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Research Article

FOUR XANTHONES FROM FRUITS OF *GARCINIA SCHOMBURGKIANA*

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ABSTRACT

*Garcinia schomburgkiana has been used as a traditional medicine in Asian countries. This plant is native to Vietnam. This study was done to investigate the phytochemicals of fruits of G. schomburgkiana grown in Tay Ninh Province. Four compounds α-mangostin (**1**), β-mangostin (**2**), fuscaxanthone A (**3**), and 9-hydroxycalabaxanthone (**4**) were isolated from the ethyl acetate extract of Garcinia schomburgkiana fruits. Their chemical structures were elucidated by comparing their spectroscopic data with reported data in the literature.*

Keywords: 9-hydroxycalabaxanthone; fuscaxanthone A; *Garcinia schomburgkiana*; *xanthone;* mangostin

1. Introduction

Garcinia schomburgkiana is popularly distributed in tropical areas of Asia, Africa, South America, Australia, and Polynesia (Lim, 2012; Nguyen et al., 2022). In Vietnam, the plant is known as the local name "Bua dong", grown widely in the provinces of South Vietnam. Different parts of *G. schomburgkiana* are widely used in traditional medicine. Fruits and some other parts are used for treatment of cough, nervous disorders menstruation, diabetes, and to improve symptoms of indigestion (Lim, 2012). In addition, *G. schomburgkiana* was used to treat scalp inflammation, bleeding, and periodontitis (Liu et al., 2016). Extracts and isolated compounds of this plant had various bioactivities such as antioxidant (Meechai et al., 2016) and cytotoxicity against cancer cell lines (Darnasmara et al., 2021; Kaennakam et al., 2019; Sukandar et al., 2016), especially against HeLa cell line (Le et al., 2016). Phytochemical data of *G. schomburgkiana* revealed the presence of xanthones, depsidones, biphenyls, benzophenones, biflavonoids, steroids, and

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phloroglucinol (Le et al., 2016; Sukandar et al., 2016). However, little is known about the chemical data of fruits of *G. schomburgkiana*. This paper reports the isolations and structural elucidation of four compounds from *G. schomburgkiana* fruits collected in Tay Ninh Province, Vietnam.

2. Experimental

2.1. General experimental procedures

The NMR spectra were recorded on a Bruker Avance spectrometer (500 MHz for ^{1}H–NMR and 125 MHz for ^{13}C–NMR) in acetone-d_6 and $CDCl_3$. Thin-layer chromatography was carried out on silica gel 60 (Merck, 40-63 μm) and spots were visualized by spraying with 10% H_2SO_4 solution, followed by heating.

2.2. Plant material

Dried, ground fruits of *Garcinia schomburgkiana* were collected in Tay Ninh Province in August 2022. The scientific name of the material was identified as *Garcinia schomburgkiana*. A voucher specimen (No UP-010) was deposited in the herbarium of the Department of Organic Chemistry, Faculty of Chemistry, Ho Chi Minh University of Education, Ho Chi Minh City, Vietnam.

2.3. Extraction and isolation

Dried, ground fruits of *Garcinia schomburgkiana* (5 kg) were extracted with methanol (10L x 3) at room temperature. The filtrated solution was evaporated at reduced pressure to obtain a crude extract (695.5 g). This extract was partitioned into EtOAc to afford the extract **EA** (295.2 g). The water-soluble layer was evaporated to provide the extract Me (358.7 g). The **EA** extract was applied to silica gel column chromatography (CC) with a gradient system using the mobile phase as *n*-hexane: EtOAc (11:1, v/v) to afford 26 fractions (coded **EA1**-**EA26**). The fraction **EA12** (1.01 g) was further subjected to silica gel CC, eluted with the solvent system of *n*-hexane: EtOAc (11:1, v/v) to give eight fractions **EA12.1**-**EA12.8**. Next, the fraction **EA12.4** (8.12 g) was rechromatographed by silica gel CC, eluted with *n*-hexane: EtOAc (7:1, v/v) to afford eight fractions S1-S8. Fraction S8 (215 mg) was applied to silica gel CC, eluted with *n*-hexane: EtOAc: $CHCl_3$: acetone: H_2O (15:2:1:1:0.01, v/v/v/v/v) to afford compounds **3** (3.1 mg) and **4** (7.2 mg). The fraction **EA12.5** (1.12 g) was separated by silica gel CC to give five subfractions **R1**-**R5**, eluted with the solvent system of *n*-hexane: EtOAc (5:1, v/v) to afford **1** (21.0 mg) and **2** (12.0 mg).

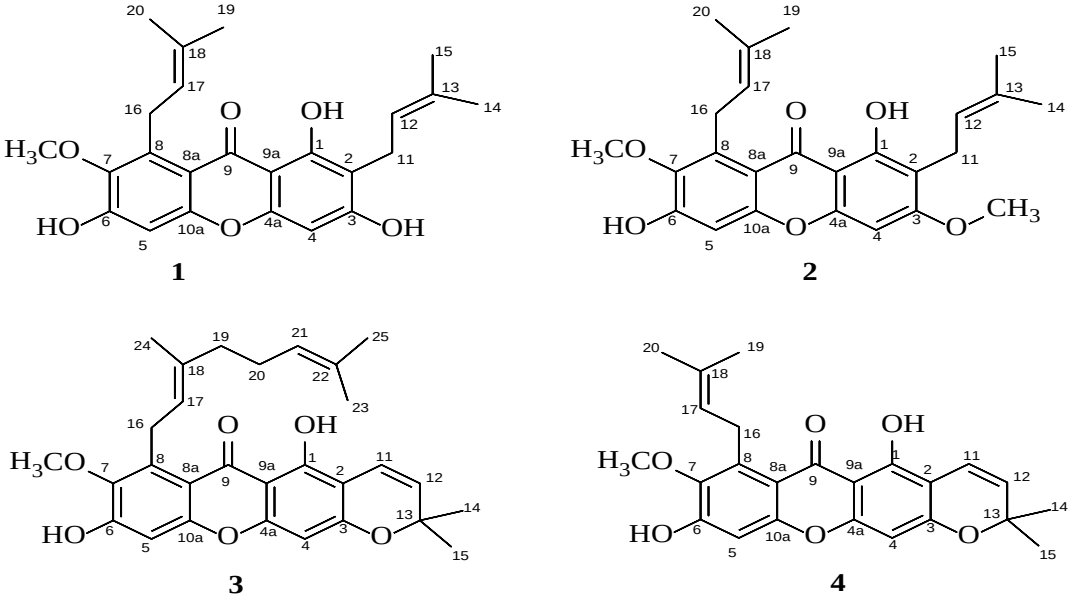

Figure 1. *Chemical structures of isolated compounds* ***1-4***

- ***α*-Mangostin** (**1**). Yellow amorphous powder. ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm, *J* in Hertz): 6.30 (1H, *s*, H-4), 6.83 (1H, *s*, H-5), 3.44 (2H, *d*, 7.0, H-11), 5.28 (1H, *t*, 7.0, H-12), 1.84 (3H, *s*, H-14), 1.83 (3H, *s*, H-15), 4.08 (2H, *d*, 6.5, H-16), 5.26 (1H, *t*, 6.5, H-17), 1.77 (3H, *s*, H-19), 1.69 (3H, *s*, H-20), 3.80 (3H, *s*, 7-OCH_3). ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 160.7 (C-1), 108.7 (C-2), 161.8 (C-3), 93.5 (C-4), 154.7 (C-4a), 103.7 (C-5), 155.9 (C-6), 142.7 (C-7), 137.2 (C-8), 112.3 (C-8a), 182.1 (C-9), 101.7 (C-9a), 155.3 (C-10a), 21.6 (C-11), 121.6 (C-12), 132.3 (C-13), 18.4 (C-14), 26.0 (C-15), 26.7 (C-16), 123.3 (C-17), 135.8 (C-18), 18.0 (C-19), 26.0 (C-20), 62.2 (7-OCH_3).
- ***β*-Mangostin (2).** Yellow amorphous powder. ^{1}H-NMR (500 MHz, $CDCl_3$, δ ppm, *J* in Hertz): 6.52 (1H, *s*, H-4), 6.87 (1H, *s*, H-5), 3.32 (2H, *d*, 7.0, H-11), 5.24 (1H, *t*, 7.0, H-12), 1.82 (3H, *s*, H-14), 1.77 (3H, *s*, H-15), 4.13 (2H, *d*, 6.6, H-16), 5.26 (1H, *t*, 6.6, H-17), 1.65 (3H, *s*, H-19), 1.82 (3H, *s*, H-20), 13.67 (1H, *s*, 1-OH), 3.97 (3H, *s*, 7-OCH_3), 3.80 (3H, *s*, 3-OCH_3). ^{13}C-NMR (125 MHz, $CDCl_3$, δ ppm): 160.7 (C-1), 111.8 (C-2), 164.4 (C-3), 89.9 (C-4), 155.6 (C-4a), 102.2 (C-5), 156.6 (C-6), 144.8 (C-7), 138.1 (C-8), 112.8 (C-8a), 182.9 (C-9), 104.4 (C-9a), 157.6 (C-10a), 21.9 (C-11), 123.3 (C-12), 131.6 (C-13), 25.9 (C-14), 17.8 (C-15), 26.7 (C-16), 123.3 (C-17), 131.5 (C-18), 25.9 (C-19), 18.4 (C-20), 61.3 (7-OCH_3), 56.6 (3-OCH_3).
- **Fuscaxanthone A** (**3**). Yellow amorphous powder. ^{1}H-NMR (500 MHz, acetone-d_6, δ ppm, *J* in Hertz): 6.26 (1H, *s*, H-4), 6.87 (1H, *s*, H-5), 6.68 (1H, *d*, 10.0, H-11), 5.72 (1H, *d*, 10.0, H-12), 1.46 (3H, *s*, H-14), (3H, *s*, H-15), 1.46, 4.13 (2H, *d*, 6.5, H-16), 5.32 (1H, *m*, H-17), 1.98 (2H, *m*, H-19), 2.05 (2H, *m*, H-20), 5.04 (1H, *m*, H-21), 1.52 (3H, *s*, H-23), 1.84 (3H, *s*, H-24), 1.56 (3H, *s*, H-25), 13.93 (1H, *s*, 1-OH), 9.71 (1H, *s*, 6-OH), 3.80 (3H, *s*, 7-OCH_3). ^{13}C-NMR (125 MHz, acetone-d_6, δ ppm): 158.9 (C-1), 104.7 (C-2), 160.7 (C-3),

94.7 (C-4), 157.2 (C-4a), 102.9 (C-5), 156.3 (C-6), 142.1 (C-7), 138.3 (C-8), 112.0 (C-8a), 182.5 (C-9), 103.6 (C-9a), 157.8 (C-10a), 116.0 (C-11), 128.5 (C-12), 78.3 (C-13), 28.5 (C-14), 28.5 (C-15), 26.8 (C-16), 124.7 (C-17), 135.3 (C-18), 40.5 (C-19), 27.3 (C-20), 125.2 (C-21), 131.6 (C-22), 17.8 (C-23), 16.5 (C-24), 25.7 (C-25), 61.4 (7-OCH_3).

- **9-Hydroxycalabaxanthone (4).** Yellow amorphous powder. ^{1}H-NMR (500 MHz, acetone-d_6, δ ppm, *J* in Hertz): 6.26 (1H, *s*, H-4), 6.87 (1H, *s*, H-5), 6.68 (1H, *d*, 10.0, H-11), 5.72 (1H, *d*, 10.0, H-12), 1.46 (3H, *s*, H-14), 1.46 (3H, *s*, H-15), 4.12 (2H, *d*, 6.5, H-16), 5.26 (1H, *t*, 6.5, H-17), 1.82 (3H, *s*, H-19), 1.65 (3H, *s*, H-20), 13.93 (1H, *s*, 1-OH), and 3.80 (3H, *s*, 7-OCH_3). ^{13}C-NMR (125 MHz, acetone-d_6, δ ppm): 158.8 (C-1), 105.2 (C-2), 160.7 (C-3), 94.6 (C-4), 157.2 (C-4a), 158.8 (C-6), 144.8 (C-7), 138.2 (C-8), 111.8 (C-8a), 183.1 (C-9), 104.5 (C-9a), 157.2 (C-10a), 116.0 (C-11), 125.5 (C-12), 78.8 (C-13), 28.5 (C-14), 28.5 (C-15), 26.8 (C-16), 124.6 (C-17), 131.6 (C-18), 18.3 (C-19), 25.9 (C-20), and 61.3 (7-OCH_3).

3. Results and discussion

Compound **1** was obtained as a yellow amorphous powder. The ^{1}H-NMR spectrum showed the presence of two isoprenyl groups characteristic of two olefinic protons [δ 5.28 (1H, *t*, 7.0, H-12) and 5.25 (1H, *t*, 6.6, H-17)], two methylenes [δ 3.44 (*d*, 7.0, H_2-11), 4.08 (*d*, 6.5, H_2-16)], and four methyls [δ 1.84 (H_3-14), 1.83 (H_3-15), 1.77 (H_3-19), and 1.69 (H_3-20)], two aromatic protons [δ 6.30 (1H, *s*, H-4) and 6.83 (1H, *s*, H-5)] and a methoxy group [δ 3.80 (*s*, 7-OCH_3)]. The ^{13}C-NMR spectrum of **1** provided 24 carbons, including a carbonyl carbon (δ 182.1, C-9), six oxygenated aromatic carbons (δ 160.7, 161.8, 154.7, 155.9, 142.7, and 155.3), other six aromatic carbons (δ 108.7, 93.5, 103.7, 137.2, 112.3, and 101.7), two quaternary olefinic carbons (δ 132.3 and 135.8), two olefinic methine carbons (δ 121.6 and 123.3), two methylene carbons (δ 21.6 and 26.7), four methyl carbons (δ 26.0, 26.0, 18.4, and 18.0), and a methoxy carbon (δ 62.2). The comparison of ^{1}H- and ^{13}C-NMR data of compound **1** indicated the consistency with those of α-mangostin reported in the literature (Trisuwan & Ritthiwigrom, 2012), thus, compound **1** was elucidated to be α-mangostin.

The comparison of the NMR data of compounds **2** and **1** pointed out that they shared the same xanthone skeleton. The difference between them is the presence of an additional methoxy group [δ_H 3.82, δ_C 55.8, 3-OCH_3]. The good compatibility between the NMR data of **2** and *β*-mangostin (Trisuwan & Ritthiwigrom, 2012) suggested the chemical structure of **2** to be *β*-mangostin.

Compound **3** was obtained as a yellow amorphous powder. The ^{13}C-NMR spectrum provided 29 carbons, including a carbonyl carbon (δ 182.9, C-9), two aromatic methine carbons (δ 94.7 and 102.9), six olefinic carbons (δ 135.3, 131.6, 128.5, 125.2, 124.7, 116.0), one methoxy carbon (δ 61.4), five methyl carbons (δ 28.5, 28.5, 17.8, 16.5, and 25.7), three methylene carbons (δ 26.8, 40.5, and 27.3), one oxygenated quaternary carbon at δ 78.3, and 10 aromatic quaternary carbons (δ 158.9, 104.7, 160.7, 157.2, 156.3, 142.1, 138.3, 112.0,

103.6, and 157.8). The ^{1}H-NMR spectrum showed a geranyl group characteristic of two olefinic methines at δ 5.32 (*m*, 1H, H-17), 5.04 (*m*, 1H, H-21), three methylenes at δ 1.98 (*m*, H_2-19), 2.05 (*m*, H_2-20), 4.13 (*d*, J = 6.5 Hz, H_2-16), three singlet methyls at δ 1.52 (H_3-23), δ 1.84 (H_3-24), and δ 1.56 (H_3-25). In HMBC analysis, the methylene protons at δ 4.13 (*d*, J = 6.5 Hz, H-16) gave cross peaks to carbons C-7 (δ 142.1), C-8 (δ 138.3), and C-8a (δ 112.0), thus defining the location of the geranyl moiety to be at C-8. Moreover, the ^{1}H-NMR spectrum also showed the presence of a hydrogen-bond hydroxy group at δ 13.93 (1H, *s*), two cis-coupled olefinic protons at δ 6.68 (1H, *d*, 10.0, H-11) and 5.72 (1H, *d*, 10.0, H-12), and two singlet methyls at δ 1.46 (H_3-14 and H_3-15). HMBC correlations of H_3-14 and H_3-15 to carbons at δ 78.3 (C-13) and 128.5 (C-12) indicated that **3** had a 2,2-dimethylchromene ring fused to the xanthone at C-2 and C-3. Finally, a methoxy group at δ 3.80 and two aromatic protons at δ 6.26 (*s*, 1H, H-4) and δ 6.87 (*s*, 1H, H-5) were defined by further HMBC correlations. The comparison of NMR data of **3** with the published ones (Ito et al., 2003) indicated that **3** was fuscaxanthone A.

The comparison of NMR spectral data of compounds **4** and **3** showed high similarity, indicating that they shared a xanthone skeleton fused with a 2,2-dimethylchromene moiety. The difference is the change of the geranyl chain at C-8 in **3** to the isoprenyl group in **4**. NMR data of **4** were consistent with those of 9-hydroxycalabaxanthone (Sen et al., 1981), thus **4** was elucidated as 9-hydroxycalabaxanthone.

4. Conclusions

From fruits of *Garcinia Schomburgkiana* collected in Tay Ninh province, four xanthones *α-mangostin* (**1**), *β-mangostin* (**2**), fuscaxanthone A (**3**), and 9-hydroxycalabaxanthone (**4**) were isolated. Their chemical structures were determined by the NMR spectroscopic method and by comparison with the literature. Further studies on this species are in progress.

❖ ***Conflict of Interest:*** *Authors have no conflict of interest to declare.*

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BỐN HỢP CHẤT XANTHONE TỪ QUẢ BỨA ĐỒNG *GARCINIA SCHOMBURGKIANA*

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TÓM TẮT

Garcinia schomburgkiana được sử dụng trong y học cổ truyền ở nhiều nước châu Á. Đây là loài cây đặc hữu ở Việt Nam. Nghiên cứu về thành phần hóa học của quả bứa đồng G. schomburgkiana thu hái ở Tây Ninh được tiến hành. Bốn hợp chất bao gồm α-mangostin (**1**)**,** *β-mangostin* (***2***)*, fuscaxanthone A* (***3***) *và 9-hydroxycalabaxanthone* (***4***) *được cô lập từ cao ethyl acetate của quả bứa đồng, thu hái tại Tây Ninh bằng các phương pháp sắc kí khác nhau. Cấu trúc hóa học của các hợp chất được xác định bằng các phương pháp phổ nghiệm đồng thời so sánh với các dữ liệu phổ trong tài liệu tham khảo.*

Từ khóa: 9-hydroxycalabaxanthone; fuscaxanthone A; *Garcinia schomburgkiana*; *xanthone;* mangostin