



Chemical Constituents from *Garcinia Maingayi*

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ABSTRACT

Studies on the stem bark of Garcinia maingayi have led to the isolation of two terpenoids stigmasterol 1 and sitosterol 2. The structures of these compounds were determined by spectroscopic methods such as mass spectroscopy (MS), ¹H & ¹³C NMR and by comparison with previous studies. These structures were isolated from hexane crude.

Keywords: *Garcinia maingayi*, stigmasterol, sitosterol

Introduction

Natural products chemists have always devoted their studies on plants to the isolation and identification of secondary metabolites. Recently, there is much interest in the application of these plant products in the field of medicine or as natural pesticides. Malaysia has 12000 species of flowering plants of which about 1300 are said to be medicinal (Burkhill, 1966). However, only about a hundred have been fully investigated for their potential.

Literature Review

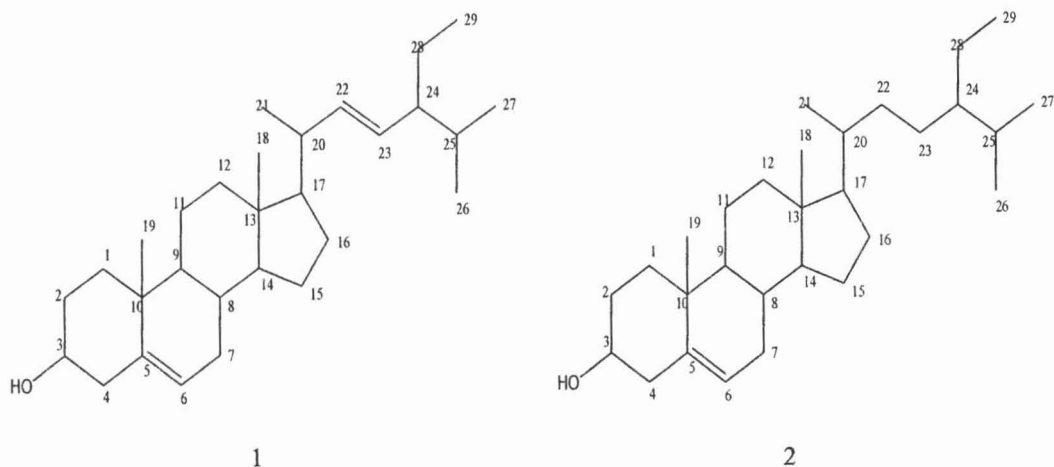
Research has shown that the genus *Garcinia* is widespread in the old world, most notably in the lowland tropical rain forest of south-east Asia and West Africa (Apofu, 1986). Extensive research exhibit a wide range of biological and pharmacological activities such as cytotoxic, antimicrobial, antimalarial and anti-HIV-1 protease inhibitory activity (Kosela S, 2000).

Detail studies on the stem bark have provided two known compounds stigmasterol 1 and sitosterol 2 from hexane crude.

Methods and Materials

The finely powdered stem bark (≈ 1.0 kg) was extracted with distilled hexane. The crude extracts were filtered and after removal of the solvents by vacuum evaporation yielded dark residues weighing 12.8g. The crude extract was subjected to a series of column chromatography over Si gel column using hexane, chloroform, ethyl acetate and methanol mixtures of increasing polarity as an eluting solvent and was further purified by preparative TLC, mini column chromatography and recrystallization. Column chromatography on the crude hexane extract yielded two terpenoids stigmasterol 1 and sitosterol 2.

Results and Discussion



Detail chemical investigation of the hexane extracts of the stem bark of *Garcini maingayi* have furnished two known compounds stigmasterol **1** and sitosterol **2**.

Compound **1** was recrystallized from hexane to afford **1** as fine white needles, melting point 168-170 °C (Lit. 170 °C, Hill *et al.*, 1991). Strong absorption at 3418 cm^{-1} in the IR spectrum confirmed the presence of hydroxyl group. The absorptions observed at 2936 cm^{-1} and 1628 cm^{-1} were assigned to carbon - hydrogen stretching for CH_3 and CH_2 and carbon - carbon double bond respectively.

Two doublet of doublets at δ 5.18 ($J = 15.2, 8.5$ Hz) and 5.04 ($J = 15.2, 8.5$ Hz) which appeared at the ^1H NMR spectrum were assigned to H-22 and H-23 of the side chain respectively. ^1H - ^1H COSY spectrum further supported these assignments. The large coupling constant value of 15.2 Hz suggested that the two protons have a trans configuration. Meanwhile a doublet at δ 5.35 ($J = 5.0$ Hz) was assigned to H-6 and a multiplet at δ 3.55 was due to the presence of a hydroxymethine group at H-3. The ^{13}C NMR spectrum showed a total of 29 carbons which confirmed the number of carbons present in **1**. The ^{13}C NMR assignments were carried out by comparing with ^{13}C NMR published data (Holland *et al.*, 1978). DEPT spectrum revealed the presence of three quaternary carbons, eleven methine carbons, nine methylene carbons and six methyl carbons which is consistent with the structure of **1** and matched well with the ^{13}C NMR chemical shift values that were reported earlier (see table 1). ^{13}C NMR signals appeared at δ 140.7, 138.3, 129.2 and 121.7. This shows that there are four olefinic carbons which were assigned to C-5, C-22, C-23 and C-6 respectively. The signal at δ 71.8 also confirmed the presence of a hydroxymethine carbon in **1**.

Table 1: ^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) Assignments of Stigmasterol 2

Position	δH	δC	δC^*	DEPT	^1H - ^1H COSY
1		37.3	37.4	CH ₂	
2		31.7	31.7	CH ₂	
3	3.55 (1H, m)	71.9	71.8	CH	H-4
4	2.29 (2H, m)	42.4	42.4	CH ₂	H-3
5		140.8	140.9	C	
6	5.35 (1H, d, $J = 5.0$ Hz)	121.8	121.7	CH	H-7
7	2.07 (2H, m)	32.0	31.9	CH ₂	H-6
8		32.0	31.9	CH	
9		50.2	50.3	CH	
10		36.6	36.6	C	
11		21.3	21.1	CH ₂	
12		39.8	39.8	CH ₂	
13		42.3	42.4	C	
14		56.9	57.0	CH	
15		24.5	24.4	CH ₂	
16		29.1	28.9	CH ₂	
17		56.0	56.0	CH	
18		12.4	12.2	CH ₃	
19		19.5	19.4	CH ₃	
20		40.6	40.5	CH	
21		21.2	21.1	CH ₃	
22	5.18 (1H, dd, $J = 15.0, 8.5$ Hz)	138.4	138.4	CH	H-23
23	5.04 (1H, dd, $J = 15.0, 8.5$ Hz)	129.3	129.4	CH	H-22
24		51.5	51.3	CH	
25		32.0	31.9	CH	
26		19.1	19.0	CH ₃	
27		21.2	21.1	CH ₃	
28		25.6	25.4	CH ₂	
29		12.1	12.0	CH ₃	

*Holland et al., 1978 in CDCl_3 at 20 MHz

Compound **2** was obtained as an amorphous powder and was crystallized from chloroform as white needles, melting point 132-134 °C (Lit. 136-137 °C, Hill *et al.*, 1991). It gave a positive iodine vapor's test. The EI-MS spectrum of **2** displayed a molecular ion peak at m/z 414, compatible with the molecular formula $\text{C}_{29}\text{H}_{50}\text{O}$ which has two hydrogen atoms more than compound **1**. Loss of a water molecule was observed at molecular ion peak of 396 m/z .

The IR spectrum exhibited a strong absorption band at 3418 cm^{-1} which indicated the presence of a hydroxyl group in **2**. Other significant bands observed at 2942 cm^{-1} and 1668 cm^{-1} supported the presence of carbon - hydrogen stretching for CH₃ and CH₂ groups and carbon - carbon double bond respectively.

Interpretation of the ^1H and ^{13}C spectra data by means of ^1H - ^1H COSY, DEPT and HSQC

experiments and comparison with published data allowed full assignments of the NMR signals which led to structure **2**. The ^1H NMR spectrum was close to that of **1**, but differed by the absence of signals for the olefinic protons of H-22 and H-23 of the side chain. A doublet signal was observed at δ 5.35 ($J = 5.1$ Hz) for the only olefinic proton at H-6. The ^1H NMR spectrum also showed a multiplet signal at δ 3.52 attributable to the proton geminal to the hydroxyl group placed at C-3.

The ^{13}C NMR spectrum contained 29 carbons corresponding to three quaternary, nine methine, eleven methylene groups and six methyl carbon atoms, which were carried out by means of a DEPT experiment. The downfield signals for C-22 and C-23 were absent in the ^{13}C NMR spectrum compared to **1**. Signals resonating at δ 140.7, δ 121.7 and δ 71.8 were assigned to C-5, C-6 and the hydroxyl bearing carbon, C-3 respectively.

The HSQC showed cross peak between the proton signal for H-6 at δ 5.35 to the carbon signal of C-6 at δ 121.7 and the proton signal for H-3 at δ 3.52 to the carbon signal for C-3 at δ 71.8. The assignments of the NMR spectra for sitosterol **2** are summarized in Table 2.

Table 2: ^1H NMR (400 MHz, CDCl_3) and ^{13}C NMR (100 MHz, CDCl_3) Assignments of Sitosterol
2

Position	δH	δC	δC^*	HMBC (H to C)
1		37.2	37.3	
2		31.6	31.6	
3	3.52 (1H, m)	71.8	71.7	
4	2.28 (2H, m)	42.3	42.3	C-3, C-6, C-5
5		140.7	140.8	
6	5.35 (1H, d, $J = 5.1$ Hz)	121.7	121.6	
7		31.9	31.9	
8		31.9	31.9	
9		50.1	50.2	
10		36.5	36.5	
11		21.1	21.1	
12		39.7	39.8	
13		42.3	42.3	
14		56.7	56.8	
15		24.3	24.3	
16		28.2	28.3	
17		56.0	56.1	
18		11.8	11.9	
19		19.4	19.4	
20		36.1	36.2	
21		18.8	18.8	
22		33.9	33.9	
23		26.0	26.1	
24		45.8	45.9	
25		29.1	29.2	
26		19.8	19.8	
27		19.0	19.1	
28		23.0	23.1	
29		12.0	12.3	

* Hill *et al.*, 1991

Conclusion

From hexane crude of *Garcinia maingayi* we have obtained two compounds stigmasterol **1** and sitosterol **2**.

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