

A TRITERPENOID COMPOUND FROM THE STEMBARK OF *Aglaiia argentea* (MELIACEAE)**A. T. Hidayat^{1,2}, K. Farabi¹, M. Muhammad¹, D. Harneti¹, Nurlelasari¹, R. Maharani^{1,2}, K. Haikal², U. Supratman^{1,2*}, Y. Shiono³.**¹*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Padjadjaran, Jatinangor 45363, Indonesia*²*Central Laboratory of Universitas Padjadjaran, Jatinangor 45363, Sumedang, West Java, Indonesia*³*Department of Food, Life, and Environmental Science, Faculty of Agriculture, Yamagata University, Tsuruoka, Yamagata 997-8555, Japan.***E-mail : unang.supratman@unpad.ac.id***ABSTRAK**

Senyawa triterpenoid, 3-epikabraleahidroksilakton (**1**) telah diisolasi dari ekstrak *n*-heksana kulit batang *Aglaiia argentea*. Struktur kimia senyawa **1** diidentifikasi berdasarkan data-data spektroskopi dan perbandingan data spektra yang diperoleh sebelumnya. Senyawa triterpenoid, 3-epikabrraleahidroksilakton (**1**) dilaporkan pada tumbuhan ini untuk pertama kali.

Kata kunci : *Aglaiia argentea*, 3-epikabraleahidroksilakton, Triterpenoid, Meliaceae

ABSTRACT

A triterpenoid compound, 3-epicabraleahydroxylactone (**1**) has been isolated from the *n*-hexane extract of the stem bark *Aglaiia argentea*. The chemical structure of compound **1** was identified based on spectroscopic data and by comparison with the spectral data previously reported. A triterpenoid, 3-epicabraleahydroxylactone (**1**), was reported from this plant for the first time.

Keywords : *Aglaiia argentea*, 3-epicabraleahydroxylactone, Triterpenoid, Meliaceae

INTRODUCTION

The genus *Aglaiia* belong to Meliaceae family consists of approximately 120 species, which are mainly distributed in the tropical rainforest especially in the Southeast Asia and on the Pacific islands (Pannell, 1992). Previous phytochemical studies have revealed the presence of a variety of compounds with interesting biological activities, including rocaglamide (Su et al., 2006), protolimonoids (Farabi et al., 2017a), bisamides (Sianturi et al., 2015), dammaran-type triterpenoids (Harneti et al., 2012), cycloartane-type triterpenoids (Awang et al., 2012), glabretal-type triterpenoids (Su et al., 2006), steroids (Harneti et al., 2014; Farabi et al., 2017b) and flavonoids (Nugroho et al., 1999).

Triterpenoids are metabolites of isopentenyl pyrophosphate oligomers and represent the largest group of phytochemicals. It has been estimated that more than 20,000 triterpenoids exist in nature (Liby et al., 2007). They predominantly are found in various plants including sea-weeds as well as in wax-like coatings of various fruits and medicinal herbs, including apples, cranberries, figs, olives, mistletoe, lavender, oregano, rosemary and thyme (Rabi et al., 2009, Laszczyk, 2009; Ovensna et al., 2004; Neto, 2007; Gerhauser, 2008). Triterpenoids are biosynthesized in plants by the cyclization of squalene, a triterpene hydrocarbon and precursor of all steroids (Phillips et al., 2006). They can further be subclassified into diverse groups including cucurbitanes, cycloartanes, dammaranes,

euphanes, friedelanes, holostanes, hopanes, isomalabaricanes, lanostanes, limonoids, lupanes, oleananes, protostanes, squalenes, tirucallanes, ursanes and miscellaneous compounds (Setzer et al., 2003; Petronelli et al., 2009; Mullauer et al., 2010). Although triterpenoid compounds of other *Aglaia* species have been investigated previously, but the triterpenoid compound of *A. argentea* is yet to be reported. We report herein the isolation and structure identification of triterpenoid compound, 3-epicabraleahydroxylactone (**1**) from the stem bark of *A. argentea*.

MATERIAL AND METHODS

Plant Material

The stem bark of *A. argentea* were collected in Bogor Botanical Garden, Bogor, West Java Province, Indonesia in January 2016. The plant was identified by the staff of the Bogoriense Herbarium, Research Center for Biology, Indonesian Institute of Science, Bogor, Indonesia and a voucher specimen (No. Bo-1288718) has been deposited at the herbarium.

General Experimental Procedure

Melting points were measured on an electrothermal melting point apparatus and are uncorrected. UV Spectra were measured by using a TECAN Infinite M200 pro with MeOH. The IR spectra were recorded on a Perkin-Elmer spectrum-100 FT-IR in KBr. Mass spectra were obtained with a Synapt G2 mass spectrometer instrument. ^1H , ^{13}C , DEPT NMR spectral data and ^1H - ^1H COSY, HMQC and HMBC experiments were performed on a JEOL ECZ-600 spectrometer at 600 MHz with CDCl_3 as a solvent, chemical shifts are given on a δ (ppm) scale and tetramethylsilane (TMS) as an internal standard. Column chromatography was conducted on silica gel 60. TLC plates were precoated with silica gel GF₂₅₄ (Merck, 0.25 mm) and detection was achieved by spraying with 10% H_2SO_4 in EtOH, followed by heating.

Extraction and isolation

The crushed and dried bark (2.5 kg) of *A. argentea* was extracted with methanol (14 L) at room temperature for 5 days. The methanol extract was evaporated under reduce pressure to give a

brown residue (140 g). The brown residue was first dissolved in H_2O and then partitioned successively with *n*-hexane (3 L), EtOAc (3 L) and *n*-butanol (3 L). The *n*-hexane soluble fraction (14.1 g) was fractionated by vacuum liquid chromatography on silica gel using a gradient *n*-hexane-EtOAc to give ten fractions (A–J). Fraction D (340 mg) was column chromatographed on silica gel, eluted with *n*-hexane:EtOAc (1:1), to give six subfractions (D01–D06). Subfraction D05 was column chromatographed on octa desyl silane, eluted with MeOH:MeCN: H_2O (6:1:3) to give **1** (20.6 mg).

3-epicabraleahydroxylactone (**1**). White crystals, m.p. (decomposed); IR (KBr) ν_{max} 3477, 2942, 2890, 1715, 1471, 1387, 1075 cm^{-1} ; ^1H NMR (CDCl_3 , 600 MHz); ^{13}C NMR (CD_3OD , 125 MHz), see Table 1. HRTOF-MS m/z 417.3105 $[\text{M}+\text{H}]^+$, calcd. for $\text{C}_{27}\text{H}_{44}\text{O}_3$ m/z 416.3290.

RESULTS AND DISCUSSION

The phytochemical test for the *n*-hexane extract showed the presence of triterpenoids. By using triterpenoid test to guide separations, the *n*-hexane fraction was separated by column chromatography over silica gel by gradient elution. The fractions were repeatedly subjected to normal-phase column chromatography and preparative TLC on silica gel GF₂₅₄ yielded a triterpenoid, **1** (Figure 1).

Compound **1**, was obtained as white crystals. The molecular formula was established to be $\text{C}_{27}\text{H}_{44}\text{O}_3$ based on The HR-TOFMS spectrum m/z 417.3105 $[\text{M}+\text{H}]^+$, calcd. for $\text{C}_{27}\text{H}_{44}\text{O}_3$ m/z 416.3290 together with NMR data (Tabel 1), thus requiring six degrees of unsaturation. The UV spectrum showed no a conjugated double based on the absorption maximum above 20 nm. IR spectrum of **1** showed the presence of a hydroxyl group (3477 cm^{-1}), aliphatic bands (2942 and 2860 cm^{-1}), a carbonyl lactone (1715 cm^{-1}), a *gem*-dimethyl (1471 and 1387 cm^{-1}) and an ether (1075 cm^{-1}).

^1H -NMR spectrum of **1** showed the presence of six tertiary methyl resonances at δ_{H} 0.92 (3H, s, H-18), 0.82 (3H, s, H-19), 1.33 (3H, s, H-21), 0.91 (3H, s, H-28), 0.81 (3H, s, H-29) and 0.87 (3H, s, H-30), which characteristic signals for a nor-triterpenoid (Phongmaykin et al., 2008) and

an oxygenated methine at δ_H 3,37 (1H, s, H-3). ^{13}C -NMR spectrum of **1** together with DEPT experiments showed the presence of twenty seven carbon signals consist of six methyls resonances at [δ_C 15.6 (C-18), 16.1 (C-19), 25.4 (C-21), 28.4 (C-28), 22.2 (C-29) and 16.4 (C-30)], an oxymethine signal at δ_C 76.3 (C-3), an oxygenated quaternary sp^3 carbon at δ_C 90,3 (C-20) and an ester signal at δ_C 176.9 (C-24), indicated opening of C-25, C-26 and C-27 carbons and formed a lactone ring at C-24/20, supporting the presence of trisnortriterpenoid dammaran (Phongmaykin et al., 2008).

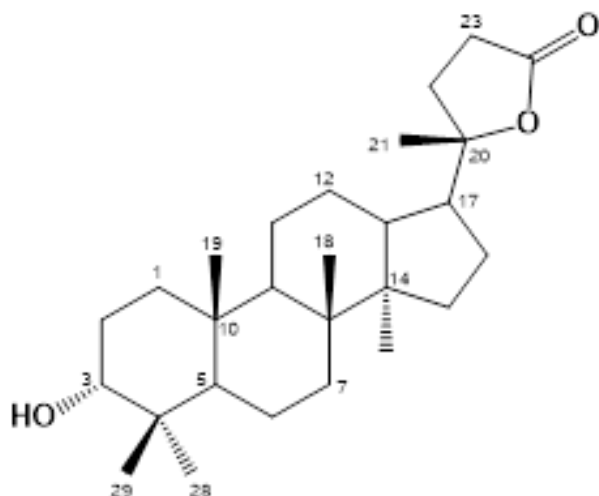


Figure 1. Chemical Structure for Compound 1

These functionalities accounted for one out of the total six degrees of unsaturation. The remaining five degrees of unsaturation were consistent with the trisnortriterpenoid dammaran with addition of a lactone ring.

In order to clarify the position of functional group in compound **1**, 1H - 1H COSY and HMBC experiments were carried out and the results was shown in Figure 2. The 1H - 1H COSY spectrum of **1** showed correlations in H_1 - H_2 - H_3 , H_5 - H_6 - H_7 , H_9 - H_{11} - H_{12} - H_{13} , H_{15} - H_{16} - H_{17} , and H_{22} - H_{23} , supporting the presence of a trisnortriterpenoid dammaran structure in **1**. In the HMBC spectrum, the correlations arising from the tertiary methyl protons to their neighboring carbons enabled the assignment of the five singlet

methyls at C-4 (2 \times), C-10, C-8, C-14 and C-20, respectively. Methylenes protons at δ_H 1.40 and 1.56 were correlated to an oxygenated carbon at δ_C 76.3 (C-3), whereas one of a *gem*-dimethyl was correlated to an oxygenated carbon at C-3 (δ_C 76.3), indicated that a secondary hydroxyl group was attached at C-3. A methylene protons at δ_H 2.52 and 2.62 were correlated to carbonyl lactone at δ_C 176.9 (C-24), whereas the methyl proton at δ_H 1.33 was correlated to oxygenated carbon at C-20 (δ_C 90.3) and C-17 (δ_C 49.5), indicated that a lactone ring was attached at C-17.

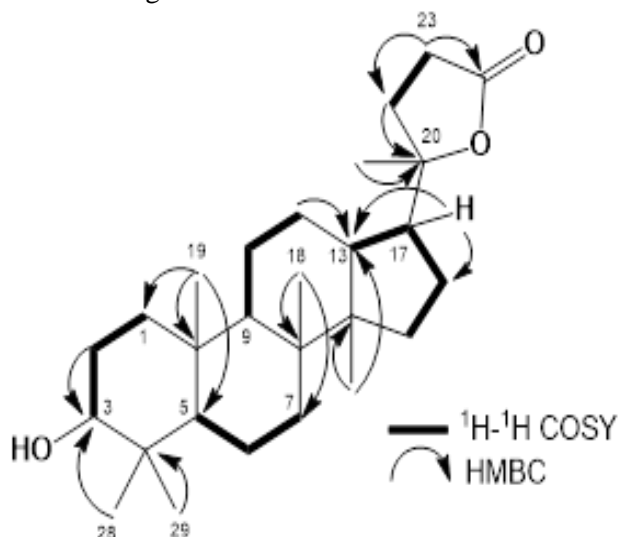


Figure 2. Selected 1H - 1H COSY and HMBC correlations for **1**

A relative stereochemistry of a hydroxyl group at C-3 was determined on the basis of coupling constant, 3J 0 Hz in the 1H NMR and δ_C 90.3 (C-20) in the ^{13}C NMR, indicating dan 3-OH as α -oriented, as well as a biogenetic point of view of the triterpenoid in the *Aglaia* genus. Consequently compound **1** was identified as a 3-epicabraleahydroxylactone, and was reported from this plant for the first time.

CONCLUSION

A trisnortriterpenoid dammaran, 3-epicabraleahydroxylactone (**1**) has been isolated from the *n*-hexane extract of the stembark *Aglaia argentea*. This investigation support the

occurrences of triterpenoid compounds in the *Aglaia* genus.

Table 1. NMR Data for Compound **1** (500 MHz for ^1H and 125 MHz for ^{13}C in CDCl_3)

Position of Carbon	^1H NMR δ_{H} (Integral., mult., $J=\text{Hz}$)	^{13}C NMR δ_{C} (mult.)
1	1.17 (1H, m) 1.50 (1H, m)	35.2 (t)
2	1.40 (1H, dd, 2.4, 9.6) 1.56 (1H, m)	33.7 (t)
3	3.37 (1H, m)	76.3 (d)
4	-	37.3 (s)
5	1.85 (1H, m)	49.4 (d)
6	1.37 (1H, m) 1.48 (1H, m)	18.3 (t)
7	1.71 (1H, m) 1.84 (1H, m)	26.9 (t)
8	-	40.6 (s)
9	1.41 (1H, dd, 2.4, 13.2)	50.4 (d)
10	-	37.7 (s)
11	1.20 (1H, m) 1.34 (1H, m)	25.4 (t)
12	1.49 (1H, m) 1.91 (1H, m)	21.3 (t) 21.3 (t)
13	1.53 (1H, m)	43.2 (d)
14	-	50.3 (s)
15	1.10 (1H, m) 1.90 (1H, m)	31.2 (t)
16	1.52 (1H, m) 1.42 (1H, m)	25.1 (t)
17	1.23 (1H, m)	49.5 (d)
18	0.92 (3H, s)	15.6 (q)
19	0.82 (3H, s)	16.1 (q)
20	-	90.3 (s)
21	1.33 (3H, s)	25.4 (q)
22	1.47 (1H, m) 2.01 (1H, m)	31.3 (t)
23	2.52 (1H, m) 2.62 (1H, m)	29.3 (t)
24	-	176.9 (s)
28	0.91 (3H, s)	28.4 (q)
29	0.81 (3H, s)	22.2 (q)
30	0.87 (3H, s)	16.4 (q)

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