SUPPLEMENTARY MATERIAL

A New Flavone from Malaysia Borneo *Marsdenia tinctoria*

Nur Atiqah Mohd Nasuha and Yeun-Mun Choo*

Chemistry Department, Faculty of Science, University of Malaya, Kuala Lumpur 50603, Malaysia.

Marsdenia tinctoria is an indigo producing plant commonly found in Borneo, Malaysia. In the present study, one new flavone kapitone (**1**) and three known compounds, *i.e.* 3,2'-dihydroxyflavone (**2**), 1-methyl cyclobutene (**3**) and dimethyl isatoate (**4**) were isolated from the Malaysia Borneo *M. tinctoria* R. Br. (Apocynaceae). These compounds were isolated and characterized using extensive chromatographic and spectroscopic methods.

Keywords: *Marsdenia tinctoria*, flavone, kapitone, 2,3-bis(2-hydroxyphenyl)-4H-chromen-4-one, spectroscopic analysis

Kapitone (**1**)

Purplish amorphous solid; UV (EtOH) $\lambda_{\max}$ (log ϵ) 570 (3.19), 280 (3.39), 240 (3.58), 230 (3.57), 220 (3.58) nm; IR (NaCl) $\nu_{\max}$ 3274, 2927, 2855, 1687, 1545, 1462, 1322 cm^{-1} ; HRESIMS m/z 313.1343 [M - OH]⁺ (calcd for C₂₁H₁₄O₄ - OH, 312.0865) and 312.1311 [M - H₂O]⁺ (calcd for C₂₁H₁₄O₄ - H₂O, 312.0786).

NMR data of kapitone (**1**)

No.	δ_{H}	δ_{C}	HMBC
2		159.5	6'
3		107.4	6''
4		187.7	5
4a		121.0	6, 8
5	7.79 brd (8)	125.8	7
6	7.07 brt (8)	122.3	8
7	7.56 brt (8)	137.0	5
8	7.13 brd (8)	112.5	6

8a		151.4	5, 7
1'		120.7	3', 5'
2'		151.2	4', 6'
3'	7.87 brd (8)	127.6	5'
4'	7.82 td (8,1)	134.7	6'
5'	7.55 brt (8)	127.5	3'
6'	8.46 dd (8,1)	127.6	4',
1''		123.7 ^a	3'', 5''
2''		138.0	4'', 6''
3''	8.70 brd (8)	116.8	5''
4''	7.51 td (8,1)	129.9	6''
5''	7.43 td (8,1)	126.8	3''
6''	9.27 brd (8)	125.7	4'', 5''
2' -OH	11.78 brs		

^aNot detected in ¹³C NMR spectrum. Value obtained from HMBC spectrum

3,2'-Dihydroxyflavone (2)

Yellowish oil; UV (EtOH) $\lambda_{\max}$ (log ϵ) 390 (3.21), 310 (3.38), 250 (4.07), 220 (3.86) nm; IR (NaCl) $\nu_{\max}$ 3387, 2926, 1697, 1598, 1459, 1317 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ 8.64 (1H, br d, J = 8 Hz, H-8), 8.54 (1H, dd, J = 8 and 1 Hz, H6'), 8.04 (1H, br d, J = 8 Hz, H-3'), 7.92 (1H, br d, J = 8 Hz, H-5), 7.86 (1H, td, J = 8 and 1 Hz, H-4'), 7.79 (1H, td, J = 8 and 1 Hz, H-7), 7.68 (1H, td, J = 8 and 1 Hz, H-5'), 7.43 (1H, td, J = 8 and 1 Hz, H-6). ¹³C NMR (CDCl₃, 150 MHz) δ 182.7 (C, C-4), 158.1 (C, C-2), 146.4 (C, C-2'), 146.2 (C, C-8a), 137.8 (CH, C-7), 134.7 (CH, C-4'), 130.1 (CH, C-3'), 129.7 (CH, C-5'), 126.9 (CH, C-6'), 126.5 (CH, C-6), 124.9 (CH, C-5), 123.9 (CH, C-1'), 121.9 (C, C-4a), 117.4 (CH, C-8); HRESIMS m/z 237.1991 [M* - OH]⁺ (calcd for C₁₅H₁₀O₄ - OH, 237.0552) and 236.1541 [M* - H₂O]⁺ (calcd for C₁₅H₁₀O₄ - H₂O, 236.0473).

1-Methylcyclobutene (3)

Yellowish oil; UV (EtOH) $\lambda_{\max}$ (log ϵ) 230 (2.55) and 215 (2.73) nm; IR (NaCl) $\nu_{\max}$ 2968, 2930, 1574, 1456, 1379, 1238, 1166, 1083, 756 cm⁻¹; ¹H NMR (CDCl₃, 600 MHz) δ 5.12 (1H, t, J = 7 Hz, H-2), 2.04 (4H, m, CH₂-3 and CH₂-4), 1.68 (3H, s, 1-Me). ¹³C NMR (CDCl₃, 150 MHz) δ 135.3 (C, C-1), 125.1 (CH, C-2), 32.3 (CH₂, C-4), 26.5 (CH₂, C-3), 23.5 (CH₃, 1-Me).

Dimethyl isatoate (4)

Yellowish oil; UV (EtOH) $\lambda_{\max}$ (log ϵ) 315 (2.77), 245 (3.32), 220 (3.70) nm; IR (NaCl) $\nu_{\max}$ 3400, 3280, 2929, 2857, 1745, 1524, 1458, 1245, 1219 cm^{-1} ; ^1H NMR (CDCl_3 , 600MHz) δ 10.35 (1H, br s, NH), 8.43 (1H, dd, $J = 8$ and 1 Hz, H-6), 8.01 (1H, dd, $J = 8$ and 1 Hz, H-3), 7.53 (1H, td, $J = 8$ and 1 Hz, H-5), 7.03 (1H, td, $J = 8$ and 1 Hz, H-4), 3.90 (3H, s, COOMe); 3.79 (3H, s, NHCOOMe); ^{13}C NMR (CDCl_3 , 150MHz) δ 168.2 (C, COOMe), 154.0 (C, NHCOOMe), 141.5 (C, C-1), 134.26 (CH, C-5), 130.3 (CH, C-3), 120.9 (CH, C-4), 118.2 (CH, C-6), 114.5 (C, C-2), 51.9 (C, COOMe and NHCOOMe); HRESIMS m/z 210.122 $[\text{M}+\text{H}]^+$ (calcd for $\text{C}_{10}\text{H}_{11}\text{NO}_4 + \text{H}$, 210.0766).

List of Figure:

Figure S1: HMBC of kapitone (1)

Figure S2: ESI-MS spectrum of kapitone (1)

Figure S3: IR spectrum of kapitone (1)

Figure S4: UV spectrum of kapitone (1)

Figure S5: ^1H NMR spectrum (CDCl_3 , 600 MHz) of kapitone (1)

Figure S6: ^{13}C NMR spectrum (CDCl_3 , 150 MHz) of kapitone (1)

Figure S7: HMBC spectrum (CDCl_3 , 600 MHz) of kapitone (1)

Figure S8: HSQC spectrum (CDCl_3 , 600 MHz) of kapitone (1)

Figure S9: ^1H NMR spectrum (CDCl_3 , 600 MHz) of 3,2'-dihydroxyflavone (2)

Figure S10: HMBC spectrum (CDCl_3 , 600 MHz) of 3,2'-dihydroxyflavone (2)

Figure S11: HSQC spectrum (CDCl_3 , 600 MHz) of 3,2'-dihydroxyflavone (2)

Figure S12: ^1H NMR spectrum (CDCl_3 , 600 MHz) of 1-methylcyclobutene (3)

Figure S13: HMBC spectrum (CDCl_3 , 600 MHz) of 1-methylcyclobutene (3)

Figure S14: HSQC spectrum (CDCl_3 , 600 MHz) of 1-methylcyclobutene (3)

Figure S15: ^1H NMR spectrum (CDCl_3 , 600 MHz) of dimethyl isatoate (4)

Figure S16: HMBC spectrum (CDCl_3 , 600 MHz) of dimethyl isatoate (4)

Figure S17: HQCC spectrum (CDCl_3 , 600 MHz) of dimethyl isatoate (4)

Figure S1: HMBC of kapitone (1)

Figure S2: ESI-MS spectrum of kapitone (1)

Figure S3: IR spectrum of kapitone (1)

Figure S4: UV spectrum of kapitone (1)

Figure S5: ^1H NMR spectrum (CDCl₃, 600 MHz) of kapitone (1)

Figure S6: ^{13}C NMR spectrum (CDCl_3 , 150 MHz) of kapitone (**1**)

Figure S8: HSQC spectrum (CDCl₃, 600 MHz) of kapitone (**1**)

Figure S9: ^1H NMR spectrum (CDCl_3 , 600 MHz) of 3,2'-dihydroxyflavone (**2**)

Figure S10: HMBC spectrum (CDCl₃, 600 MHz) of 3,2'-dihydroxyflavone (**2**)

Figure S11: HSQC spectrum (CDCl₃, 600 MHz) of 3,2'-dihydroxyflavone (2)

Figure S12: ^1H NMR spectrum (CDCl_3 , 600 MHz) of 1-methylcyclobutene (**3**)

Figure S13: HMBC spectrum (CDCl_3 , 600 MHz) of 1-methylcyclobutene (**3**)

Figure S14: HSQC spectrum (CDCl₃, 600 MHz) of 1-methylcyclobutene (**3**)

Figure S15: ^1H NMR spectrum (CDCl_3 , 600 MHz) of dimethyl isatoate (**4**)

Figure S16: HMBC spectrum (CDCl₃, 600 MHz) of dimethyl isatoate (4)

Figure S17: HSQC spectrum (CDCl₃, 600 MHz) of dimethyl isatoate (**4**)