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Prenylation of Xanthone Extract from Mangosteen (*Garcinia mangostana* L.) Rind by Using Superbase Catalyst of γ-Alumina/NaOH/Na and Antioxidant Activity Test

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Interest has been shown in the xanthone compounds from waste of fruit processing of mangosteen (*Garcinia mangostana* L.) because of their interesting pharmacological activities. In an effort to develop novel antioxidant agent, the prenylation reaction of xanthone-rich mangosteen have been tried and studied by using super base catalyst. The heterogeneous superbase catalyst γ-Al_2O_3/NaOH/Na was prepared using industrial waste of aluminium scrap and was analyzed using XRD. This catalyst was then applied under mild condition. The identification of the new prenylated xanthone-rich mangosteen were established by IR, UV and LC-MS techniques. The result showed, pericarp of mangosteen contained four xanthone derivatives and the LC-MS data of the products reaction showed a molecular ion at *m/z* 478.425 and the present results suggested that xanthone derivative *i.e.*, α-mangosteen linking a new prenyl group. The prenylated products enhanced their antioxidant activity.

Keywords: Xanthone, Prenylation, *Garcinia mangostana* L., Superbase catalyst.

INTRODUCTION

One of the metabolite plants family that is fascinating to be researched is compound with prenyl structure (3-methylbut-2-en-1-yl), because it has antitumor and anticancer bioactivity[1-4]. Indonesia has rich biodiversity, mangosteen for example in this research, which specifically has xanthone structure framework. This metabolite compound is found within mangosteen rind (*Garcinia mangostana* L.) which is a prenyl-xanthone compound. This compound is fascinating to be synthesized using heterogenic catalyst of Na/NaOH/ γ-alumina super base. Super base catalyst consists of alkali metal and its hydroxide which is supported by γ-alumina, with general formula; MOHx/My/γ-Al_2O_3. One of the super base catalysts is Na/NaOH/ γ-Al_2O_3 with base level more[3] than 37. This research is aimed to study binding model of 3,3-dimethylalyl bromide compound on xanthone compound which was extracted from mangosteen (*Garcinia mangostana*) rind using superbase catalyst of γ-Al_2O_3/NaOH/Na, followed by researching bioactivity as antioxidant compound using radical scavenging activity method.

EXPERIMENTAL

Ingredients used within this research were mangosteen rind (*Garcinia mangostana* L.), methanol, ethanol, *n*-hexane, ethyl acetate, silica gel, γ-Al_2O_3, Na, NaOH, prenyl bromide, acetone and DPPH.

Extraction of xanthone compound from mangosteen rind: Mangosteen rind was chopped and then dried by sun rays. The dry-pericarp-skin was pureed by blender and then sifted. 1000 g of mangosteen pericarp skin powder, which has been dried and pureed. Later, it was immersed in 2 L of methanol and left for 7 days while stirred occasionally. This composition was filtered with gauze and separated from its residue. The methanol extract was concentrated and kept in vial bottle at ± 40 °C.

Partial isolation of xanthone compound from mangosteen rind extract: 10 g of crude mangosteen rind extract was fractionated with column chromatography by eluent *n*-hexane: ethyl acetate with gradient system (polarity increase). Each 10 mL fractions was stored and then grouped based one similarity of colour solution. KLT analysis later was conducted to each fraction. Fraction dot visualization from KLT result was conducted by UV lamp with 254 and 366 nm wavelengths.

Making of superbase catalyst γ-Al_2O_3/NaOH/Na: 10 g of calcinized γ-Al_2O_3 was heated while stirred at 400 °C within nitrogen atmosphere. After 2 h heated, 1.75 g of NaOH was added at the same temperature while stirred using stirrer until NaOH melt and evenly stirred. The stirring process was continued for 20 min to produce white solid. 0.5 g of sodium (metal) later was added into the composition and then continued by 1 h stirring at the same temperature to produce dark-blackish solid which faded into grey.

Prenylation reaction between isolate xanthone with superbase catalyst: 0.25 g of isolate xanthone was diluted within 45 mL acetone and then stirred at 28 °C. 0.40 g of prenyl bromide and 0.34 of γ-Al_2O_3/NaOH/Na superbase catalyst were later added and stirred for 2 h. This composition was filtered until filtrate was obtained. This filtrate was later removed from its solvent and diluted again into ethyl acetate. Its residue was then diluted again with methanol. This ethyl acetate and methanol fractions were later steamed and stored at 4 °C. Xanthone compound from prenylation product was being measured by FT-IR, UV-visible spectroscopy and LC-MS.

RESULTS AND DISCUSSION

Yellowish mass can be obtained from extraction product of mangosteen rind, in which yellow crystal can be obtained in partial purification.

From prenylation reaction result towards xanthone component of mangosteen rind using superbase catalyst of γ-Al_2O_3/NaOH/Na, two fractions from separation result were obtained. The separation used silica-gel with two kinds of solvents (ethyl acetate and methanol) as shown in Fig. 1.

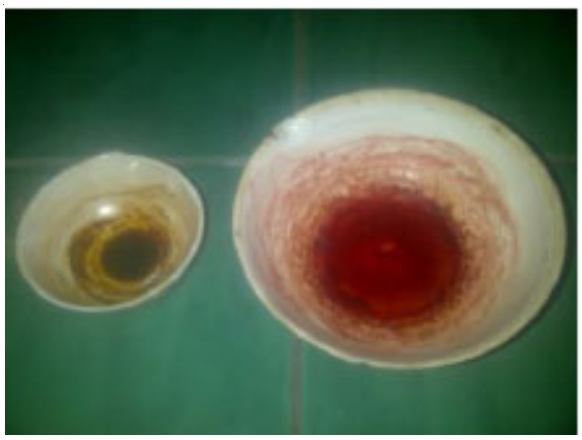

Fig. 1. Prenylation product from xanthone in ethyl acetate and methanol solubility

It can be noted from the IR analysis that the three xanthone samples still showed existence of hydroxide cluster. However, prenylation result from methanol fraction and isolate xanthone showed different IR spectrum; no peak on 1722.46 cm^{-1} wavelength in IR spectrum from prenylation result of methanol fraction. Absence of the wavelength indicated that there was no C=O cluster. Therefore, possibility of xanthone compound, either in form of isolate xanthone or prenylation result, was not found within methanol fraction. Spectrum band around 3200 cm^{-1} wavelength showed dilation (addition of -OH bound). Therefore, it was believed that prenyl cluster didn't distribute H atom on -OH xanthone cluster.

From the UV spectrum (Fig. 2), there was shift towards direction of longer wavelength. Therefore, there was red shift (bathochromic). Isolate xanthone peak was found in 221 nm wavelength with 3.252 absorbance. On the other hand, prenylation result peak from ethyl acetate fraction was found in 229 nm wavelength with 3.931 absorbance level. Wavelength shift (8 nm) was suspected due to additional C=C which came from dimethylalyl cluster after prenylation result.

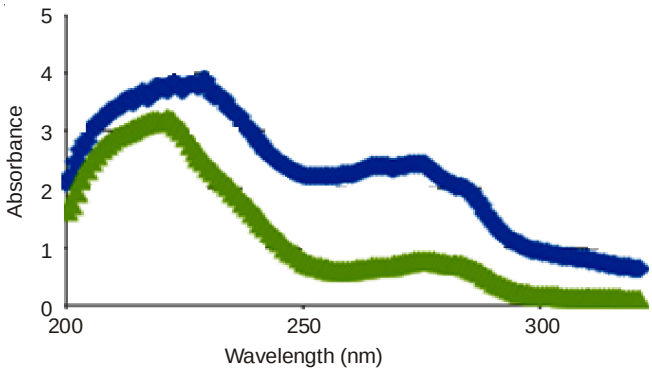

Fig. 2. UV-visible spectrum of isolatedxanthone (■) and prenylated xanthone (■)

Mass spectrum (MS) analysis of xanthone component from mangosteen rind and prenylation reaction from xanthone component in shown in Fig. 3. From the MS data, three components of derivate xanthone were identified. There were quad-

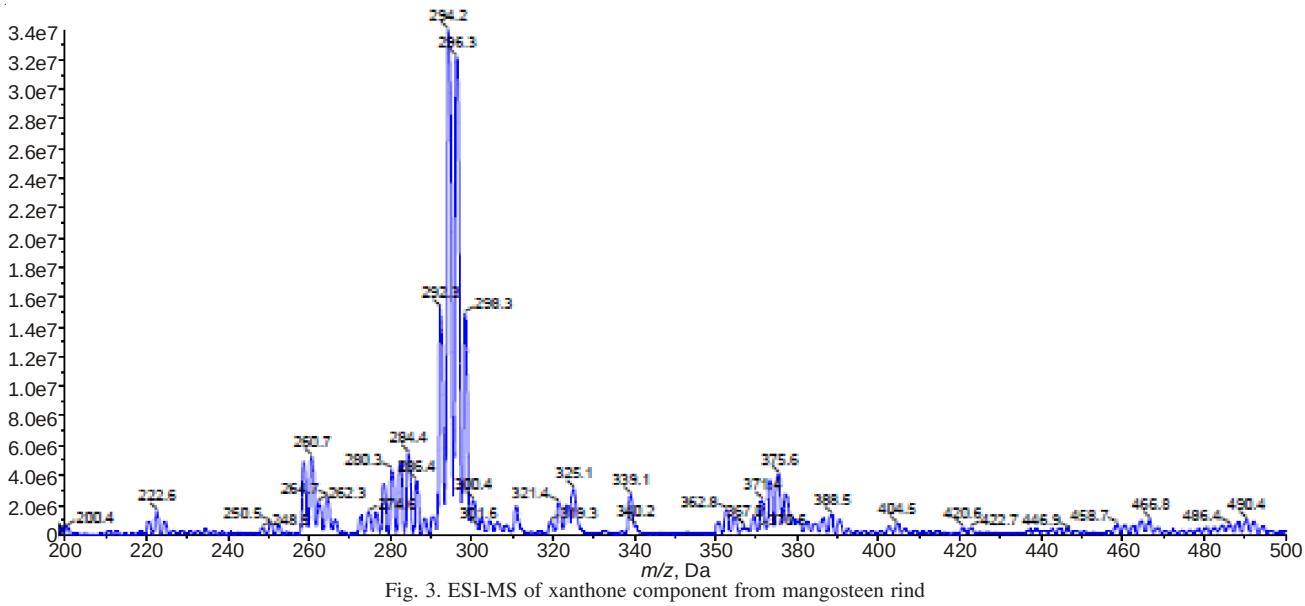

Fig. 3. ESI-MS of xanthone component from mangosteen rind

TABLE-1
ANTIOXIDANT ACTIVITY OF XANTHONE EXTRACT AND PRENYLATION RESULT

Fraction	Scavenging activity (%)				IC_{50} (ppm)
	1 (ppm)	1 (ppm)	5 (ppm)	10 (ppm)	
Isolated xanthone	17.590	26.235	38.885	65.120	7.185
Prenylated xanthone	16.715	26.380	65.335	87.115	4.890

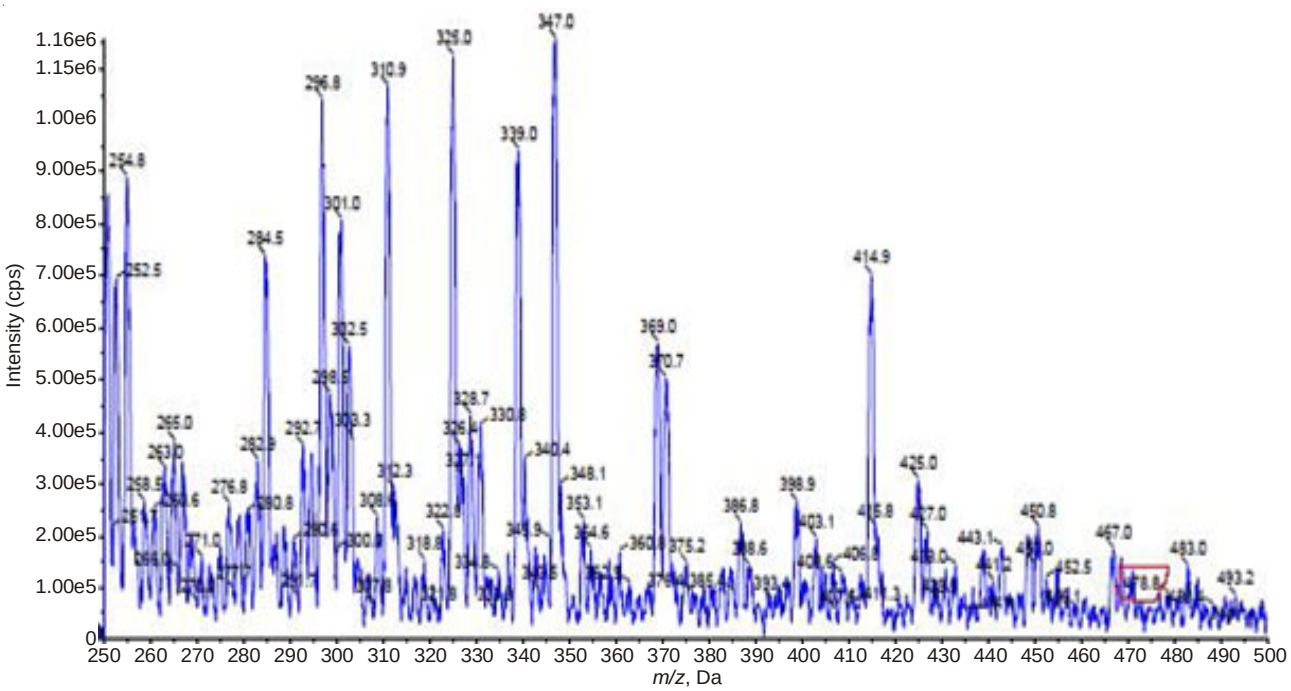

Fig. 4. ESI-MS from reaction result of prenylationxanthone

raxanthone G (*m/z* = 326); 1,5,8-trihydroxide-3-metoxide-2-(3-methylbut-2-enhylxanthone (*m/z* = 342.1) and α-mangosteen (*m/z* = 410.3). ESI-MS identification from xanthoneprenylation in shown in Fig. 4. From data, *m/z* = 478.35 was found. This was believed related to derivate xanthone structure; 1,5,8-trihydroxide-3-methoxide-2-(3-methylbut-2-enhyl)xanthone (Fig. 5).

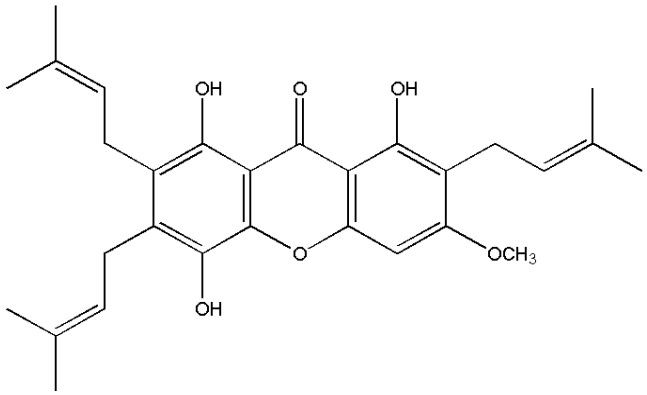

Fig. 5. Prediction of derivate xanthoneprenylation

Antioxidant activity results of xanthone component from mangosteen rind and its prenylation result using radical scavenging (DPPH) method are given in Table-1. From the data above, it can be concluded that prenylation can increase antioxidant ability. This was due to increase in stability of radical fenoction xanthone by additional prenyl cluster existence.

Conclusion

Heterogeneous superbase catalyst of γ-alumina/NaOH/Na succeed to be synthesized and can be used for prenylation reaction of derivate xanthone from mangosteen rind. Xanthone-prenylation result can increase its ability as an antioxidant.

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