

Synthesis and Characterization of C-Cinnamal Calix [4] Resorsinarena from Cinnamon Oil Waste West Sumatra

S B Etika*, E Nasra, I Rilaztika

Chemistry Department Faculty of Mathematics and Natural Science, Universitas Negeri Padang, Jln. Prof.Dr.Hamka Air Tawar Padang, Indonesia

*sribentietika67@gmail.com

Abstract. Synthesis and characterization of compound C-Cinnamal Calix [4] Resorsinarena (CCCR) of cinnamon oil waste have been done. This study was aimed to synthesis and characterize C- Cinnamal Calix [4] Resorsinarena from cinnamaldehyde isolated cinnamon oil waste. C-Cinnamal Calix [4] Resorsinarena was synthesized by electrophilic substitution reaction of cinnamaldehyde isolated by the acid and resorcinol at 77oC temperature for 2 hour. The data analysis spectrum UV-VIS and FT-IR showed that the compound isolated cinnamaldehyde same as pure cinnamaldehyde compound. The characterization of C-Cinnamal Calix [4] Resorsinarena in the form of reddish-colored solids with melting point 3580C by using UV-VIS showed the presence of double bond, FT-IR showed the absorption at the wave number 3323,94 cm⁻¹ indicating the –OH group, the wave number 1610,94 cm⁻¹ showed the vibration C=C, the strong region absorption of 1500,86 cm⁻¹ indicating the presence of an aromatic ring, the at 1442,88 cm⁻¹ wave number indicating the presence of CH₃.

1. Introduction

Environmental issues related to water pollution have been a hot topic in recent decades. One of the water pollution is cause by bad industrial disposal. The waste will cause the damage of the environment (Harera, 2015). One of the environmental parameters associated with water pollution is the heavy metal.

In the last decade, determination of low levels of heavy metals in sea-water has received particular attention as a way to assess the early impact of human activities on the marine environment. The determination of trace elements in sea-water is difficult. Electrothermal Atomic Absorption Spectrometry (ETAAS) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) have been widely used for the determination of trace elements in different samples because the available data are highly precise and accurate; however, with se-water, the co-volatilization of matrix salts produce severe interference owing to intense background absorption signals. Also, ICP-AES methods sometimes suffer from problems with signal suppression and clogging of the sample introduction system when the sample contains dissolved solids at concentrations greater than 0.2 % m/v. further, ICP-AES methods are less sensitive than ETAAS. (Rudner, P.C et al, 1998)

The use of preconcentration step is one of the more effective ways of increasing sensitivity. One of these preconcentration methods used to measure the heavy metals in very small concentration is solid phase extraction. Solid Phase Extraction (SPE) is one of the concentrating techniques through the sorption (adsorption-desorption) process which is still being developed.



The previous research used solid phase extraction methods with resin and “ligating bracelets” as the supporting polymer material that can be used for copper ion analysis. But, the supporting polymer materials used in that research is expensive and limited.

A research based on natural products as a supporting polymer material for retention of heavy metals. One of can be an alternative to overcome the problem the natural products that can be used is cinnamon oil. *Cinnamomum vermicelli* (*Cinnamomum verum*) is derived from plants growing in different countries in Asia, such as Indonesia, West Sumatra. There are many benefits of cinnamon, such as immune system.

Cinnamon comes from Indonesia, which in trade is better known as cassia vera. Indonesian cinnamon is well known having a good smells. The main product of cinnamon is the outer skin of cinnamon used as a spice for food seasoning. In addition, the other products of cinnamon are powder, cinnamon essential oil and cinnamon oleo resin which is widely used in food beverage, pharmaceutical and cosmetics industry (Guenther, 1972). The chemical composition of with cassia, microscopically is similar. Sclerenchyma cells in the cassia are present in the outer shell, The inner sclerenchyma cells are thicker and the thickening is detected in the cassia skin. The outer skin cells of cork are smaller than the inner skin. The amount of starch particles on the skin of the two types of cinnamon is equal, but slightly larger in cassia.

The main components of cinnamon are cinnamaldehyde, eugenol and some aldehydes in relatively small percentage quantity. Essential oils can be obtained by steam distillation and water for 4 -5 hours. First, the material in distillation process is chopped making oil evaporation faster. The wet and dry materials has no effect to the oil component. The highest essential oil concentration is in the stem, but there is also in the root leaves, and flowers in small percentage. The chemical composition in the volatile oil of cassia Indonesia are cinnamaldehyde, cinnamyl acetate, salicylaldehyde, cinnamic acid, salicylic acid, ortho-methoxy, benzaldehyde (methyl salicylaldehyde), methyl-ortho-cinnamaldehyde (o-methoxy Cinnamaldehyde) and phenylpropyl acetate. The concentration of Indonesian cassia cinnamaldehyde is 80%-90%. This cinnamaldehyde is a yellow liquid, volatile, slightly soluble in water, soluble in alcohol and ether, insoluble in petroleum ether and has a molecular formula C_8H_7CHO with Mr. 132,15 (Guenther, 1987).

Cinnamaldehyde was isolated from cinnamon essential oil in 1834 by Dumas and Peligot and synthesized in the laboratory by the Italian chemist Luigi Chiozza in 1854. The natural product was trans-cinnamaldehyde. The cinnamaldehyde molecule consists of a benzene ring attached to an unsaturated aldehyde. Many synthesis methods are used in the laboratory, but the most efficient method is the distillation of cinnamon bark oil vapor. Cinnamaldehyde is a cinnamic derivative with is a major component of cinnamon oil. The chemical structure of cinnamaldehyde consists of a benzene substituted by a conjugated carbonyl system. Cinnamaldehyde can be isolated from cinnamon using sodium bisulfite solvent. Some of the benefits of the cinnamaldehyde is flavoring in chewing gum, ice cream, candy, and beverage drinks. Usage levels range from 9 to 4900 ppm. It is also used in some natural, sweet, or fruit fragrance cinnamaldehyde can be used as food seasoning, it can be marketed as cinnamon powder.

The cinnamaldehyde reacted with resorcinol will give C-Cinnamal Calix [4] Resorsinarena (CCCR). CCCR has twelve benzene residues, eight hydroxyl groups, and four alkenyl groups (double bonds).

C-Cinnamal Calix [4] Resorsinarena (CCCR) is a cyclic macromolecule compound contained aromatic group. The aromatic groups are connected to each other through a methylene bridge forming a cavity with an active group therein, this compound to be used as a host molecule for another guest, either anion, cation, or neutral compound. Based on the reaction mechanism, the CCCR synthesis reaction is an electrophilic substitution reaction (Handayani, 2014). The reaction between cinnamaldehyde and resorcinol produce C-Cinnamal Calix [4] Resorsinarena. CCCR has twelve benzene residues, eight hydroxyl groups, and four alkenyl groups (double bonds). The presence of electron pair in the hydroxyl group, as well as the presence of electrons in aromatic residues and double bonds is predicted to have special activity on heavy metal cations.

The synthesis of CCCR from cinamon oil can be used to retain heavy metal ions by solid phase extraction methods. The purpose of this study was to synthesize CCCR from cinnamaldehyde in cinnamon oil and characterize CCCR with FTIR, UV-VIS, RMI and Melting Point.

2. Experimental section

2.1. Materials and Equipments

The equipments used in this research are reflux set, buchner funnel, FTIR (Jasco 460 plus Spectroscopy), rotary evaporator (HeidolphLaborota 4000), Desiccator,Ultravioletspectroscopic Agilent 8453 UV-Vis. The materials are NaOH (merck), HNO₃ (merck), resorcinol (merck), cinnamaldehyde, HCl 5%, ethanol (merck), diethyl ether (merck), NaHSO₃ (merck), Ether (merck), Na₂SO₄ (merck), Sweetwood Oil (PT STS).

2.2. Research Procedures

2.2.1. Isolation of cinnamaldehyde from cinnamon oil. Isolation of cinnamaldehyde from cinnamon oil has done by adding saturated sodium bisulfite until there is no more precipitation. The precipitate does not increase. The precipitate was filtered and washed with ethanol 10 ml and diethyl ether 10 ml. Then, the precipitate was added HCl 5% 250 ml and refluxed at 60 ° C for 30 minutes. The mixture was twice extracted with ether and the extraction coating was combined and dried with anhydrous Na₂SO₄. After the filtration, the solution was evaporated by using a rotary evaporator and produced cinnamaldehyde

2.2.2. Characterization of Cinnamaldehyde. Further examination, the double bond of the isolated cinnamaldehyde was confirmed by UV-VIS Spectroscopy, the functional group was confirm by using FTIR, Isolated cinnamaldehyde the amont of hydrgen atoms used by RMI, was confirmed the boiling point used melting Point.

2.2.3. Synthesis of CCCR. The isolated cinnamaldehyde was mixed with a resistor with a ratio (1: 1) in ethanol 90% 50 ml and added of HCl 5 %. The solution was stirred and refluxed at 77 ° C for 2 hours. The precipitate was filtered and washed by using 10 ml ethanol and 10 ml of water and dried to obtain CCCR solids of 3.245 g.

2.2.4. CCCR Characterization. The double bonds in CCCR synthesis was confirmed by using UV-VIS spectroscopy, the functional groups was confirm by using FTIR, the number of hydrogen was confirm by using RMI and the melting point was conform Melting point.

3. Results and Discussion

3.1. The isolation of cinnamaldehyde from Cinnamon Oil

The cinnamaldehyde in the concentrated high cinnamon oil (51.6% - 56.0%) gives the easing isolation process take place quite easily. The isolation result was 8,234 g with 27,72% from 30 g of cinnamon oil rendemen.

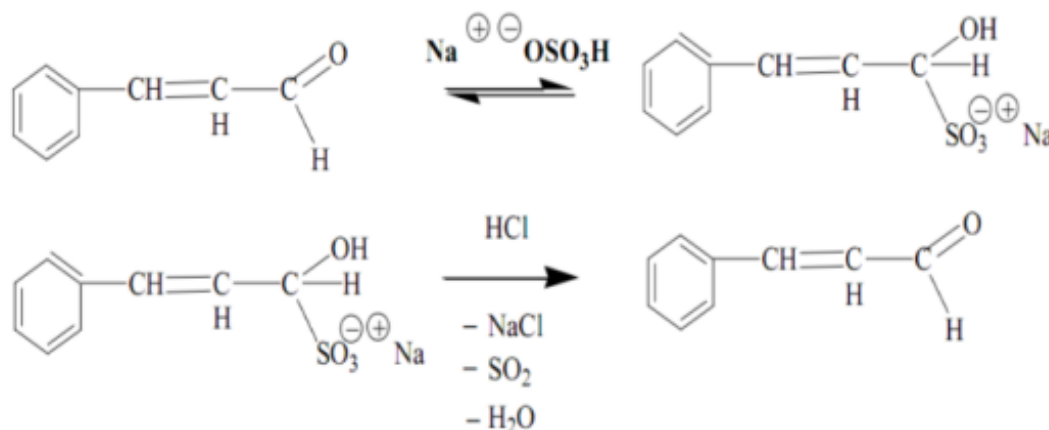


Figure 1. The reaction of cinnamaldehyde with sodium bisulfite (Ngadiwiyanana, et al, 2004).

In Figure 1, the cinnamaldehyde can be removed from cinnamon oil by addition of saturated sodium bisulfite. Bisulfite the product is a salts and the reaction is reversible so reaction, the aldehyde can be produced by the addition of acids (Anam, Khairul, 2004).

3.2. The Characterization of Isolated Cinnamaldehyde

The isolation of cinnamaldehyde from 30 g of cinnamon oil gives 8.234 g, 27.72 %. ^1H -NMR spectrum (400 MHz, acetone) δ 5.6 (1H, dd), 6.5-6.7 (1H, m), 7.0 (1H, d), 8.7 (1H, CHO, d).

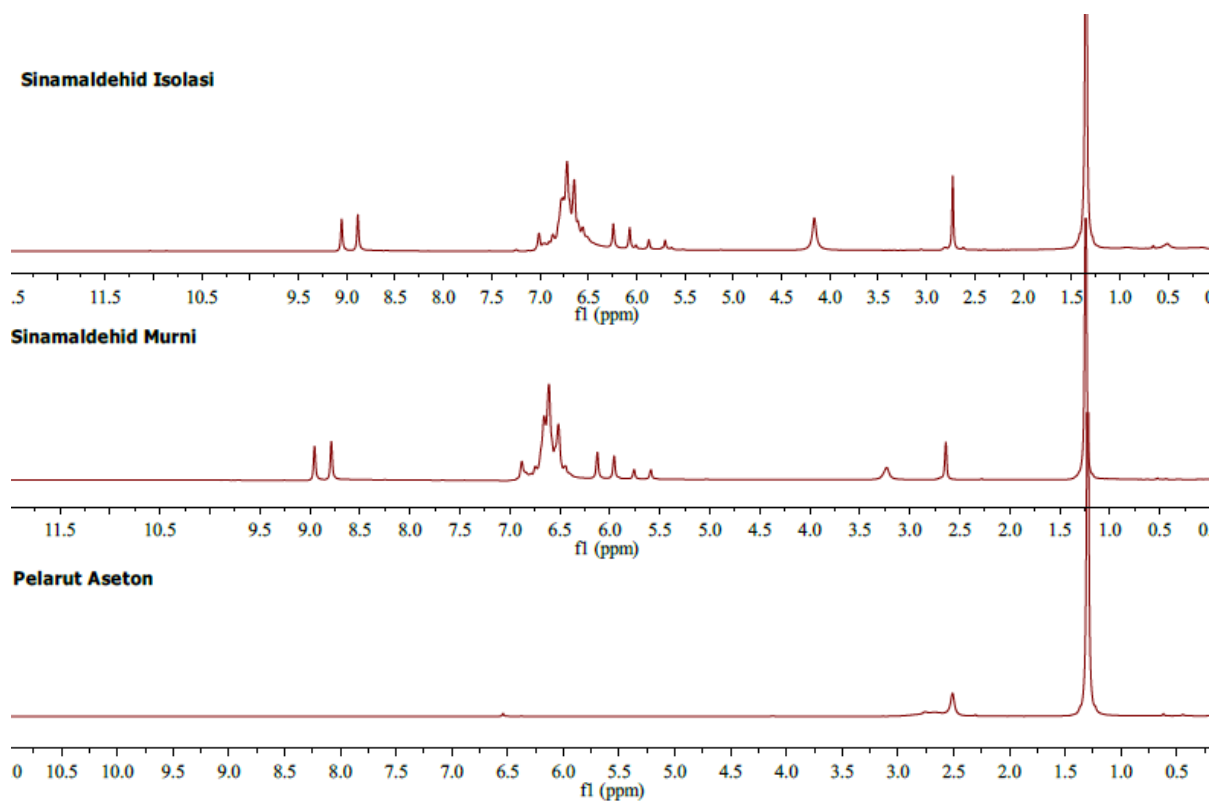


Figure 2. The ^1H NMR of Cinnamaldehyde from isolation, pure, and the NMR solvent

The cinnamaldehyde was characterized by FTIR. From the IR spectra in Figure 3 there is sharp peak at $1668,72\text{ cm}^{-1}$ wavelength indicating the presence of carbonyl uptake ($\text{C}=\text{O}$). These structurally carbonyl clusters are conjugated with double bonds. The wave number $2929,48\text{ cm}^{-1}$ refers to (CH_2). The wave number $3044,89\text{ cm}^{-1}$ refers to (C-H) and amplify the isolation result. The existence of an aromatic ring is indicated by the wave number $1450,60\text{ cm}^{-1}$. The presence of a bond ($\text{C}=\text{C}$) is indicated by data on the fingerprint region in absorption of wave number $689,09\text{ cm}^{-1}$ (Sastrohamidjojo, 1992). This result is the same as the pure cinnamaldehyde FTIR spectrum.

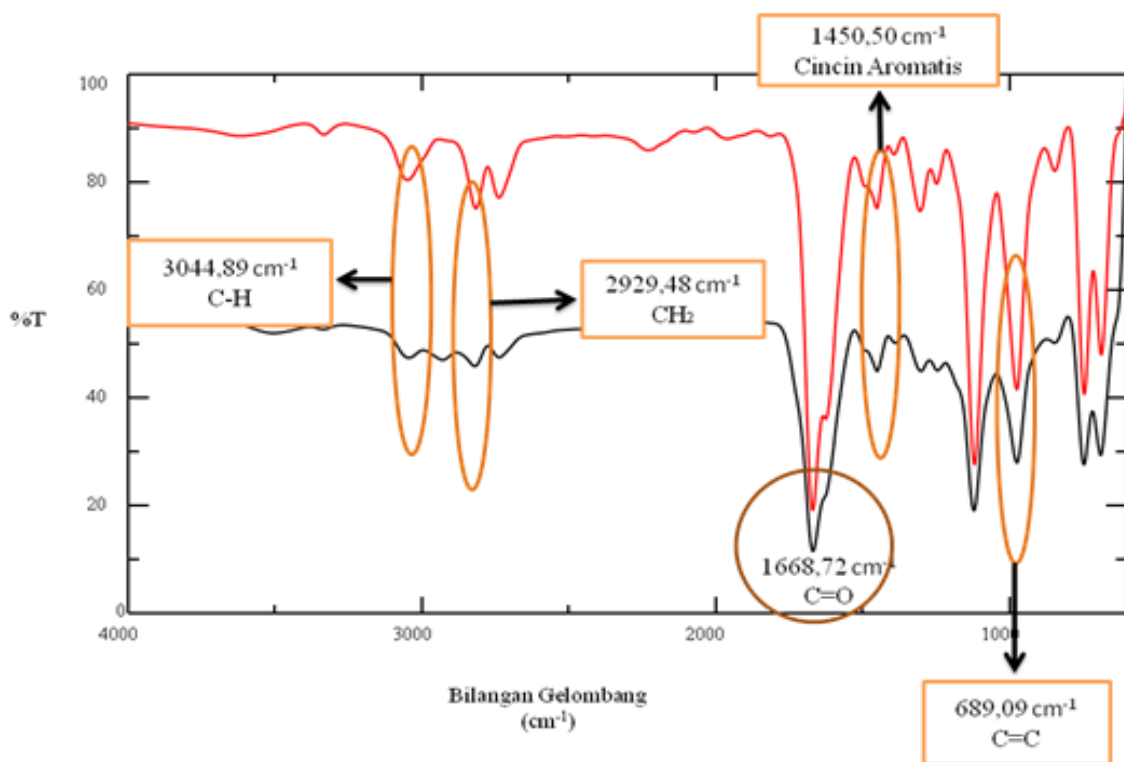


Figure 3. The IR Spectrum Cinnamaldehyde

In the other side, UV-VIS spectroscopy measurements of cinnamaldehyde were absorbed at 320 nm wavelengths with an absorbance of 1,72 indicating the presence of the conjugated double bond of the cinnamaldehyde compound shown in Fig 4. The results are similar to the UV-VIS cinnamaldehyde spectrum constructed from cinnamaldehyde pure.

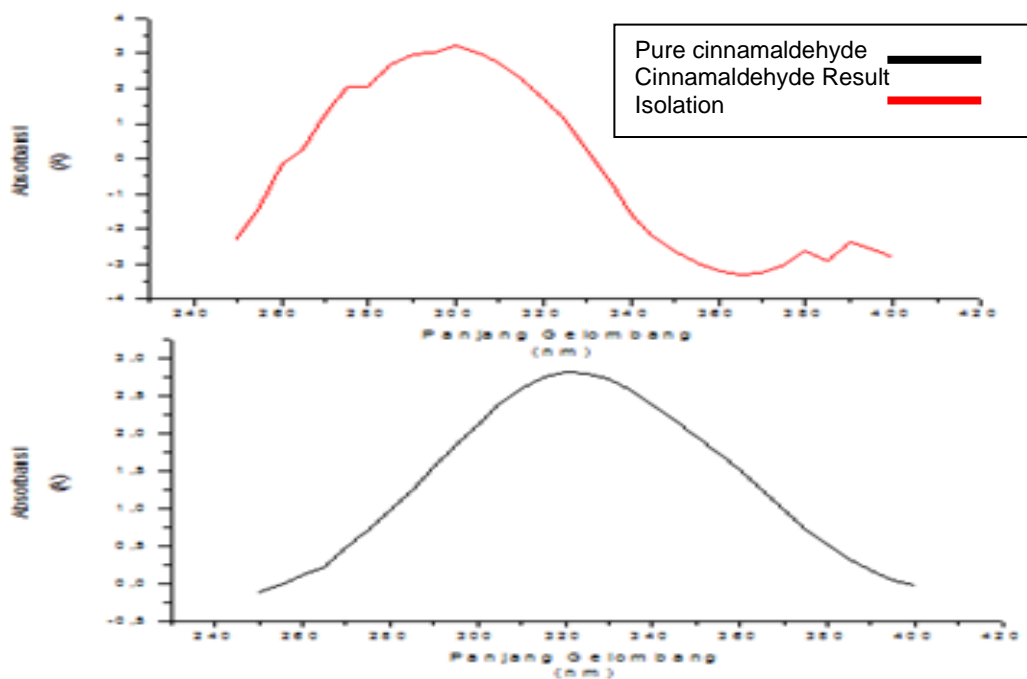


Figure 4. The UV-Vis Spectrum of cinnamaldehyde

3.3. The Synthesis of CCCR

The synthesis of CCCR is done by reacting cinnamaldehyde with resorcinol in the acidic atmosphere, (Figure 5). The synthesis of CCCR is prepared at temperature 77°C with in 2 hours.

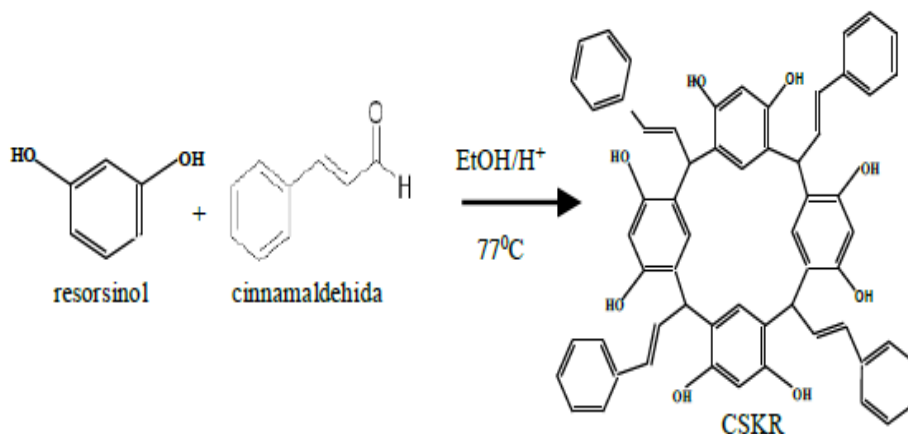


Figure 5. Synthesis of CCCR (Sardjono, 2008)

The synthesis product is directly removed from the reaction mixture as a reddish solid as much as 3.245 g. The CCCR synthesis results were characterized using FTIR, UV-VIS spectroscopy and melting Point.

3.4. The Characterization of CCCR

The synthesis of CCCR gives 3.245 g as a reddish solid. ^1H NMR spectrum (400 MHz, acetone and ethyl acetate) δ 0.7 (1H, d), 1.3 (1H, d), 2.5 (1H, s), 2.7 (1H, s), 6.6 (1H, OH).

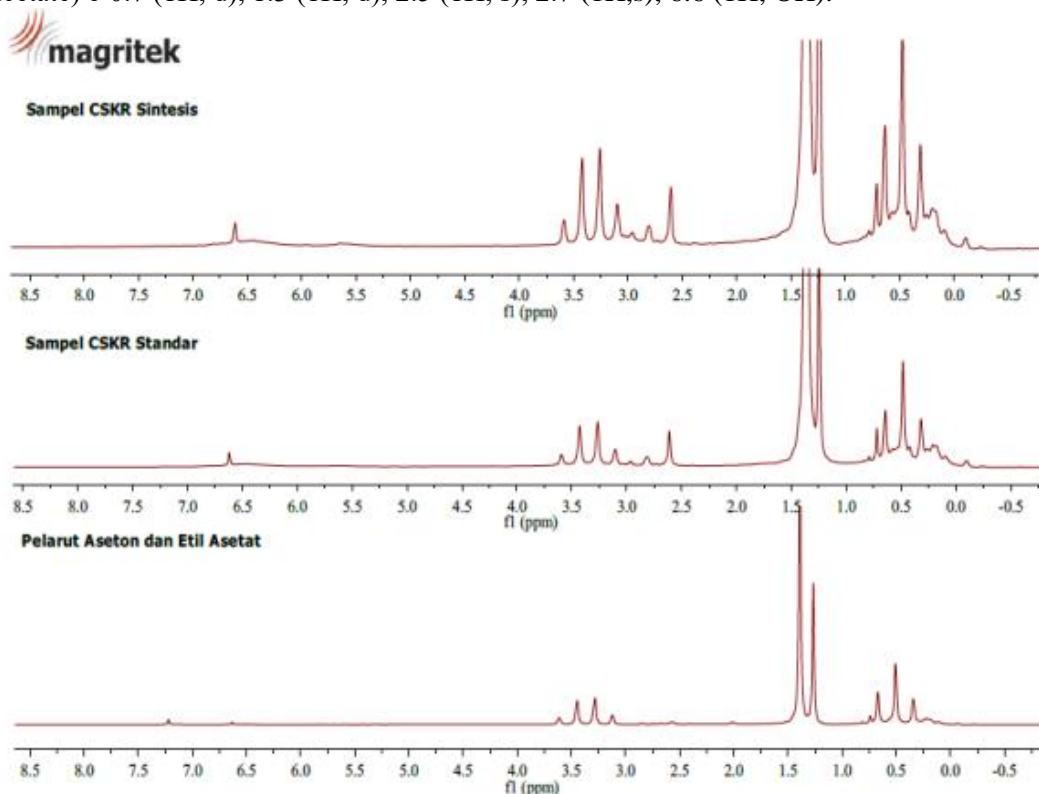


Figure 6. The ^1H NMR of synthesized CCCR, pure, and the NMR solvent

The characterization of CCCR with FTIR shows a wide and strong peak at 3323.94 cm^{-1} wavelength indicating O-H span of vibration. The wave number 1610.94 cm^{-1} shows the vibration of (C = C). A strong absorption area of 1500.86 cm^{-1} denotes the existence of an aromatic ring. Furthermore, the IR spectrum also features absorption bands derived from vibrations (CH_2) located on the fingerprint $695.52\text{ cm}^{-1} - 839.60\text{ cm}^{-1}$ (Sastrohamidjojo, 1992), as shown in Figure 5. Characterization of CCCR of pure of cinnamadehyde shows the same results as CCCR from the synthesis,

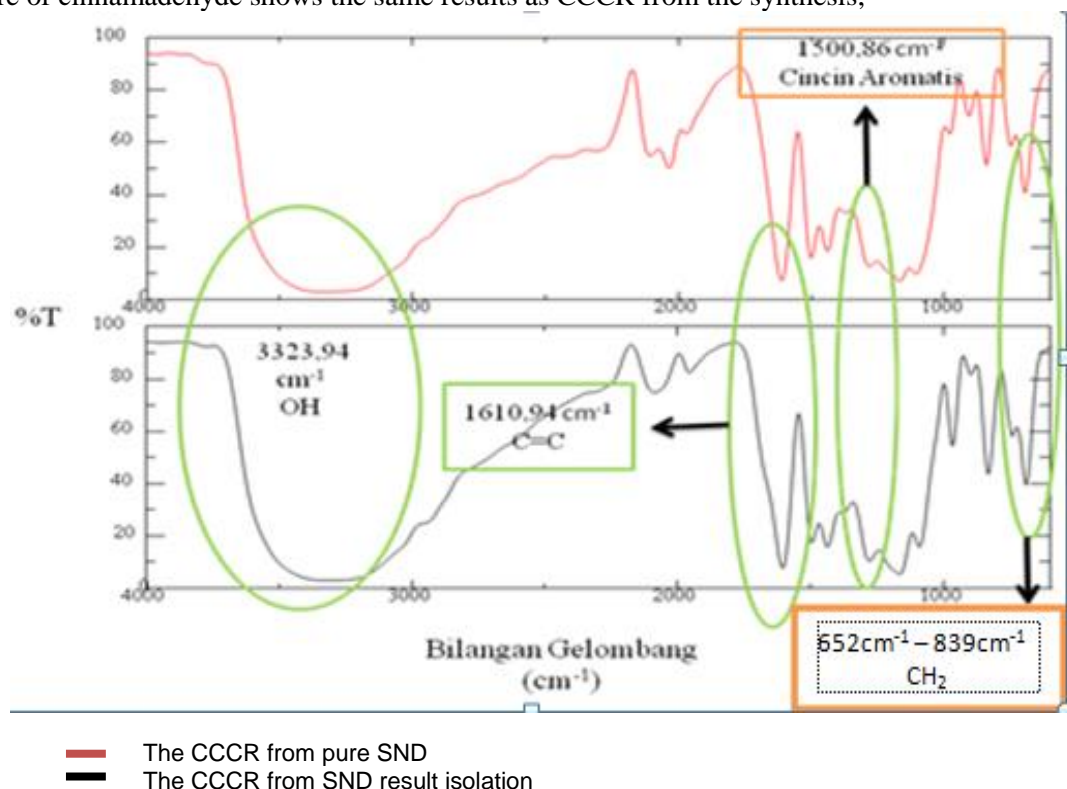


Figure 7. The Infrared Spectrum of CCCR

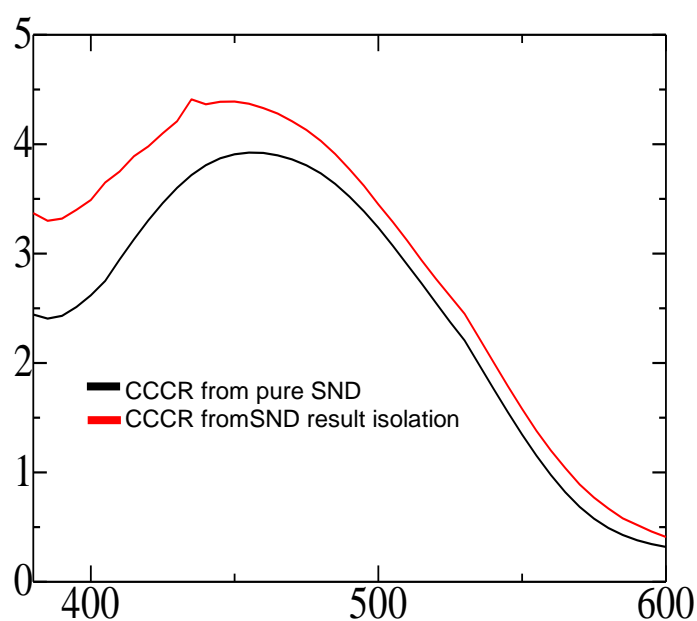


Figure.8. The Spectrum UV-VIS of CCCR

To support the result data of from cinnamaldehyde isolation, the melting point measurements were compared with the synthesis result from pure cinnamaldehyde. The synthesized CCCR melting point is 358 ° C and the melting point of CCCR of pure cinnamaldehyde is 359°C. In the other side, UV-VIS spectroscopy measurements of CCCR were absorbed at 440 nm wavelengths with an absorbance of 4.365 indicating the presence of the conjugated double bond of the CCCR compound shown in Figure 8. The results are similar to the UV-VIS CCCR spectrum constructed from cinnamaldehyde pure.

4. Conclusion

Based on the results of the synthesis and Characterization of C-CinnamalCalix [4]Resorsinarena from Cinnamon Oil, the conclusion are: 1. The isolation cinnamaldehyde produced as much (27,72%) 8,324 g from 30 g and 2. Synthesized CCCR produced as much as 3.245 g in the form of reddish solids

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