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Short Communication

A New Natural Product Compound Benjaminin from *Calophyllum benjaminum*

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ABSTRACT

Our detailed study on the chemical constituents of the stem bark of *Calophyllum benjaminum* and *Calophyllum javanicum* has resulted in one new coumarin benjaminin (1), five xanthones fuscaxanthone C (2), β-mangostin (3), thwaitesixanthone (4), dombakinaxanthone (5) and caloxanthone A (6), together with four common triterpenes friedelin (7), β-sitosterol (8), lupeol (9) and stigmasterol (10). The structures of these compounds were elucidated using NMR, FTIR and GCMS.

Keywords: Benjaminin, *Calophyllum benjaminum*, *Calophyllum javanicum*, Clusiaceae, coumarin, xanthone

INTRODUCTION

Calophyllum genus is one of the many genera of the *Guttiferae* family. This particular genus comprises more than 180 species that are widely distributed in Southeast Asia. *Calophyllum benjaminum* and *Calophyllum javanicum* are among the many *Calophyllum* species that grow in Malaysia. Some *Calophyllum* species are used in folk medicine to treat rheumatism, wound and inflammation. Previous studies have indicated this genus as rich in secondary metabolites such as xanthones (Morel *et al*. 2000), coumarins (Ee *et al*. 2011), and chromanone acids (Cottiglia *et al*. 2004). Some of the compounds isolated from *Calophyllum* species exhibited significant biological effects such as cytotoxic activities (Guilet *et al*. 2001), anti-human immunodeficiency virus (HIV), antimicrobial (Yimdjo *et al*. 2004) and anti-

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tumour promoter activities (Itoigawa *et al*. 2001). As part of our ongoing research on *Calophyllum* species from Malaysia, we reported here the first phytochemical study on *Calophyllum benjaminum* and *Calophyllum javanicum*.

MATERIALS AND METHODS

Extraction and Isolation

The ground stem bark of both plants was extracted with a series of solvents in increasing polarity, starting with hexane, followed by chloroform, ethyl acetate and methanol respectively for three days for each solvent. The extracts were evaporated to dryness using a rotary vacuum evaporator and the dry extract purified and isolated using column chromatography (Merck silica gel). Eluting solvents, which were of increasing polarity, ranged from 100% hexane to mixtures of hexane and chloroform, mixtures of chloroform and ethyl acetate, ethyl acetate with methanol and 100% methanol. Repeated purifications of the chloroform extract of *Calophyllum benjaminum* gave benjaminin (1) (11mg) together with fuscaxanthone C (2) (9mg). Meanwhile, β – mangostin (3) (5mg) and calaxanthone A (6) (10mg) were obtained from the methanol extract. The chloroform extract of *Calophyllum javanicum* gave dombakinaxantone (5) (7mg) and thwaitesixanthone (4) (8mg). Meanwhile, the ^{1}H and ^{13}C NMR spectral data for compounds 2 - 6 (see Fig.2) are in agreement with the data given in the literature (Ito *et al*., 2003; Mahabusarakam *et al*., 1987; Iinuma *et al*., 1994; Ranjith *et al*., 1997; Dahanayake *et al*., 1974).

Benjaminin (1): Yellowish Oil; FTIR: 3296,2930, 1706, 1621 cm^{-1}

^{1}H-NMR($CDCl_3$, 400MHz): *d* 12.28 (7-OH, s), 5.19 (1H, *t*, *J* = 6.29 Hz, H-2″), 4.13 (1H, *m*, H-3‴), 3.72 (3H, *s*, 5-OCH_3), 3.51 (1H, *m*, H-4), 3.25 (2H, *m*, H-1″), 2.74 (2H, *d*, *J* = 6.85 Hz, H-3), 2.53 (1H, *m*, H-2‴), 1.74 (3H, *s*, H-5″), 1.70 (2H, *m*, H-1′), 1.67 (3H, *s*, H-4″), 1.49 (3H, *d*, *J* = 6.87, H-CH_3-3‴), 1.24 (2H, *m*, H-3′), 1.22 (2H, *m*, H-4′), 1.19 (3H, *d*, *J* = 6.87 Hz, H- CH_3-2‴), 1.11 (2H, *m*, H-2′), 0.82 (3H, *t*, *J* = 6.87, H-5′).

^{13}C-NMR ($CDCl_3$, 100MHz): *d* 200.42 (C-1‴), 179.27 (C-2), 164.96 (C-5), 160.17 (C-7), 158.60 (C-8a), 131.80 (C-3″), 122.90 (C-2″), 115.26 (C-6), 115.19 (C-4a), 78.76 (C-3‴), 61.92 (OCH_3), 46.21 (C-2‴), 39.20 (C-3), 33.87 (C-1′), 32.67 (C-4), 31.95 (C-3′), 27.78 (C-2′), 25.80 (C-4″), 22.68 (C-1″), 22.64 (C-4′), 19.69 (C-CH_3-3‴), 17.99 (C-5″), 14.15 (C-5′), 10.34 (C-CH_3-4‴)

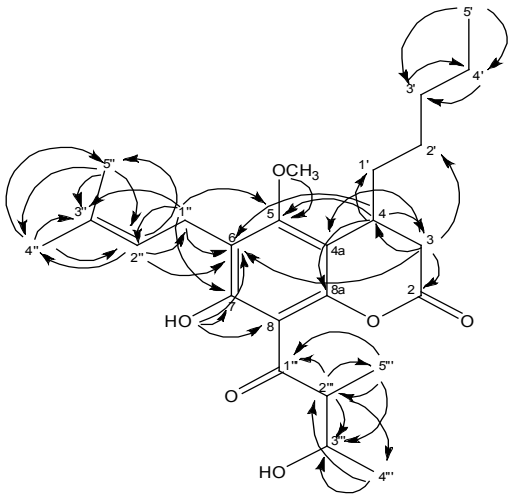
RESULTS AND DISCUSSION

Benjaminin (1) was obtained from the chloroform extract of *Calophyllum benjaminum* as a yellowish oil with molecular formula $C_{25}H_{36}O_6$. The EIMS spectrum gave a molecular ion peak at m/z 432. The FTIR spectrum of benjaminin displayed absorbtion peaks at 3296, 2925, 1705, 1626 cm^{-1}, while the UV spectrum gave a maximum absorbtion at 400nm.

The ^{1}H NMR signals were assigned through their COSY and HMBC correlations. The ^{1}H-NMR spectrum gave one singlet signal at δ 12.28 implying a hydroxyl peak. One olefinic proton signal at δ 5.19 (*t*, 1H,

J = 6.30 Hz), three methine signals at δ 2.53 (*m*, 1H), 3.51 (*m*, 1H), and 4.13 (*m*, 1H) and six methylene signals at δ 1.70 (*m*, 2H), 1.11 (*m*, 2H), 1.24 (*m*, 2H), 1.22 (*m*, 2H), 3.25 (*m*, 2H) and 2.74 (*d*, 2H, J = 6.87 Hz) were also observed. The olefinic signal was assigned to the olefinic (H-2″) proton of the prenyl side chain at C-6 while the methylene signals belong to the four methylene protons of the n-pentyl side chain at C-4 (H-1′, H-2′, H-3′ and H-4′) and the prenyl group (H-1″) and H-3, respectively. Five methyl signals at 0.82 (*t*, 3H, J = 6.87 Hz, 5′-CH_3), 1.74 (*s*, 3H, 5″-CH_3), 1.67 (*s*, 3H, 4″-CH_3), 1.19 (*d*, 3H, J = 6.87 Hz, 2‴-CH_3) and 1.49 (*d*, 3H, J = 6.87 Hz, 3‴-CH_3) were duly assigned to the five methyl groups of the side chains at C-4, C-6 and C-8. One methoxyl group at δ 3.72 (*s*, 3H) was seen to be attached to C-5 through their ^3J correlation in the HMBC spectrum. The ^{13}C-NMR spectrum gave 25 signals and from the analysis of the DEPT experiment, it was concluded that the molecule had five methine carbons, six methylenes, and six methyls plus nine quaternary carbons including the two carbonyl carbons at δ 179.27 and 200.42.

The complete elucidation of the structure was achieved with the aid of the HMBC analysis (Fig.1) after assigning the protons to their direct bonding carbons by the HMQC spectrum. The attachment of the n-pentyl group to C-4 was justified by the ^2J correlation between H-4 and C-1′. H-1″of the prenyl group was seen to have a cross peak with C-6 (^2J) and a ^3J correlation with C-7 and C-5. Hence, the attachment of this prenyl side chain to C-6 is obvious. C-7 was concluded to be bonded to an OH group from its ^3J correlations with C-8 and C-6 and its ^2J correlation with C-7. The methoxyl protons correlated to C-5 via a ^3J correlation hence proving its attachment. The doublet signal at δ 2.74, which integrated for



(1)

Fig.1: HMBC correlations in benjaminin (1)

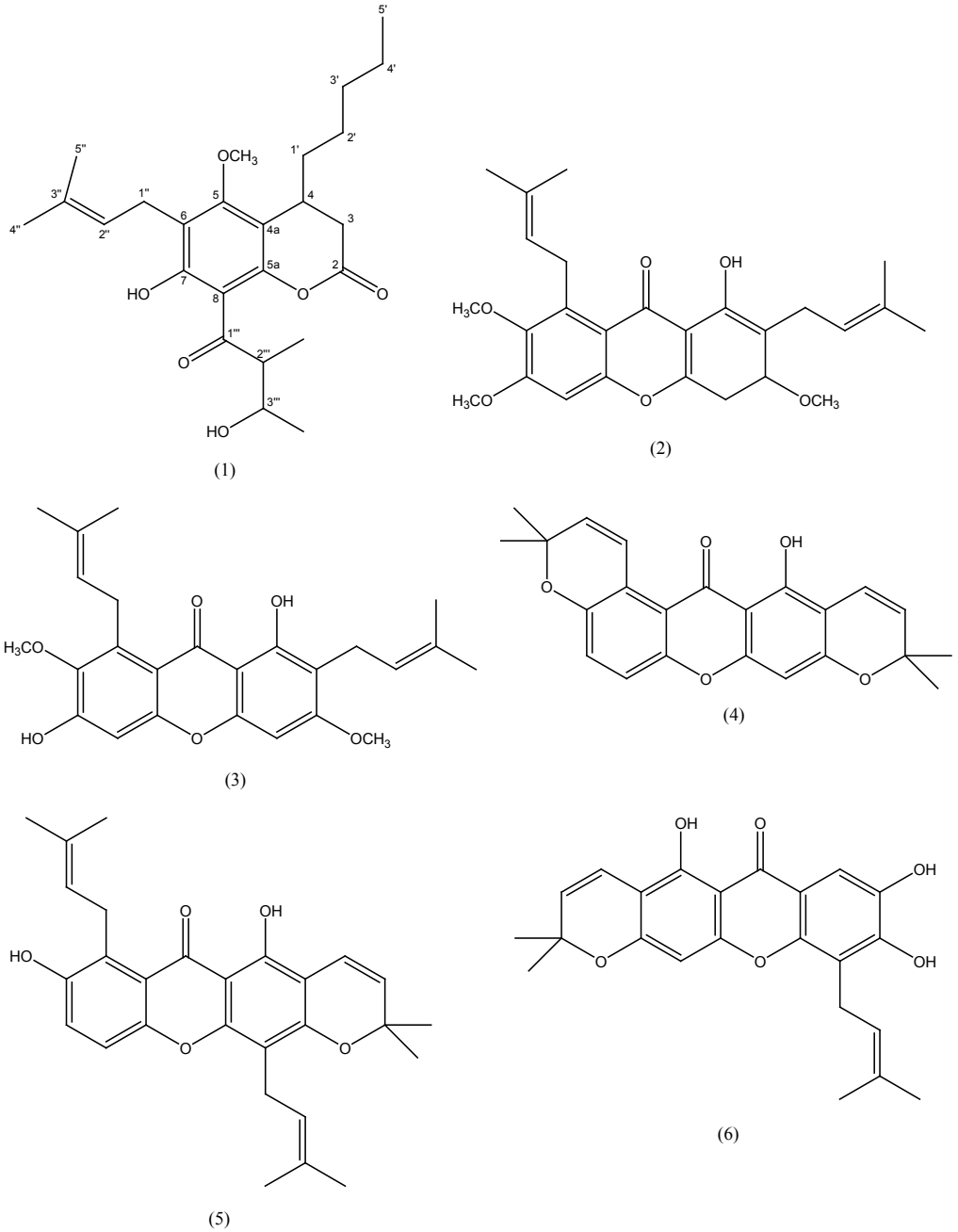


Fig.2: Structures of compounds 1-6

2 protons and correlated to C-2 and C-4 via ^{2}J correlations and to C-4a via a ^{3}J correlation, indicated C-3 to be a methylene carbon. The HMBC correlation of the methoxyl proton at δ 3.72 with δ 164.96 (C-5) confirmed its attachment at C-5. Hence, the remaining carbon, which is C-8, could be shown to be attached to a 3-hydroxy-2-methylbutanoyl moiety via HMBC correlations (see Fig.1). The C-2″′proton gave cross peaks with the C-2″′ methyl and C-3″′ methyl groups thus justifying its location. Meanwhile, a HMBC correlation was observed between the C-3″′ methine proton and the carbonyl carbon at position C-1″′. Thus, compound **1** was deduced to be benjaminin with the IUPAC name 7-hydroxy -8-(3-hydroxy-2-methylbutanoyl)-5-methoxy-6-(3-methylbut-2-enyl)-4-pentylchroman-2-one.

CONCLUSION

The detailed isolation work on the stem bark of *Calophyllum benjaminum* and *Calophyllum javanicum* have resulted in one new coumarin benjaminin (1), five xanthones fuscaxanthone C (2), β-mangostin (3), thwaitesixanthone (4), dombakinaxanthone (5), and caloxanthone A (6), together with four common triterpenes friedelin (7), β-sitosterol (8), lupeol (9) and stigmasterol (10). There was no report available on this particular plant before.

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