Synthesis and characterization of dialkanolamides from castor oil (Ricinus communis) as nonionic surfactant

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Abstract. Nonionic surfactant of dialkanolamide derivates was synthesized and characterized from castor oil (Ricinus communis). Ricinoleic acid was isolated from castor oil by hydrolysis in alkaline (KOH) condition at 65 °C. Oxidation of ricinoleic acid by dilute potassium permanganate (KMnO4) in alkaline condition at 75-90 °C gave dicarboxylic acid which was then reacted with ethanolamine at 140-160 °C for 6 hours. The product was recrystallized with isopropanol, and the structure elucidation was performed by FTIR, 1HNMR spectrometer, and GC-MS with silylation method. Characterization of surfactants was carried out by surface tension measurement (capillary rise method), Critical Micelle Concentration (CMC) based on turbidity method and calculation of Hydrophilic-Lipophilic Balance (HLB) value with Griffin method and Bancroft rule. The result showed that ricinoleic acid in castor oil is 86.19 % and it is oxidation give an azelaic acid and octanedioic acid in 53.25 %. Amidation of a dicarboxylic acid and ethanolamine at 140-160 °C for 6 hours yielded of N1,N9-bis(2-hydroxyethyl)nonadiamide in 49.35 %. Surfactant characterization indicates that dialkanolamide derivates can be used as a surfactant due to its ability to reduce the surface tension of ethanol with CMC at 1.2 g/L, HLB value is 5.58 and can be used as emulsifier water in oil (W/O).

1. Introduction
Surfactants are being used in a broad variety of applications, among in the household cleaning, agricultural crop protection, cosmetics, pharmacy, remediation, petroleum additive, enhanced oil recovery [1], food additive and processing [2]. Based on a 2016 Acmitie Market Intelligence report [3], the global market of surfactants reached at approximately US$30.65 billion in 2015. Increasing by 4.4% annually, the market is expected to reach US$39.69 billion by 2021. So far, the most surfactant made from edible oil or petroleum. The production of surfactant from edible oils has increased seriously affect on food security. Several non-edible oils such as jatropha [4], castor, thumba oil and sal fat [5] were reported for surfactant preparation. One of the non-edible oil that is abundant in Indonesia is castor oil. The largest fatty acid composition of castor oil is ricinoleic acid, which is approximately 87-90% of the...
total fatty acids [6]. Ricinoleic acid is an 18-carbons unsaturated fatty acid which having an hydroxyl group on the 12th carbon atom. The hydroxy group and the double bond are easily oxidized to yield a broad range of products depend on the type of oxidant and reaction conditions. By condensing the fatty acids, methyl esters, or triglycerides with some alkanolamines produced alkanolamides [7]. These compounds are commonly used as biosurfactants or biolubricants, rush inhibitors, ink formulation, in the pharmaceutical industry and anti-inflammatory [8].

The chemical properties of alkanolamide derivatives vary greatly, depending on the length of the hydrocarbon chain and the substituent properties in the nitrogen atom [9]. Alkanolamides have a large function, especially as a stable emulsifier, due to the amide bond are not easy to decompose in an acidic condition [10] and easy to biodegrade [11]. Fatty alkanolamides can be synthesized from alkanolamines with fatty acids, fatty acid esters, and fatty acyl halide [11-12]. By breaking the double bond on the ricinoleic acid with cleavage oxidation produced a dicarboxylic acid. The dicarboxylic acid (azelaic acid) is a compound of nine carbon atoms with two carboxylate groups at both ends. Amidation of the azelaic acid produced dialkanolamide compound (N1, N9-bis (2-hydroxyethyl) nonadiamide) (Scheme 1). In addition, the products were characterized by Fourier transform infrared spectroscopy (FTIR), GCMS and H1NMR.

![Scheme 1. Synthesis of the nonionic surfactant from castor oil](image)

2. Experimental Section

2.1. General

Castor oil was purchased from Brataco and N, O-bis (trimethylsilyl) trifluoroacetamide (BSTFA) from Aldrich Chemical Co. Potassium hydroxide, potassium permanganate, ethanol, petroleum ether, diethyl ether, isopropanol, ethanolamine, acetonitrile, sulfuric acid, and sodium sulfate anhydrous were purchased from Merck with an analytical grade and were used without further purification. The synthesis products were identified by infrared spectrophotometer (FTIR, Shimadzu-8201PC), spectrometers Nuclear Magnetic Resonance Proton (1H NMR, JEOL JNM-ECA 500, 500 MHz, CDCl3, TMS) and Gas Chromatography (GC Hawlet Packard-5890), Gas Chromatography - Mass Spectrophotometer (GCMS, Shimadzu QP-5000, and Shimadzu QP-2010). GC analysis of ricinoleic acid methyl esters was
carried out using HP-5 column, 30 m x 0.025 mm id. The samples for GCMS analysis were prepared by using BSTFA as silylation agent and injected to Rtx-5MS column, 30 m x 0.025 mm id, 40 mL/min of flow rate and 60 kPa of inlet pressure. Silylation process: 200 μL sample (0.3 g in 0.6 mL acetonitrile) and 100 μL BSTFA was heated at 60-65 °C for 60 min.

2.2. Procedure

2.2.1. Hydrolysis of Castor Oil
Castor oil (14 g, 14 mmol) was introduced into KOH solution (11 g, 196 mmol) in 40 mL of ethanol and were refluxed for four h. The mixture was poured into an ice cube and acidified with sulfuric acid solution (20%/v/v) under stirring until pH 2. The ricinoleic acid was produced by separated them from aqueous layer with diethyl ether. The extract was dried over anhydrous sodium sulfate, and the solvent was evaporated under vacuum to give yellow liquid of ricinoleic acid with 82.48% of yield. νmax : 3348 (-OH, str.), 3008 (-H) and 1712 (C=O acid, str.) cm⁻¹. The GC chromatogram as its ester form showed 4 peaks with the highest at tR 8.3 minutes (86.19%).

2.2.2. Cleavage Oxidation
The mixture of fatty acid hydrolyzed from castor oil (12 g, 40 mmol) was dissolved in 90 mL potassium hydroxide solution (3.5 g). With a strong stirring, 316 g (200 mmol) potassium permanganate dissolved in 350 mL of distilled water and the salt of fatty acid mixture solution was added carefully at 75 °C for 30 minutes until permanganate color was disappeared. The mixture was amounted to 3 M sulfuric acid solution, and heated at 90 °C for 15 min to form a brown precipitate and filtered in a hot condition. The filtrate was cooled in an ice bath until a precipitate is formed and recrystallized with hot water. The solid white product was 4.07 g with m.p 104.2-108 °C. νmax : 2939 and 2854 (-H, str.), 1697 (C=O carboxylic acid, str.) and 1411 (-CH 2-, deformation) cm -1. The GC chromatogram as its ester form showed 2 peaks dominant at tR 12.77 (35.7%; m/z 110, 97, 69, 55 and 41(base peak) ) and 14.08 minutes (45.91%; m/z 152, 124, 111, 83, 60, 55 (base peak) and 41).

2.2.3. Dialkanolamide synthesis
The oxidation product (2.85 g) and ethanolamine (2.88 g, 45 mmol) were heated for 6 hours at 160 °C. The formed product was dissolved in 50 mL of isopropanol and cooled in an ice bath to yield solid N1, N9-bis(2-hydroxyethyl)nonadiamide (2.05 g) with m.p. 119 ºC. νmax: 3266 (-O-H, str.), 2916 (-C-H, str.), 2855 (-C-H, str.), 11643 (C=O amide, str.), 1558 (N-H, bend) and 1049 (-C-N) cm⁻¹. The GC chromatogram (reverse phase) with silylation shows 1 peak (100% abundance) at tR = 20.8 min. Mass spectrum (EI) : m/z 403, 375, 35, 286, 196, 172, 166, 101, 73 (base peak), 44, and 41. 8H (500 MHz, CDCl3) 1.21 (6H, s, -CH2-), 1.44 (4H, t, -CH2-), 2.03 (4H, t, -CH2-), 3.08 (4H, m, -CH2-), 3.36 (4H, m, -CH2-), 7.78 (2H, s, NH).

2.2.4. Surfactant Characterization Test
Critical Micelle Concentration (CMC) was evaluated by using Lamotte 2020 Portable Turbidity Meter with AMCO as a standard and surface tension by capillary rise method according to Cabral [13]. The HLB (Hydrophilic-Lipophilic Balance) value is calculated using the equations proposed by Davies-Rideal with the Bancroft rule [14]:

\[
\text{HLB} = 7 + \Sigma H + \Sigma L
\]

With, Σ H = Amount of x hydrophilic group values, Σ L = Amount of x hydrophobic group value

3. Result and Discussion
The synthesis of dialkanolamide derivates from castor oil consisted of several steps. First, castor oil was hydrolysis to obtain its fatty acids. Second, the mixture of fatty acids which most consisted by ricinoleic acid (86,19%) was strongly oxidized to break down the alkene bonds and to produce its corresponding acid groups. The final steps, the oxidation products were reacted with ethanolamine to give N1, N9-bis(2-
hydroxyethyl)nonadiamide. The aim of this research was to produce some nonionic surfactant from castor oil and characterized its physicochemical properties.

Saponification of castor oil was accomplished in ethanol as a solvent and acidified to produce a yellowish liquid of fatty acids with 82.48% of conversion. Elucidation of the product was done by FTIR and GC analysis. The infrared spectrum showed the appearance of a broad peak at 3348 cm\(^{-1}\) as a stretching of O-H group and shifting of carbonyl bond to 1712 cm\(^{-1}\). GC chromatogram showed four dominant peaks with the highest abundance was a ricinoleic acid with 86.19% at 8.3 min of retention time.

The oxidation of fatty acid with concentrated potassium permanganate at 75-90 °C is performed to cleavage the double bond on the ricinoleic acid to its dicarboxylic form. This reaction is carried out under an alkaline condition and with high stirring so that the ricinoleic acid can be mixed well into water layer. The infrared spectra exhibited the appearing absorbance of the carbonyl group of carboxylic acids at 1697 cm\(^{-1}\). The absence of alkene absorption at 3008 and 725 cm\(^{-1}\) indicated that ricinoleic acid was successfully broken down to produce azelaic acid (nonadioic acid). The GC chromatogram showed that the oxidation product was given two dominant peaks at retention time 12.77 and 14.08 min respectively were octanedioic (36%) and azelaic acid (46%) with a total yield of 53.25%.

Alkanolamides can be synthesized from carboxylic acid derivatives with hydroxylamine. The synthesis dialkanolamides carried out by heating ethanolamine and oxidation products with a molar ratio 3:1 at 140-160 °C for 6 hours. Recrystallization with isopropanol resulted in white solids with 119 °C of m.p. The appearance of peaks at 1049, 1558 and 3266 cm\(^{-1}\) were respectively characterized as C-N, N-H, and N-H/O-H bonds of alkanolamides. The shifting of carbonyl peak from 1697 to 1643 cm\(^{-1}\) indicated that amides group was presented with the product. Those data confirmed with MS of the silylated product gave a fragment at m/z 403 occurred when molecular ion (m/z 562) released two trimethylsilyls and a methyl radical. This fragment furthermore released two methyl radicals into m/z 375, which is further fragmented resulting in m/z 196, 44, and 41. The McLafferty rearrangement of molecular ion produced fragments with m/z 315, 286, 172, 166, 101, and 73. The purity of product confirmed by appearing only one dominant peak on GC chromatogram at 20.8 min of retention time. The GC chromatogram showed that recrystallization with isopropanol eliminated impurities from the product. \(^1\)H-NMR spectrum confirmed the single product with the appearance protons with a chemical shift at 7.78 ppm as two hydrogen atoms of secondary amides. Multiplet signals at 3.08-3.36 ppm.
equivalent to eight protons from the methine group of ethanolamides. Moreover, fourteen methine protons from long chain fatty acid appeared at 1.21-2.03 ppm. Based on the elucidation structure with FTIR, GCMS, and NMR, it can be concluded that reaction between oxidation products of castor oil fatty acid and ethanolamine than recrystallized with isopropanol produced \(N_1,N_9\)-bis(2-hydroxyethyl)nonadiamide with the percentage of yield was 49.35\%.

Surfactant characterization was evaluated by using capillary rise method and turbidimetry to determine surface tension and CMC, respectively. The surface tension of ethanol was decreased in the greater addition concentration of \(N_1,N_9\)-bis(2-hydroxyethyl)nonadiamide. It has the same results with ricinoleic acid and tween 80 (Fig 1.). At a concentration of 0.5 g/L, \(N_1,N_9\)-bis(2-hydroxyethyl)nonadiamide was able to provide a greater decrease in surface tension than ricinoleic acid and tween 80, but when the concentration increased to 1 g/L and 1.5 g/L, tween 80 gave a better result than others.

The CMC value was determined by measuring the average turbidity of the sample at various concentration. The value of CMC was evaluated where the addition concentration of the sample dramatically change the turbidity gradient (Fig. 2). The critical micelles concentration of \(N_1,N_9\)-bis(2-hydroxyethyl)nonadiamide formed at a concentration of 1.2 g/L, whereas tween 80 will form CMC at a concentration of 1.1 g/L. In the other hand, ricinoleic acid can not be a good surfactant at a concentration of 0.5 - 2 g/L due to no critical micelles concentration in the solution.

HLB (Hydrophilic-Lipophilic Balance) is a value that describes the power of hydrophilicity or lipophilicity in some substances. In this empirical method, the surfactant is rated by using a number based on its solubility in water. The HLB value for a compound is fixed under all reaction conditions, so in this study, the determination of HLB was performed using the Griffin method with Bancroft rule. The calculation results obtained HLB value of \(N_1\), \(N_9\)-bis(2-hydroxyethyl)nonadiamide, tween 80, and ricinoleic acid were 5.58, 3.45 and 2.93, respectively. Theoretically, the range of HLB values 3-4 is a non-dispersed type of surfactant in water, whereas the range of HLB 4-6 values can be utilized as emulsifiers for water emulsions in oil (emulsifier W/O) [15].

4. Conclusion
\(N_1\), \(N_9\)-bis(2-hydroxyethyl)nonadiamide can be prepared from castor oil with several steps such as hydrolysis, cleavage oxidation with concentrated potassium permanganate and amidation with ethanolamine. Based on elucidation analyses as described above, it was concluded that all compounds were successfully synthesized. Surfactant characterization showed that \(N_1\), \(N_9\)-bis(2-hydroxyethyl) nonadiamide could be used as an emulsifier for water emulsion in oil (W/O).

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