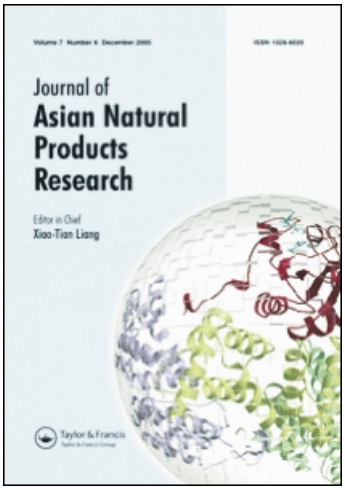

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Daphnifolin, a new xanthone from *Mesua daphnifolia* (Guttiferae)

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Note

Daphnifolin, a new xanthone from *Mesua daphnifolia* (Guttiferae)

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A new tetraoxygenated xanthone, daphnifolin (1,3,5-trihydroxy-4-methoxyxanthone), along with three other xanthones, were isolated from the stem bark extracts of *Mesua daphnifolia*. Their structures were characterized on the basis of 1D and 2D NMR spectral data.

Keywords: *Mesua daphnifolia*; Guttiferae; Xanthone; Daphnifolin

1. Introduction

Mesua, a small genus of stove evergreen shrubs, belongs to the Guttiferae family. Plants from this family are known to be abundant sources of oxygenated and prenylated xanthones. Until today, only a few studies have been done on the *Mesua* species. Most of these studies are related only to the species *Mesua ferrea* [1–6], *Mesua racemosa* [7] and *Mesua thwaitesii* [8]. These studies have led to the isolation of xanthones [1–3,8], coumarins [4,5,7], biflavonoids [6] and triterpenoids [6]. However, there has been no report on the bioactivity of these secondary metabolites. We recently worked on the stem bark of *M. daphnifolia* and a new xanthone, daphnifolin, which when isolated is 1,3,5-trihydroxy-4-methoxyxanthone. This paper reports the isolation and identification of daphnifolin and three other xanthones from the stem bark of *M. daphnifolia*.

2. Results and discussion

Daphnifolin, 1,3,5-trihydroxy-4-methoxyxanthone (**1**), was isolated as yellow crystals with a mp 240–242°C. This compound gave a dark green colour with methanolic ferric chloride, indicating it to be a phenolic compound. The UV spectrum exhibited characteristic absorption bands of a xanthone. The IR spectrum showed absorption bands at ν_{max} 3470

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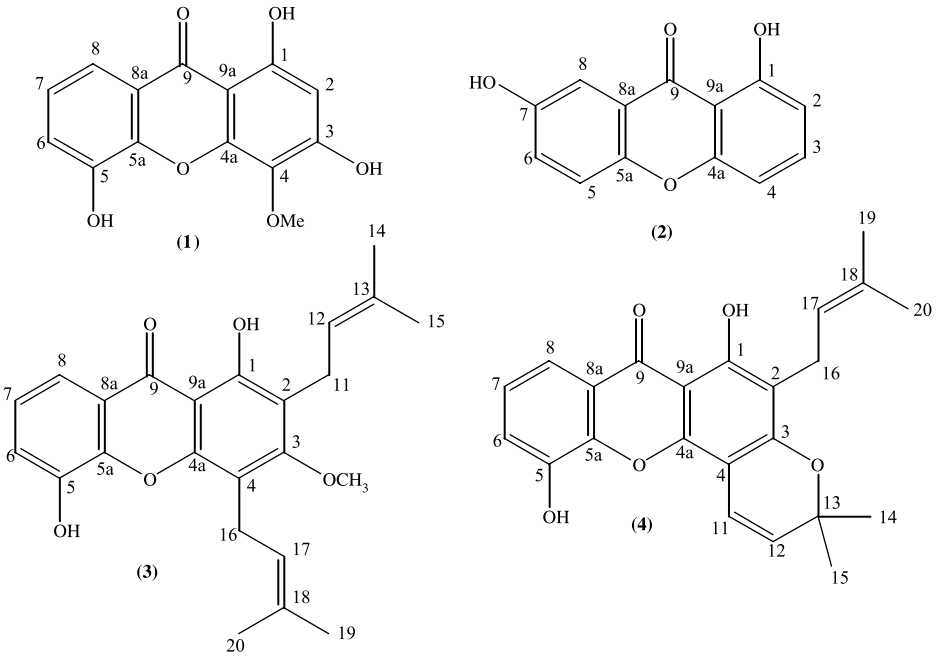
(O—H), 1658 (chelated C═O), 1582 (aromatic ring), 1218 (C—O) cm^{-1} and the EI-MS gave a molecular ion peak at *m/z* 274, corresponding to the molecular formula $C_{14}H_{10}O_6$.

The ^1H NMR spectrum of daphnifolin exhibited a downfield singlet at δ 13.23 for the chelated hydroxyl group attached to C-1. The aromatic region of the spectrum indicated three signals at δ 7.63 (1H, dd, $J = 7.4$, 1.8 Hz), 7.30 (1H, dd, $J = 7.4$, 1.8 Hz) and 7.24 (1H, t, $J = 7.4$ Hz) which were assigned to the aromatic protons H-8, H-6 and H-7, respectively.

The lone aromatic proton H-2 gave a singlet at δ 6.51 and the remaining singlet at δ 3.83 (3H, s) was therefore attributed to the methoxy protons at position 4. The ^{13}C NMR spectrum indicated a total of 14 carbon signals. The presence of a carbonyl carbon, 6 oxygenated aromatic carbons, 4 protonated aromatic carbons, 2 substituted aromatic carbons and a methoxy carbon was supported by DEPT spectral data.

The structure of daphnifolin was further confirmed by COSY, HSQC and HMBC spectral data (table 1). From the HMBC spectrum, it was observed that the lone aromatic proton (H-2) correlated to three oxygenated aromatic carbons (δ 159.4, δ 153.8, δ 131.5) and a substituted aromatic carbon (δ 103.9), which had to be C-1, C-3, C-4 and C-9a, respectively. Both the protons H-6 and H-8 correlated to a substituted aromatic carbon (δ 146.1), that is, C-5a (figure 1). Connectivity was also observed between proton H-8 and carbon C-9, and thus confirmed the location of the hydroxyl group at C-5. The presence of the ABX system protons in the xanthone ring B was confirmed by the $^1H—^1H$ COSY spectral data, which showed correlations between H-6 and H-7, and H-7 and H-8. This was further supported by their similar coupling constant value in the ^1H NMR spectrum. The structure of daphnifolin was therefore unambiguously assigned to be 1,3,5-trihydroxy-4-methoxyxanthone.



The other three xanthones **2**, **3** and **4** had spectral data that agree with published data.

Table 1. ^{1}H NMR and ^{13}C NMR data for 1,3,5-trihydroxy-4-methoxyxanthone (**1**) and their 2D correlations.

Position	δH	δC	*^{1}H-^{1}H COSY*	*HMBC (correlation)*
1	–	159.4	–	–
2	6.51 (1H, s)	94.8	–	C-1 (^{2}J), 3(^{2}J), 4 (^{3}J), 9a (^{3}J)
3	–	153.8	–	–
4	–	131.5	–	–
4a	–	146.9	–	–
5	–	155.3	–	–
6	7.30 (1H, dd, $J = 7.4$, 1.8 Hz)	121.3	7.24 (H-7)	C-5a (^{3}J)
7	7.24 (1H, t, $J = 7.4$ Hz)	124.8	7.30 (H-6), 7.63 (H-8)	–
8	7.63 (1H, dd, $J = 7.4$, 1.8 Hz)	116.0	7.24 (H-7)	C-5a (^{3}J), 9(^{3}J)
8a	–	121.7	–	–
9	–	182.1	–	–
9a	–	103.9	–	–
5a	–	146.1	–	–
4-OMe	3.83 (3H, s)	60.7	–	C-4 (^{3}J)
1-OH	13.09 (1H, s)	–	–	–

3. Experimental

3.1 General experimental procedures

Infrared spectra were measured in KBr/NaCl pellets on a Perkin-Elmer FTIR Spectrum BX spectrometer. EI-MS were recorded on a Shimadzu GCMS-QP5050A spectrometer. NMR spectra were obtained using a Unity INOVA 500 MHz NMR/JEOL 400 MHz FT NMR spectrometer using tetramethylsilane (TMS) as internal standard. Ultraviolet spectra were recorded on a Shimadzu UV-160A, UV-Visible Recording Spectrophotometer.

3.2 Plant material

The stem bark of *Mesua daphnifolia* was collected from Fraser's Hill in Pahang, Malaysia. The plant was identified by Dr. Rusea Go of the Biology Department, University Putra Malaysia, Malaysia. A voucher specimen (specimen no. SK96/02) is deposited at the same department.

3.3 Extraction and isolation

The powdered stem bark of *M. daphnifolia* (2.0 kg) was extracted successively with n-hexane, chloroform and acetone. The acetone extract of *M. daphnifolia* (16.0 g) was

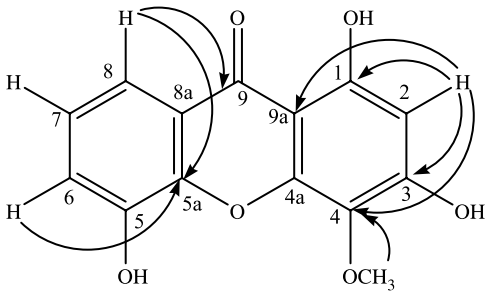


Figure 1. HMBC correlations for daphnifolin (**1**).

subjected to silica gel column chromatography and eluted with hexane, hexane/chloroform, chloroform, chloroform/acetone and acetone. Daphnifolin (1,3,5-trihydroxy-4-methoxy-xanthone) (**1**) (5 mg) and euxanthone (**2**) (8 mg) were obtained. The hexane extract of *M. daphnifolia* (16.0 g) was chromatographed on a silica gel column, eluted with hexane, hexane/chloroform, chloroform, chloroform/acetone and acetone to give 50 fractions. Further separations using Sephadex LH-20 column chromatography and eluting with methanol yielded cudraxanthone G (**3**) (10 mg) and ananixanthone (**4**) (12 mg).

3.3.1 Daphnifolin, 1,3,5-trihydroxy-4-methoxyxanthone (1). Yellow crystals, mp 240–242°C. UV (EtOH) λ_{max} nm (log ε): 207.0 (0.65), 222.0 (0.69), 244.5 (0.90), 313 (0.49). IR ν_{max} cm^{-1} (KBr): 3470, 2948, 1658, 1582, 1218. EI-MS *m/z* (rel. int.): 274 [M^+, 100], 259 (90), 245 (11), 231 (66), 202 (14), 147 (9), 136 (23), 118 (3), 93 (12), 77 (7), 65 (12), 51 (15). HREI-MS: 274.04817 [M^+] (calcd for $C_{14}H_{10}O_6$, 274.04774). ^{1}H NMR and ^{13}C NMR: see table 1.

3.3.2 Euxanthone (2). Yellow needles, mp 237–238°C. UV (EtOH) λ_{max} nm (log ε): 205.0 (0.44), 235.5 (0.84), 260.0 (1.05), 286.5 (0.21), 386.5(0.21). EI-MS *m/z* (rel. int.): 228 [M^+, 100], 200 (17), 171 (4), 144 (7), 136 (3), 115 (18), 107 (7), 89 (6), 72 (5), 63 (23), 53 (4), 43 (5). IR, ^{1}H NMR and ^{13}C NMR data were identical to literature values [1].

3.3.3 Cudraxanthone G (3). Fine yellow needles, mp 130–132°C. UV (EtOH) λ_{max} nm (log ε): 215.0 (1.00), 259.0 (1.58), 315.0 (0.47), 379.5 (0.47). EI-MS *m/z* (rel. int.): 394 [M^+, 37], 379 (11), 351 (100), 339 (90), 323 (29), 309 (10), 295 (23), 281 (18), 269 (40), 265 (6), 241 (5), 169 (6), 152 (6), 137 (11), 115 (8), 107 (6), 91 (5), 77 (10), 69 (13), 43 (14), 41 (36). IR, ^{1}H NMR and ^{13}C NMR data were identical to literature values [9].

3.3.4 Ananixanthone (4). Fine yellow needles, mp 172–173°C. UV (EtOH) λ_{max} nm (log ε): 253.5 (1.04), 272.0 (0.98), 331.5 (0.38), 383.5 (0.09). EI-MS *m/z* (rel. int.): 378 [M^+, 37], 364 (23), 363 (100), 336 (26), 323 (31), 307 (29), 154 (11). IR, ^{1}H NMR and ^{13}C NMR data were identical to literature values [10].

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