)-*p*-methoxycinnamide compounds was greater than *N*-(*p*-chlorophenyl)-*p*-methoxycinnamide under the same reaction conditions.

Acknowledgments

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