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## New Chemical Constituent from the Rhizomes of *Johannesteijsmannia altifrons* (Juzuk Kimia Baru daripada Rizom *Johannesteijsmannia altifrons*)

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### ABSTRACT

A new compound namely 2-[(1'E)-3'-hydroxyl-1'-methyl-1'-propen-1'-yl]-6-methoxy-7-[(2''-methylheptyl)oxy]-5-benzofurancarboxylic acid and three known compounds of  $\beta$ -sitosterol,  $\gamma$ -taraxasterol and stigmasterol were isolated from the *n*-hexane extracts of the rhizomes and fruits of *Johannesteijsmannia altifrons* using vacuum liquid, column and radial chromatography. The structures of the isolated compounds were determined by means of 1D and 2D NMR, FT-IR, UV-VIS spectroscopy and mass spectrometry.

**Keywords:** *Arecaceae*;  $\beta$ -sitosterol; *Johannesteijsmannia altifrons*; new compound, 2-[(1'E)-3'-hydroxyl-1'-methyl-1'-propen-1'-yl]-6-methoxy-7-[(2''-methylheptyl)oxy]-5-benzofurancarboxylic acid; stigmasterol;  $\gamma$ -taraxasterol

### ABSTRAK

Satu sebatian baru yang dikenal pasti sebagai asid 2-[(1'E)-3'-hidroksil-1'-metil-1'-propen-1'-il]-6-metoksi-7-[(2''-metilheptil)oksi]-5-benzofurankarbosilik dan tiga sebatian yang telah dikenali iaitu  $\beta$ -sitosterol,  $\gamma$ -taraksasterol dan stigmasterol telah dipisahkan daripada ekstrak *n*-heksana rizom dan buah *Johannesteijsmannia altifrons* dengan menggunakan kromatografi cecair vakum, turus dan radial. Struktur sebatian yang terpisah ditentukan melalui kaedah spektroskopi RMN 1D dan 2D, IM-JF, UL-BN dan spektrometri jisim.

**Kata kunci:** *Arecaceae*; asid 2-[(1'E)-3'-hidroksil-1'-metil-1'-propen-1'-il]-6-metoksi-7-[(2''-metilheptil)oksi]-5-benzofurankarbosilik;  $\beta$ -sitosterol; *Johannesteijsmannia altifrons*; sebatian baru, stigmasterol;  $\gamma$ -taraksasterol

### INTRODUCTION

*Johannesteijsmannia* belongs to the *Arecaceae* family comprises of four species, *J. altifrons*, *J. lanceolata*, *J. magnifica* and *J. perakensis*. *Johannesteijsmannia altifrons* is also known as Daun Sang (Malay) and Joey Palm (English) can be found in various parts of Peninsular Malaysia namely in Kelantan, Perak, Terengganu, Pahang, Johor and Kedah. These fan palms are usually found growing under shade or in dappled light without a trunk and can grow up to 10-20 feet tall and 15 feet wide. In the forest, the leaves drop down to the base of the palm and form compost. The leaves are also commonly used as material for roof building by the local people (Ng 2006).

The family of *Arecaceae* has been reported to contain flavonoids (Muhaisen 2014), alkaloids (Dyana & Kanchana 2012), terpenoids, steroids, fatty acids and tannins (Benmehdi et al. 2012). However, to the best of our knowledge, no chemical constituent has ever been isolated or characterized from this genus. Thus, a phytochemical investigation on *J. altifrons* is done to further enrich our knowledge on this species. In this study, the *n*-hexane extracts from the rhizomes and fruits of *J. altifrons* were purified and led to the discovery of known  $\beta$ -sitosterol (1),  $\gamma$ -taraxasterol (2), stigmasterol (3) and new 2-[(1'E)-3'-hydroxyl-1'-methyl-1'-propen-1'-yl]-6-methoxy-7-[(2''-methylheptyl)oxy]-5-benzofurancarboxylic acid (4) as in Figure 1.

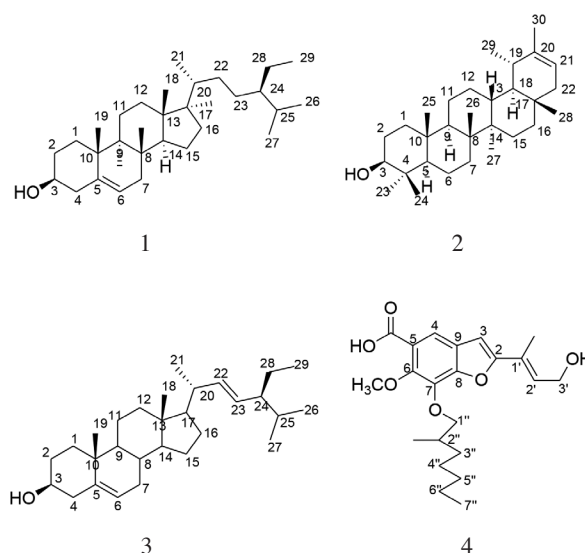


FIGURE 1. Compounds isolated from the rhizomes and fruits of *J. altifrons*

### MATERIALS AND METHODS

#### GENERAL

There are different spectroscopic methods used to elucidate the structures of  $\beta$ -sitosterol,  $\gamma$ -taraxasterol, stigmasterol and 2-[(1'E)-3'-hydroxyl-1'-methyl-1'-

propen-1'-yl]-6-methoxy-7-[(2''-methylheptyl)oxy]-5-benzofurancarboxylic acid including UV-VIS, mass spectrometry, FT-IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using Avance III 600 MHz Bruker. Deuterated chloroform ( $\text{CDCl}_3$ ) was used as the NMR solvent with the chemical shifts  $\delta_{\text{H}}$ , in ppm and the values of coupling constants,  $J$ , in Hz. Mass spectra were recorded by using the LC-mass spectrometer (LC-MS) on the Dionex/Bruker Micro ToFQ. The infrared spectra were recorded on the Perkin-Elmer Spectrum 400 and the UV-VIS spectra were obtained in chloroform using UV-2400PC. Vacuum liquid chromatography (VLC) was prepared by using silica gel of Merck 7747. For column chromatography (CC) and radial chromatography (RC), silica gel with PF<sub>254</sub> containing gypsum (Merck 7749) was used. Thin layer chromatography (TLC) was performed on commercially pre-coated aluminum silica gel 60 F<sub>254</sub> of Merck 5554.

#### PLANT MATERIALS

The rhizomes and fruits of *J. altifrons* were collected at Pelagat Forest Reserve, Besut, Terengganu in February 2015. A voucher specimen (UKMB 40309) was deposited at the Herbarium of Universiti Kebangsaan Malaysia, Bangi (UKMB).

#### EXTRACTION AND ISOLATION

The air-dried, ground rhizomes (3.22 kg) and fruits (786 g) of *J. altifrons* were extracted for 3 days in methanol at room temperature, followed by filtration to give methanol solutions. They were then extracted with *n*-hexane several times, combined and reduced under pressure to afford 19.62 g (0.61%) and 4.42 g (0.56%) of greenish brown of rhizome and fruit *n*-hexane extracts. Both extracts were fractionated by VLC, eluted with increasing polarity of *n*-hexane and ethyl acetate. The fractions were combined based on their silica gel TLC profiles. For the fruit extract, the VLC gave sixteen fractions (F<sub>1</sub>-F<sub>16</sub>). Fractions F<sub>4</sub> to F<sub>7</sub> were combined and further fractionated using RC to produce four combined fractions (F<sub>41</sub>-F<sub>44</sub>). The third fraction (F<sub>43</sub>) contained  $\beta$ -sitosterol (**1**) (4.6 mg). Subsequently, fractions F<sub>9</sub>-F<sub>12</sub> were combined and purified by RC to yield seven combined fractions (F<sub>91</sub>-F<sub>97</sub>); fractions F<sub>94</sub> and F<sub>96</sub> contained  $\gamma$ -taraxasterol (**2**) (2.5 mg) and stigmasterol (**3**) (0.55 g), respectively. For the rhizome extract, the fractionation through VLC yielded eleven fractions (F<sub>1</sub>-F<sub>11</sub>). Fraction F<sub>4</sub> contained stigmasterol (**3**) (2.92 g). Fractions F<sub>5</sub> and F<sub>6</sub> were combined and further fractionated using CC to yield five combined fractions (F<sub>51</sub>-F<sub>55</sub>). Fraction F<sub>53</sub> was purified using RC to produce four combined fractions (F<sub>531</sub>-F<sub>534</sub>). The third fraction (F<sub>533</sub>) was identified as 2-[(1'*E*)-3'-hydroxyl-1'-methyl-1'-propen-1'-yl]-6-methoxy-7-[(2''-methylheptyl)oxy]-5-benzofurancarboxylic acid (**4**) (7.5 mg).

#### RESULTS AND DISCUSSION

A new compound namely 2-[(1'*E*)-3'-Hydroxyl-1'-methyl-1'-propen-1'-yl]-6-methoxy-7-[(2''-methylheptyl)oxy]-5-benzofurancarboxylic acid (7.5 mg) was isolated from the rhizomes of *J. altifrons* as a yellow powder. On TLC plate, the compound gave dark shades of purple color when viewed under UV light. Its molecular formula  $\text{C}_{22}\text{H}_{30}\text{O}_6$  was derived from ESI-MS which gave pseudomolecular ion at  $m/z$  413.2677  $[\text{M}+\text{Na}]^+$ . The UV-VIS spectrum in chloroform which gave absorbance peak at 317 nm indicates the occurrence of parent benzofuran ring in the molecule. The IR spectrum displayed a broad absorbance peak at  $3211\text{ cm}^{-1}$  which represents hydroxyl group. Absorption band which appeared at  $1607\text{ cm}^{-1}$  indicated the presence of carbonyl group and peak at  $1460\text{ cm}^{-1}$  represents benzofuran aromatic ring. Absorption peaks at  $1162$  and  $1280\text{ cm}^{-1}$  represent C-O stretches of the hydroxyl, methoxy and ester groups.

$^1\text{H}$  NMR spectrum of 2-[(1'*E*)-3'-hydroxyl-1'-methyl-1'-propen-1'-yl]-6-methoxy-7-[(2''-methylheptyl)oxy]-5-benzofurancarboxylic acid showed two highly-deshielded signals at  $\delta_{\text{H}}$  6.84 and 6.31 ppm which indicated the presence of respective protons H-3 and H-4 that were attached to benzene and furan rings of the benzofuran (Table 1). A deshielded doublet signal at  $\delta_{\text{H}}$  4.10 represents the methylene protons located next to the oxygen of phenyl ether (H-1''). A multiplet signal at  $\delta_{\text{H}}$  5.30 indicated the existence of vinylic proton (H-1'). A singlet signal at  $\delta_{\text{H}}$  3.82 indicated the existence of phenyl methoxy group. The appearance of highly overlapped proton signals at  $\delta_{\text{H}}$  1.29 indicated the presence of four terminal methylenes in the *n*-heptyl chain of the benzofuran ring (H-3'', H-4'', H-5'' and H-6'').

The  $^{13}\text{C}$  NMR spectrum showed that 2-[(1'*E*)-3'-hydroxyl-1'-methyl-1'-propen-1'-yl]-6-methoxy-7-[(2''-methylheptyl)oxy]-5-benzofurancarboxylic acid contained 22 different carbons consisting of three methyls, six methylenes, four methines, one methoxy and eight quaternary carbons (Table 1). One most deshielded signal at  $\delta_{\text{C}}$  182.1 indicated the presence of carbonyl group and signals at  $\delta_{\text{C}}$  121.5 and 125.1 represent carbon-carbon double bond. Besides these, eight highly-deshielded signals of  $\delta_{\text{C}}$  between 101.6 and 155.1 ppm show the presence of benzofuran ring. One signal at  $\delta_{\text{C}}$  62.1 indicated the presence of one methoxy group on benzene ring. Signals at  $\delta_{\text{C}}$  31.6, 29.7, 26.6, and 21.5 showed the presence of four terminal methylenes in the *n*-heptyl chain. Correlations of  $^1\text{H}$ - $^1\text{H}$  in COSY and  $^1\text{H}$ - $^{13}\text{C}$  in HMBC for the compound **4** are tabulated in Table 1 and shown in Figure 2.

A new compound (**4**) was isolated as benzofuran derivative was isolated for the first time from the Arecaceae family. Stigmasterol and  $\beta$ -sitosterol were found in many species of Arecaceae family, but were isolated for the first time from *J. altifrons*. Garcia et al. (1981) isolated stigmasterol and  $\beta$ -sitosterol from the leaves of *Phoenix canariensis*. Besides,  $\beta$ -sitosterol was the major sterol found in *Phoenix theophrasti*, *Phoenix dactylifera* (Malhi

TABLE 1.  $^1\text{H}$ ,  $^{13}\text{C}$  APT NMR data and COSY, HMBC correlations of compound **4** ( $\text{CDCl}_3$ , 600 MHz)

Position	$\delta_{\text{H}}$ ppm (number of protons, multiplicity, J Hz)	$\delta_{\text{C}}$ ppm	COSY	HMBC
2		155.1		
3	6.84 (1H, s)	101.6		C-4, C-8, C-2
4	6.31 (1H, s)	113.3		C-3, C-2, C-5, C=O
5		161.7		
5-CO <sub>2</sub> H	13.78 (1H, s)	182.1		
6		144.1		
6-OCH <sub>3</sub>	3.82 (3H, s)	62.1		C-7
7		137.1		
8		142.6		
9		132.2		
1'		125.1		
1'-CH <sub>3</sub>	1.60 (3H, s)	25.9		C-2'
2'	5.30 (1H, m)	121.5	H-3'	1'-CH <sub>3</sub>
3'	3.47 (2H, d)	51.1	1'-CH <sub>3</sub> , H-2'	C-2', C-2
1''	4.10 (2H, d)	64.5	H-2''	C-6, C-8
2''	1.29 (1H, m)	25.8	H-1''	
2''-CH <sub>3</sub>	1.85 (3H, d)	18.2		C-4''
3''	1.29 (2H, m)	31.6		
4''	1.29 (2H, m)	29.7		
5''	1.29 (2H, m)	26.6		
6''	1.29 (2H, m)	22.7	H-7''	C-7''
7''	0.89 (3H, t)	14.1	H-6''	C-6''

et al. 2014) and *Corypha taliera* (Shoeb et al. 2013). On the other hand,  $\gamma$ -taraxasterol was also isolated for the first time from *J. altifrons*. However, this compound has never been reported to be isolated from Arecaceae family.

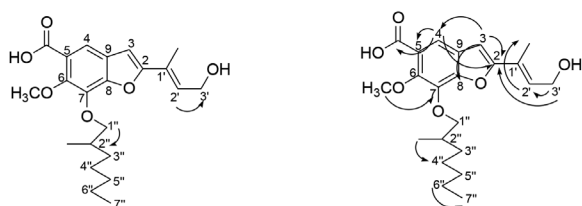


FIGURE 2. 2D NMR correlations of 2-[(1'E)-3'-hydroxyl-1'-methyl-1'-propen-1'-yl]-6-methoxy-7-[(2''-methylheptyl)oxy]-5-benzofuran-3-carboxylic acid, (a) COSY and (b) HMBC

## CONCLUSION

The investigation on chemical constituents from rhizomes and fruits of *J. altifrons* resulted in the isolation of a new compound namely 2-[(1'E)-3'-hydroxyl-1'-methyl-1'-propen-1'-yl]-6-methoxy-7-[(2''-methylheptyl)oxy]-5-

benzofuran-3-carboxylic acid (**4**), along with three known compounds of  $\beta$ -sitosterol (**1**),  $\gamma$ -taraxasterol (**2**) and stigmasterol (**3**). Compound **4** is the first benzofuran found in the Arecaceae family. The skeleton of benzofuran has been reported to possess many medical use. For example anti-cancer, anti-ulcer, anti-alzheimers, anti-viral and anti-inflammatory (Reshma et al. 2015).

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