

SYNTHESIS OF BENZOYL C-PHENYLCALIX[4]RESORCINARYL OCTAACETATE AND CINNAMOYL C-PHENYLCALIX[4]ARENE FOR UV ABSORBERS

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Received November 8, 2013; Accepted May 28, 2014

ABSTRACT

A new upper rim-functionalized benzoyl C-phenylcalix[4]resorcinaryl octaacetate and cinnamoyl C-phenylcalix[4]resorcinarene have been synthesized and evaluated as the absorbers for ultraviolet radiation. The benzoyl C-phenylcalix[4]resorcinaryl octaacetate was synthesized in 3 steps. They were synthesis of C-phenylcalix[4]resorcinarene via acid-catalyzed-condensation of resorcinol and benzaldehyde, followed by O-acetylation and Friedel-Craft benzoylation. The cinnamoyl C-phenylcalix[4]resorcinarene was synthesized in 4 steps. They were synthesis of C-phenylcalix[4]resorcinarene via acid-catalyzed-condensation of resorcinol and benzaldehyde, followed by O-acetylation, Friedel-Craft cinnamoylation and hydrolysis. Spectroscopic analysis (UV) showed that the target molecule absorbed the ultraviolet radiation between 200 and 400 nm with the maximum absorption at 240.50 nm ($\epsilon = 10.135 M^{-1} cm^{-1}$) and 243.50 nm ($\epsilon = 12.135 M^{-1} cm^{-1}$).

Keywords: synthesis; benzoyl; absorbers; ultraviolet

ABSTRAK

Senyawa benzoil C-fenil kaliks[4]resorsinaril oktaasetat dan sinamoil C-fenilkaliks[4]arena telah berhasil disintesis, serta dievaluasi kemampuannya sebagai penyerap radiasi sinar ultraviolet. Senyawa benzoil C-fenilkaliks[4]resorsinaril disintesis dalam tiga langkah reaksi yaitu; sintesis C-fenilkaliks[4]resorsinarene melalui kondensasi antara resorsinol dan benzaldehid, diikuti oleh O-asetilasi dan benzoilasi Friedel-Craft. Sinamoil C-fenilkaliks[4]resorsinarene disintesis dalam empat langkah reaksi yaitu; sintesis C-fenilkaliks[4]resorsinarene melalui kondensasi antara resorsinol dan benzaldehid, diikuti oleh O-asetilasi sinamoilasi Friedel-Craft dan hidrolisis. Analisis spektroskopi menunjukkan bahwa kedua senyawa target menyerap radiasi ultraviolet diantara 200 nm sampai 400 nm, dengan serapan maksimum masing-masing pada 240,50 nm dengan absorptifitas molar ($\epsilon = 10.135 M^{-1} cm^{-1}$) dan 243,50 nm ($\epsilon = 12.135 M^{-1} cm^{-1}$).

Kata Kunci: sintesis; benzoil; sinamoil; penyerap; ultraviolet

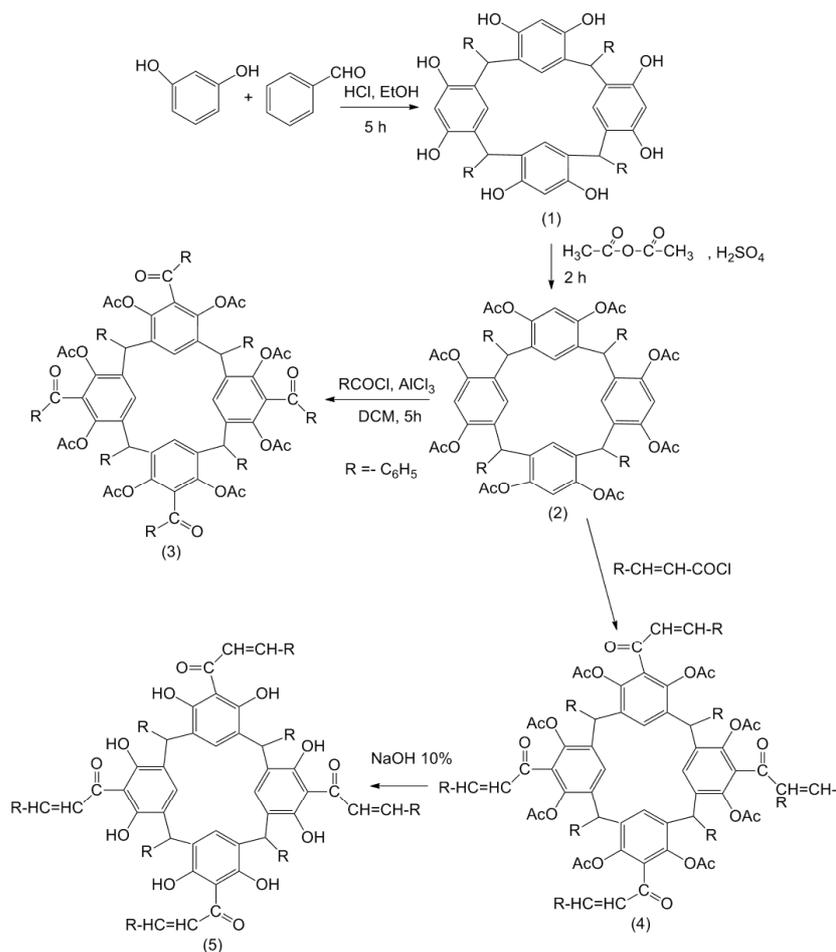
INTRODUCTION

Solar radiation in the spectral range between 290 and 400 nm is regarded as potentially dangerous for human skin, where the harmful effects strongly increase with smaller wavelength or higher energy of radiation. Primarily sunscreens are expected to protect against sunburn, also called UV erythema [1]. The purpose of UV filters used in cosmetic sunscreen formulations is to attenuate the UV radiation of the sun by absorption of UV radiation. Organic UV absorbers are transferred to an excited electronic state from which the energy may dissipate after internal conversion into molecular

vibrations and further into heat via collisions with surrounding molecules.

Research and development on sunscreen have recently gained more attention as one million people are suffered by skin cancer and 10.000 of them die because of malignant melanoma. Skin cancer particularly occurs on the area of body which is frequently exposed to the solar radiation, such as face, neck, head and back of the hand [2]. The harmful effects of the radiation are predominantly due to ultraviolet (UV) B (λ , 290-320 nm). However, several studies indicated that UV A (λ , 320-400 nm) could also lead the skin damage [3]. With the thinning of the ozone

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Scheme 1. Synthesis of benzoyl C-phenylcalix[4]resorcinaryl octaacetate and cinnamoyl C-phenylcalix[4]resorcinarene

layer, increased level of UV C radiation-related adverse heat effects such as sunburn and skin cancer [4]. UV C possesses the highest energy and has the greatest potential for biological damage such as skin cancer [5-6]. We can also encounter UV C from artificial source such as lamp and welding equipment [7].

Structurally, sunscreen possesses double bond functional group conjugated with carbonyl group (C=O) and aromatic ring [8]. One recent class organic compound which displays activity as sunscreen is calix[4]resorcinarene.

Calix[4]resorcinarene is cyclic tetramers, and classified to the class of [1₄] metacyclophanes. These compounds are synthesized by acid-catalyzed cyclocondensation of resorcinol with various aliphatic or aromatic aldehyde [9-11]. The ease for the synthesis access of calix[4]resorcinarene could give its various applications but the application as a sunscreen very limited. Sukwattanasinitt et al. [12] have reported photoswitchable calix[4]arene incorporating different regioisomers of stilbena and azobenzene. It has been

observed that the stilbena bridged derivative isomerized only under UV irradiation while azobenzene derivatives undergo thermal or photochemically induced isomerization [12].

In this study, in order to afford structural requirements for organic sunscreen, the unique properties of calix[4]resorcinarene framework and benzoyl, sinamoyl group would be combined to give benzoyl and cinnamoylcalix[4]resorcinarene (the benzophenone derivative). The benzophenone derivative has been reported and widely applied as potential sunscreen [7].

The synthesized compound was expected to have functions as sunscreen and as carrier to encapsulate the established sunscreen [13]. The photo-protection afforded by topical sunscreens against UV radiation exposure can be determined by *in vivo* or *in vitro* assays. The synthesized calix[4]resorcinarene would be *in vitro* characterized by measuring the absorption of UV radiation into the compound. The route of molecule target synthesis as scheme 1. There are four

new compound produced in this research i.e. C-phenylcalix[4]resorcinaryl octaacetate (**2**), benzoyl C-phenylcalix[4]resorcinaryl octaacetate (**3**), cinnamoyl C-phenylcalix[4]resorcinaryl octaacetate (**4**) and cinnamoyl C-phenylcalix[4]resorcinarene (**5**). The compound **1** it doesn't new compound, it has been synthesized by Tunstad et al. [11].

EXPERIMENTAL SECTION

Materials

All reagents used were dichloromethane, acetic anhydride, resorcinol, benzaldehyde, benzoyl chloride, aluminum chloride anhydrous, sodium sulfate anhydrous, sulfuric acid, hydrochloric acid, dichloromethane and ethanol 96%. The reagents were commercially obtained from E. Merck with P.A. grade and directly used without any further purification.

Instrumentation

Structure elucidation of the synthesized compounds was performed using $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ (Agilent 400), as well as FT-IR (Shimadzu, Prestige 21) spectrophotometers. Characterization of benzoyl calix[4]resorcinarene as sunscreen was conducted using Lambda 35 UV/Vis spectrometer (Perkin Elmer Inc. USA) with 10 mm quart.

Procedure

Synthesis of C-phenylcalix[4]resorcinarene

C-phenyl calix[4]resorcinarene **1** was synthesized based on the method described in literatures [6-7]. The C-phenylcalix[4]resorcinarene was obtained as a yellow solid. Yield 84.17%, melting point $>390\text{ }^\circ\text{C}$, IR (KBr pellet) wave number in cm^{-1} : 3387 (-OH), 1500 and 1600 (Ar-C=C) and 1427 (C-Hbridge), H-NMR (DMSO) δ in ppm from TMS: 5 (H-bridge), 6.1, 6.25, 6.65, 7.0 (Ar-H) and 8.2 (H of Ar-OH), m/z 792.

Synthesis of C-phenylcalix[4]resorcinaryl octaacetate

Into 100 mL round bottomed flask, compound **1** (0.79 g, 0.001 mol), acetic anhydride (12 mL, 0.127 mol) and two drops of sulfuric acid was than added. The mixture was heated for 2 h at $60\text{ }^\circ\text{C}$. The solution was cooled and crushed ice was added. The product was collected as yellow solid and washed by water. The C-phenylcalix[4]resorcinaryl octaacetate was obtained as a yellow solid. Yield 90.03%, melting point $285\text{-}288\text{ }^\circ\text{C}$, IR (KBr pellet) wave number in cm^{-1} : 1750 (C=O ester), 1500 and 1600 (Ar-C=C) and 1489 (C-H bridge), H-NMR (DMSO) δ in ppm from TMS: 5.4 (H-bridge), 1.6 (H-CH₃, acetyl group), 6.1, 6.8, 7.1 and 7.25 (Ar-H).

Synthesis of benzoyl C-phenylcalix[4]resorcinyl octaacetate

Into 100 mL round bottomed flask compound **2** (0.816 g, 0.001 mol) and benzoyl chloride (2.248 g, 0.016 mol) were dissolved in 50 mL CH_2Cl_2 . The solution was cooled to $10\text{-}20\text{ }^\circ\text{C}$ and AlCl_3 (2.60 g, 0.0192 mol) was then added in five portion for 2 h. Reaction mixture was refluxed for 5 h. The content of round bottomed flask was poured into a mixture of 10 g of crushed ice and 1 mL concentrated hydrochloric acid. The product was extracted from the solution by CH_2Cl_2 (3x50 mL). Organic layer was collected, washed with water (3x50 mL) and dried with anhydrous Na_2SO_4 . The dichloromethane was removed by rotary vacuum evaporator and the yellow solid was collected. The benzoyl C-phenylcalix[4]resorcinaryl octaacetate was obtained as a yellow solid. Yield 90.67%, melting point $325\text{-}327\text{ }^\circ\text{C}$, IR (KBr pellet) wave number in cm^{-1} : 1750 (C=O ester), 1689 (C=O benzoyl), 1500 and 1600 (Ar-C=C), H-NMR (DMSO) δ in ppm from TMS: 5.4 (H-bridge), 1.6 (H-CH₃, acetyl group), 6.0, 6.8, 7.1 and 7.25 (Ar-H), 7.5 and 8.2 (H-benzoyl), $^{13}\text{C-NMR}$ (DMSO) δ in ppm from TMS: 20 (C-methyl), 116, 126, 130, 140, 146 and 168 (Ar-C). 272 nm (λ_{max}) and $10.135\text{ M}^{-1}\text{ cm}^{-1}$ (ϵ).

Synthesis of cinnamoyl C-phenylcalix[4]resorcinyl octaacetate

Cinnamoyl chloride (2.686 g, 0.016 mol) were dissolved in 50 mL CH_2Cl_2 , poured in to 100 mL round bottomed flask consisted compound **2** (0.816 g, 0.001 mol). The solution was cooled to $10\text{-}20\text{ }^\circ\text{C}$ and AlCl_3 (2.60 g, 0.0192 mol) was then added in five portion for 2 h. Reaction mixture was refluxed for 5 h. The content of round bottomed flask was poured into a mixture of 10 g of crushed ice and 1 mL concentrated hydrochloric acid. The product was extracted from the solution by CH_2Cl_2 (3x50 mL). Organic layer was collected, washed with water (3x50 mL) and dried with anhydrous Na_2SO_4 . The dichloromethane was removed by rotary vacuum evaporator and the yellow solid was collected. The cinnamoyl C-phenylcalix[4]resorcinaryl octaacetate was obtained as a yellow solid. Yield 89.0%, melting point $275\text{-}278\text{ }^\circ\text{C}$, IR (KBr pellet) wave number in cm^{-1} : 1766 (C=O ester), 1643.35 (C=O cinnamoyl), 1500 and 1600 (Ar-C=C), H-NMR (DMSO) δ in ppm from TMS: 5.4 (H-bridge), 1.6 (H-CH₃, acetyl group), 6.1, 6.9, and 7.0 (Ar-H), 7.5 and 7.8 (H-cinnamoyl).

Synthesis of cinnamoyl C-phenylcalix[4]resorcin arene

Cinnamoyl C-phenylcalix[4]resorcinarene (**5**) synthesized by hydrolyzed compound **4** with NaOH 10% for 3 h (mol ratio 1:100) at $65\text{ }^\circ\text{C}$. The product was

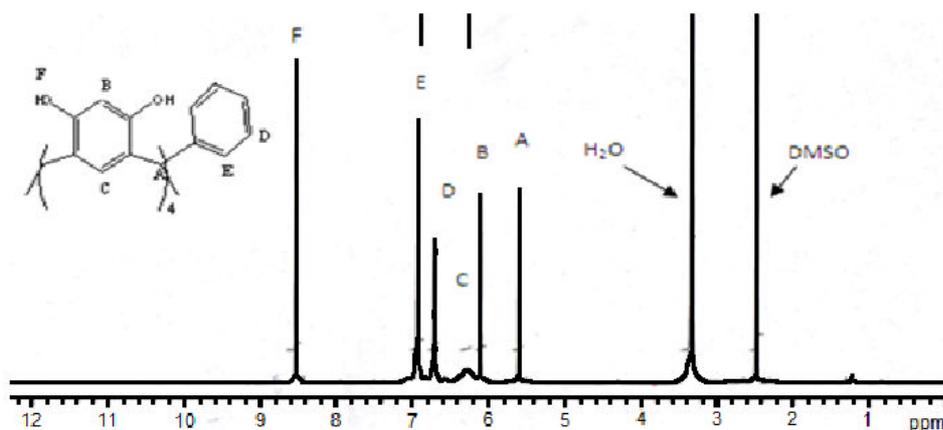


Fig 1. $^1\text{H-NMR}$ of C-phenylcalix[4]resorcinarene

characterized by IR and $^1\text{H-NMR}$. The cinnamoyl C-phenylcalix[4]resorcinarene was obtained as a orange solid. Yield 61.60%, melting point $>390^\circ\text{C}$, IR (KBr pellet) wave number in cm^{-1} : 1689 (C=O cinnamoyl), 1500 and 1600 (Ar-C=C), 3440 (-OH) and 1427 (H-bridge), H-NMR (DMSO) δ in ppm from TMS: 3.8 (H-bridge), 4.4, 6.5, and 7.4 (Ar-H), 7.5 and 7.9 (H-cinnamoyl).

Ultraviolet Analysis

Maximum wavelength (λ_{max}) and molar absorption (ϵ) were determined as follows: two solution of **3** and **5** in the concentration 10^{-3} , 0.25×10^{-3} , 0.5×10^{-3} , 0.75×10^{-3} and 10^{-4} M were prepared in dichloromethane. Their absorbance (A) was recorded at respective peak wavelengths (λ_{max}) using quartz curvetts of 1 cm path length. A plot of A versus molar concentration at λ_{max} was prepared and ϵ was obtained from the slope of straight line. The absorption spectra of samples in solution were obtained in the range of 200 to 400 nm using 1 cm quartz cell, and dichloromethane as a blank. The maximum wave length and molar absorption of **3**: 240.50 nm (λ_{max}) and $10.135 \text{ M}^{-1} \text{ cm}^{-1}$ (ϵ). The maximum wave length and molar absorption of **5**: 243.50 nm ($\epsilon = 12.135 \text{ M}^{-1} \text{ cm}^{-1}$). The UV spectrum of benzoyl C-phenylcalix[4]resorcinarene octaacetate and cinnamoyl C-phenylcalix[4] arene as displayed in Fig. 7 and 8.

RESULT AND DISCUSSION

The parent C-phenylcalix[4]resorcinarene **1** was synthesized via acid catalyzed-condensation and cyclization of resorcinol and benzaldehyde. Acetylation catalyzed by sulfuric acid of **1** produced acyl-protected-calix[4]resorcinarene **2**. Friedel-Craft benzoylation of **2** was conducted using benzoyl chloride/ AlCl_3 to give benzoyl C-phenylcalix[4]resorcinarene octaacetate **3** (Scheme 1). The yield of every step of the reactions i.e.; 84.17% (**1**); 90.03% (**2**) and 90.67% (**3**). The yield of

compound **4** is 89.04% and the yield of compound **5** is 61.60%.

Synthesis of C-Phenylcalix[4]resorcinarene

The synthesized C-phenylcalix[4]resorcinarene was characterized by IR, $^1\text{H-NMR}$ and mass spectrometers. The IR spectrum showed strong absorptions at 3387 and 1427 cm^{-1} indicated the presence of the hydroxyl and C-H bridge of calix[4]resorcinarene, respectively.

As shown in $^1\text{H-NMR}$ spectrum (Fig. 1), the peak at 5 ppm could be considered as the H-bridge. The aromatic proton gave four singlets at 6.1, 6.25, 6.65 and 7.0 ppm. The appearance of peak at 8.2 ppm could be ascribed to the hydroxyl proton. $^1\text{H-NMR}$ spectrum of **1** was similar to the literature 7.

The MS spectrum of **1** showed the appearance of a molecular peak at m/z 792 [M^+] which indicated the molecular mass of C-phenyl calyx[4]resorcinarene. The high melting point of **1** which was $> 390^\circ\text{C}$ caused by hydrogen bonding in the compound.

Synthesis of C-phenylcalix[4]resorcinarene Octaacetate

Acetylation of **1** was the protection of phenolic group from the Friedel-Craft benzoylation on the next step. The acetylation product gave IR absorptions at 1750 and 1489 cm^{-1} describing the carbonyl ester and C-H bridge, respectively. As displayed in $^1\text{H-NMR}$ spectrum (Fig. 2), the peak at 5.4 ppm described the H-bridge. The aromatic proton appeared as four signals; at 6.1, 6.8, 7.1 and 7.25 ppm. The disappearance of peak at 8.2 ppm showed that hydroxyl protons were replaced by acetyl group.

The proton integration was not good enough, it is caused by the complexity of calix[4]resorcinarene molecule. The chemical shift of the target molecule is not

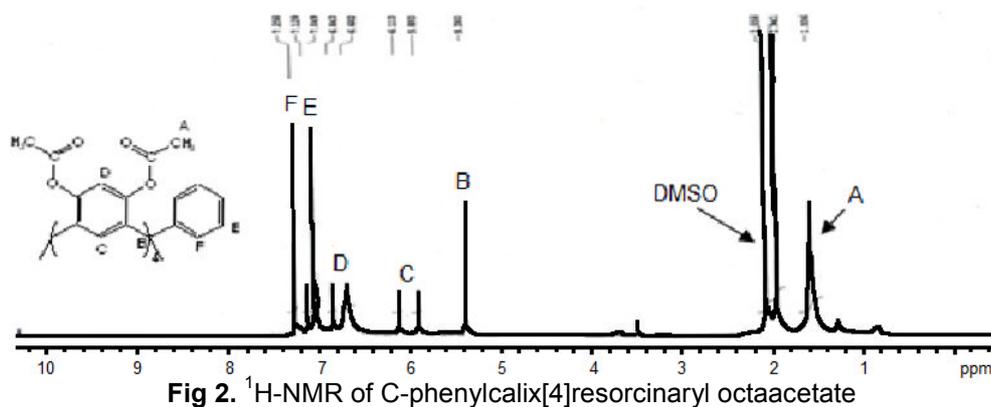


Fig 2. $^1\text{H-NMR}$ of C-phenylcalix[4]resorcinyl octaacetate

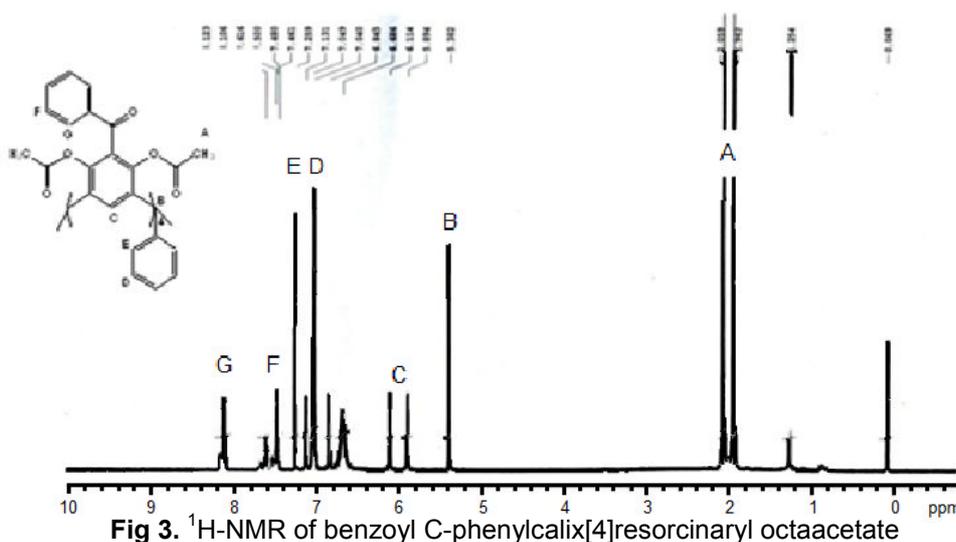


Fig 3. $^1\text{H-NMR}$ of benzoyl C-phenylcalix[4]resorcinyl octaacetate

too different with the theoretical chemical shift (A, 2.0; B, 5.34; C, 6.25; D, 7.0; E, 7.3 and F, 7.41 ppm).

The melting point of **2** was 285-288 °C. The lower melting point (comparing to the reactant) indicated that the reaction has taken place due to the disappearance of hydrogen bonds between the phenolic groups.

Synthesis of Benzoyl C-phenylcalix[4]resorcinyl Octaacetate

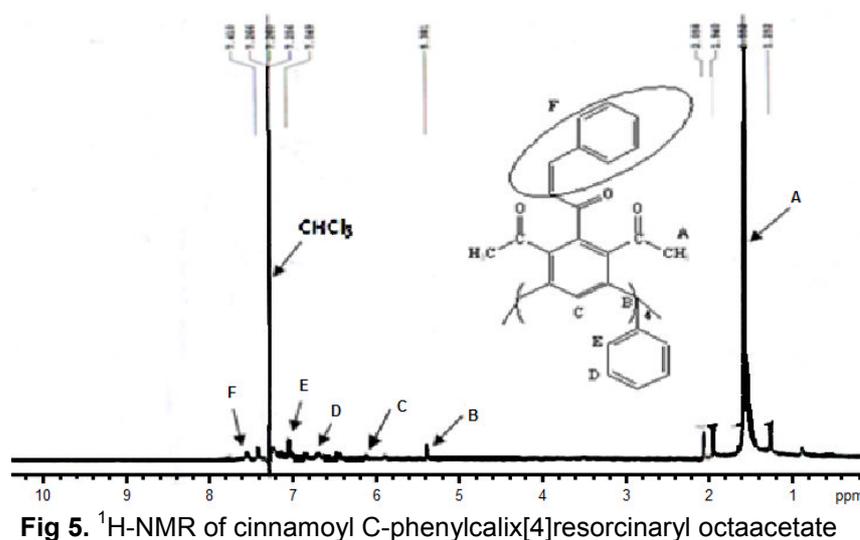
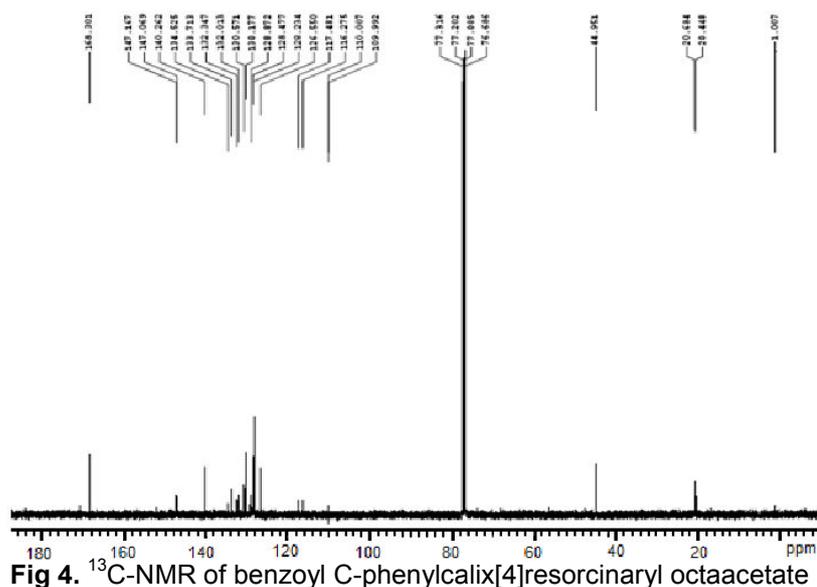
Having protected the phenolic groups of C-phenylcalix[4]resorcinarene, the Friedel-Craft benzoylation was then conducted. FT-IR spectrum of the benzoylation product showed strong absorption at 1750 cm^{-1} (C=O ester) and weak at 1689 cm^{-1} (C=O benzoyl). Two carbonyl (C=O) peaks showed that benzoylation has been conducted.

As presented in $^1\text{H-NMR}$ spectrum (Fig. 3), the peak at 5.4 ppm could be considered to be the H-bridge. The aromatic proton appeared as six signals; at 6.0, 6.8, 7.1, 7.25, 7.5 and 8.2 ppm. The appearance of the new aromatic proton at 7.5 and 8.2 ppm was represented by the benzoyl protons.

The $^{13}\text{C-NMR}$ data (Fig. 4) also showed that benzoylation has been conducted. The peak at 76 ppm could be considered to be the C-bridge. The methyl carbon appeared at 20 ppm. The aromatic carbon appeared as six signals; at 116, 126, 130, 140, 146 and 168 ppm.

Synthesis of Cinnamoyl C-phenylcalix[4]resorcinyl Octaacetate

The FT-IR spectrum of the cinnamoylation product showed strong absorption at 1766 cm^{-1} (C=O ester) and medium 1643.35 (C=O benzoyl). Two carbonyl (C=O) peaks showed that cinnamoylation has been conducted. As presented in $^1\text{H-NMR}$ spectrum (Fig. 5), the peak at 5.4 ppm could be considered to be the H-bridge. The aromatic proton appeared as six signals; at 6.1, 6.9, 7.0, 7.4, 7.5 and 7.8 ppm. The new aromatic proton at the chemical 7.4, 7.5 and 7.8 ppm were represented by the cinnamoyl protons. The low signal of the protons may be caused by the low solubility of the compound in dimethyl sulfoxide (DMSO).



Synthesis of Cinnamoyl C-phenylcalix[4]resorcin arene

Hydrolyzed cinnamoyl C-phenylcalix[4]resorcinaryl octaacetate is conducted at 65 °C for 2 h. The FT-IR spectrum showed strong absorption at 1689 cm^{-1} ($\text{C}=\text{O}$ cinnamoyl). Disappear of carbonyl ($\text{C}=\text{O}$) ester indicated that hydrolysis of cinnamoyl C-phenylcalix[4]resorcinaryl octaacetate has been conducted. As presented in ^1H -NMR spectrum (Fig. 5), the peak at 3.8 ppm could be considered to be the H-bridge.

The cinnamoyl proton appeared at 7.5 ppm to 7.9 ppm. The signals were similar to the cinnamoyl protons in literature [13], because cinnamoyl group of the compound **5** was also bonded at the aromatic ring of the calix[4]arene. The aromatic proton appeared as three signals; at 4.4, 6.5, and 7.4 ppm. The proton

signals of cinnamoyl C-phenylcalix[4]resorcinaryl octaacetate and cinnamoyl C-phenylcalix[4]resorcin arene were not strong enough so that the ^{13}C -NMR identification was not be conducted.

The UV analysis of the synthesized benzoyl C-phenylcalix[4]resorcinaryl octaacetate and cinnamoyl C-phenylcalix[4]resorcinarene were conducted in the region from 200 to 400 nm. It were obtained that the two dominant wavelength of **3** are 240.50 nm (λ_{max}) and 275.50 nm ($\epsilon = 10.135 \text{ M}^{-1} \text{ cm}^{-1}$) and could be classified as UV C region. The cinnamoyl C-phenylcalix[4]resorcinarene was also has two dominant wavelength, 243.50 (λ_{max}) and 274.50 nm ($\epsilon = 12.135 \text{ M}^{-1} \text{ cm}^{-1}$). The UV spectrum of benzoyl C-phenylcalix[4]resorcinaryl octaacetate and cinnamoyl C-phenylcalix[4]resorcinarene as displayed in Fig. 7 and 8.

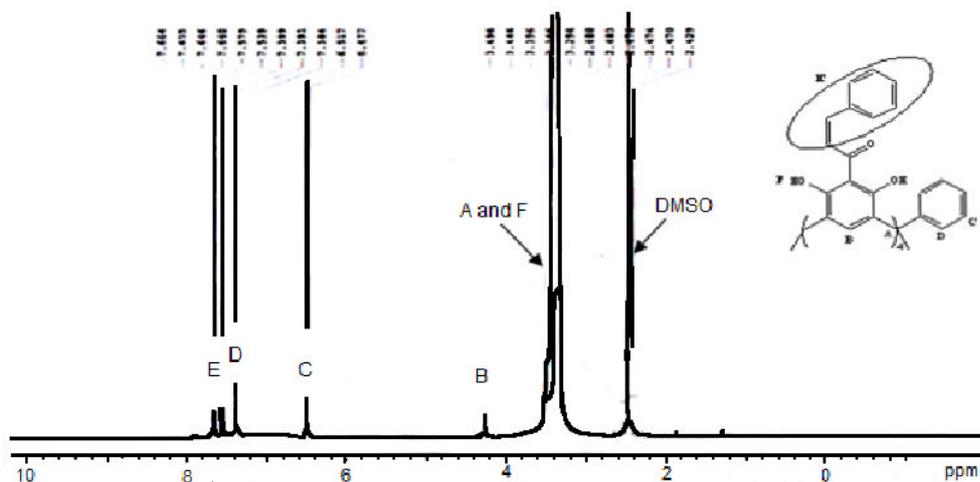


Fig 6. $^1\text{H-NMR}$ of cinnamoyl C-phenylcalix[4]resorcinarene

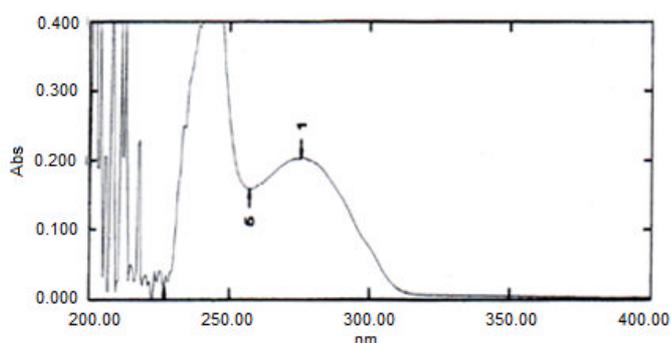


Fig 7. The UV spectrum of benzoyl C-phenylcalix[4]resorcinaryl octaacetate

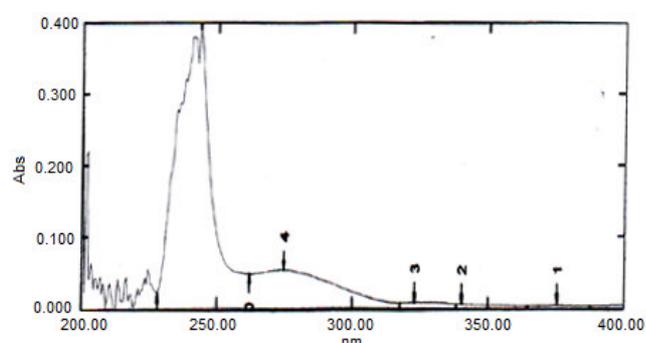


Fig 8. The UV spectrum of cinnamoyl C-phenylcalix[4]resorcinarene

The UV spectrum of the target compounds showed that, the benzoyl C-phenylcalix[4]resorcinaryl octaacetate and cinnamoyl C-phenylcalix[4]resorcinarene could absorb UV C light well. The compounds were also absorbed UV B, but not as strong as in UV C region.

UV C possesses the highest energy and has the greatest potential for skin damage. Rapid increasing of the non-melanoma skin cancer phenomena may be not only caused by UV A and UV B but also by UV C. Because recently, it has been observed that the ambient level of harmful ultraviolet (UV) rays emitted by the sun is increasing due to ozone layer depletion. Deeply research is needed to use benzoyl C-phenylcalix[4]resorcinaryl octaacetate and cinnamoyl C-phenylcalix[4]resorcinarene as an active component of the sunscreen product, to protect skin from the UV C exposure.

CONCLUSION

Benzoyl C-phenylcalix[4]resorcinaryl octaacetate and cinnamoyl C-phenylcalix[4]resorcinarene could be synthesized in a good yield and displayed good

absorption maxima at UV C region 240.50 nm ($\epsilon = 10.135 \text{ M}^{-1} \text{ cm}^{-1}$) and 243.50 nm ($\epsilon = 12.135 \text{ M}^{-1} \text{ cm}^{-1}$).

ACKNOWLEDGEMENT

The authors gratefully acknowledged the financial support received from the Universitas Gadjah Mada by Postgraduate Research Program with the contract number: LPPM-UGM/1441/LIT/2013 June 18th 2013.

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