CHEMICAL CONSTITUENTS FROM THE STEM BARK OF Alangium kurzi, Craib

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ABSTRACT

*Three new chemical constituents have been isolated from the stem bark of Alangium kurzii Craib. The structures were respectively determined to be 4-cyclohexene-1,2,3-triol **1**, 3-β-stigmast-5-en-3-ol (β-sitosterol **2**), and 3-O-β-D-glucopyranosyl-stigmast-5-ene (daucosterol **3**). These compounds are preliminary isolated from this plant.*
Keyword*:* Alangium kurzii, Alangiaceae, 4-cyclohexene-1,2,3-triol, β-sitosterol, daucosterol.

INTRODUCTION

Alangium kurzii Craib (Alangiaceae) is a traditional Indonesian medicine. The stem bark of this plant is used for treatment of rheumatism. It has also been widely used to treat some skin diseases in Jambi region, Indonesia [1]. Phytochemical work has been done on the alkaloid compounds of this plant, and a benzoquinolizine alkaloid, ankorine, together with a pyridine alkaloid, anabasine have been identified [2]. The leaves constituents of this plant have also been investigated and the presence of isoquinoline alkaloids and flavonoid glycosides have been reported [3]. In a previuos paper, we reported the isolation and identification of iridoid and isoquinoline alkaloid glycosides from the stem bark of this plant [4]. We have continued our investigations on the stem bark constituents of this species and have isolated three compounds, 4-cyclohexene-1,2,3-triol **1**, β-sitosterol **2**, and daucosterol **3**. The present paper deals with the isolation and identification of this compounds.

EXPERIMENTAL

1. General Experimental Procedures.

EIMS was carried out on a VG Auto Spec-3000 Spectrometer. ^{1}H and ^{13}C NMR were recorded on a Bruker DRX-500 Spectrometer. All NMR data were measured in pyridine-d_5, and chemical shifts were expressed in δ (ppm). TLC were performed on plates precoated with silica gel F_{254} (Qingdao Marine Chemical Ltd., People Republic of China).

2. Plant Material.

The stem barks of *Alangium kurzii* Craib were collected on 1997 in Bungo Tebo region, Jambi Province, Indonesia. This plant was identified by Dr. Djunaedi Gandawidjadja and a voucher specimen is kept in the Herbarium Bogoriense, Centre for Research and Development in Biology-LIPI, Bogor, Indonesia.

a. Extraction and Isolation.

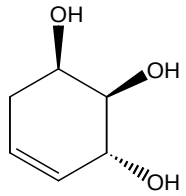
The dried stem barks of *A. kurzii* (6 kg) were extracted with MeOH at room temperature. The MeOH extracts were concd *in vacuo* and the resulting residue (200 g) was diluted in hot Ac_2O (5x300 mL) and filtered to yield an acetone fraction (30 g) and an acetone insoluble residue (170 g). The acetone fraction was subjected to CC on si gel using $CHCl_3$, $CHCl_3$ + 2% of MeOH, and MeOH as eluents. The eluates were combined on the basis of TLC analysis to provide a total of 14 fractions, and fraction 2 was a single pure of **2** (946 mg). Fraction 12 was futher separated by CC over si gel using EtOAc to obtained **1** (90 mg). The methanol residu (170 g) was diluted in MeOH (4x200 mL) and filtered to obtained 158 g of extract. This extract was subjected to CC on si gel using $CHCl_3$-MeOH (10:1), mixt. (1:1) of $CHCl_3$-MeOH (10:1) and $CHCl_3$-MeOH (7:3), MeOH, and

EtOH as eluents. The eluates were combined on the basis of TLC analysis to provide a total of 14 fractions. Evaporation of solvents from fraction 3, yielded **3** (2170 mg).

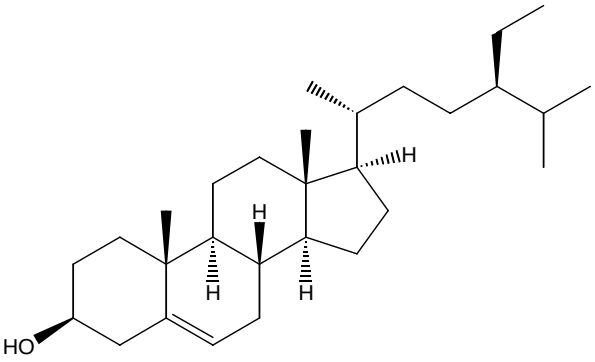
Compound **1**. White amorphous solid, 90 mg, $C_6H_{10}O_3$. ^{1}H NMR (500 MHz, pyridine-d_5): 5.85 (1H, d, *J* = 13.0 Hz, H-4), 5.55 (1H, ddd, *J* = 3.2; 6.3; 9.3 Hz, H-5), 4.58 (1H, m, H-3), 4.08 (1H, m, H-2), 4.02 (1H, m, H-1), 2.57 (1H, ddd, *J* = 6.4; 13.0; 16.5 Hz, H-6b), 2.28 (1H, ddd, *J* = 3.4; 13.0; 17.0 Hz, H-6a). ^{13}C NMR (125 MHz, pyridine-d_5): 131.7 (d, C-4), 125.5 (d, C-5), 79.7 (d, C-3), 73.9 (d, C-2), 70.8 (d, C-1), 34.9 (t, C-6).

Compound **2**. Crystal, 946 mg, $C_{29}H_{50}O$. EIMS *m/z* (intensity) : 414 [M^+] (100), 396 (50.0), 381 (23.3), 329 (31.3), 303 (33.3), 273 (24.0), 255 (25.3), 231 (13.3), 213 (16.7).

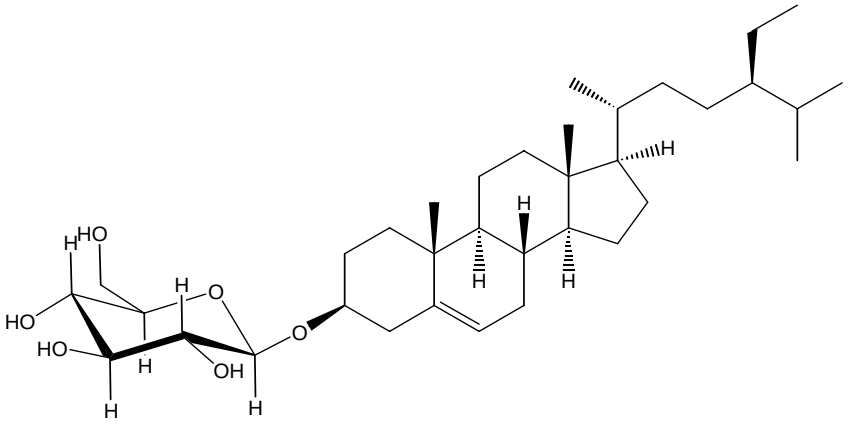
Compound **3**. White amorphous solid, 2170 mg, $C_{35}H_{60}O_6$. ^{1}H NMR (500 MHz, pyridine-d_5): aglycone part 5.33 (1H, d, *J* = 4.7 Hz, H-6), 3.97 (1H, ddd, *J* = 3.2; 6.2; 12.1 Hz, H-3), 1.00 (3H, s, H-18), 0.97 (3H, d, *J* = 6.5 Hz, H-21), 0.92 (3H, d, *J* = 6.0 Hz, H-27), 0.88 (3H, d, *J* = 5.7 Hz, H-26), 0.85 (3H, t, *J* = 7.8 Hz, H-29), 0.65 (3H, s, H-19); sugar part 5.04 (1H, d, *J* = 7.7 Hz, H-1'). ^{13}C NMR (100 MHz, pyridine-d_5): aglycone part 71.6 (d, C-3), 141.0 (s, C-5), 121 (d, C-6), 20.0 (q, C-27), 19.5 (q, C-19), 19.4 (q, C-26), 19.1 (q, C-21), 12.2 (q, C-29), 12.0 (q, C-18); sugar part 102.6 (d, C-1'), 78.6 (d, C-5'), 78.4 (d, C-3'), 75.4 (d, C-2'), 71.7 (d, C-4'), 62.9 (t, C-6'). EIMS *m/z* (intensity) : 414 [M^+ – 162] (50), 396 (100).



Compound **1**



Compound **2**
Compound **3**



RESULTS AND DISCUSSION

A methanol extract of the dried stem bark of *A. kurzii* was diluted in hot acetone and filtered to yield an acetone fraction and an acetone insoluble residue, respectively. The acetone fraction was subjected to column chromatography on silica gel to yield compounds **1** and **2**. The acetone insoluble residue was respectively separated and purified using silica gel, MPLC, afforded compound **3**.

Compound **1** (90 mg) was obtained as a white amorphous solid, had a molecular formula of $C_6H_{10}O_3$. The ^1H and ^{13}C NMR spectra of **1** showed two olefinic protons and carbons at δ 5.85 (1H, d, J = 13.0 Hz, H-4), 5.55 ppm (1H, ddd, J = 3.2; 6.3; 9.3 Hz, H-5), and δ 131.7 (d, C-4), 125.5 ppm (d, C-5), respectively. Three secondary alcoholic carbons present in **1** at δ 70.8, 73.9, and 79.7 which were leter determined to be C-1, C-2, C-3 respectively, were also observed, indicating a cyclohexentriol structure. By comparison of this data with that in the literature [5], it could be identified that **1** is 4-cyclohexen-1,2,3-triol.

Compound **2** (946 mg) was isolated as a white crystal. Its molecular formula, $C_{29}H_{50}O$, was established by EIMS *m/z* 414 $[M]^+$ (100) and DEPT ^{13}C NMR data. The mass fragmentation patern (see experimental section) features of **2** coincided very closely with a sterol, β-sitosterol [6].

Compound **3** (2170 mg) was suspected to be a sterol glycoside, as deduced from initial examination of the spectral data. However, the ^1H and ^{13}C NMR spectrum showed a doublet signal at δ 5.04 and 102.7 ppm are present indicating the anomeric proton and carbon, respectively. Moreover, the presence a hydroxymethyl signal at δ 62.9 ppm, indicated that the sugar residue in **3** was a β-D-glucopyranosyl residue. The β configuration was assigned by the $^3J_{H\text{-}1,H\text{-}2}$ value of its anomeric proton. This indication was also supported by the presence of $[M^+ -162\ ]$ ion at *m/z* 414 (45) in the EI-mass spectrum. By comparison of the mass fragmentation patern of **3** with compound **2**, it could be assigned that the aglycone moiety of **3** was β-sitosterol. A detailed comparison of this data with respective values reported in the literatures [7,8], indicated that **3** was 3-*O*-β-D-glucopyranosyl-sitosterol, also known as daucosterol.

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