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Flavonoids from the Leaves of *Melastoma malabathricum* L.

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ABSTRACT Chemical studies on the leaves of *Melastoma malabathricum* with white petals (senduduk putih) have been carried out. Purification of the methanolic extract by chromatographic methods afforded quercetin **1** and quercitrin **2**.

(*Melastoma malabathricum*, flavonoid, quercetin, quercitrin)

INTRODUCTION

Melastoma malabathricum L. (senduduk) is very common herbs or shrubs found throughout the tropic, in the moist parts, mostly from India, Thailand and Malaysia. The plants have been used in traditional Malay medicine for the treatment of diarrhoea, astringent, post-partum treatment and hemorrhoids [1].

Senduduk has at least three varieties, i.e. large, medium size and small flower with dark purple-magenta petals, light pink-magenta petals, and the rare variety white petals.

In our research, we have investigated the chemical components of the leaves of *M. malabathricum* with white flower that has miraculous healing properties [2], to the best of our knowledge there has been no report on the phytochemicals of this plant.

In this paper, we wish to report the isolation and structural elucidation of two flavonoids (**1-2**) from the methanol extract of the leaves of *M. malabathricum*.

EXPERIMENTAL

General

Mps. (uncorr.) were determined using Leica Gallen III apparatus. UV was recorded on Shimadzu UV-160 spectrophotometer in methanol. IR spectra were recorded on Perkin Elmer 1650 FTIR spectrophotometer. NMR spectra were recorded on JEOL JNH A500 Spectrometer measured at 500 MHz and 125 MHz, respectively. Vacuum Liquid Chromatography (VLC) and Column Chromatography (CC) were carried out using silica gel 230-400 mesh, Merck 9385 and 70-230 mesh, Merck 7734.

Plant Material

The plants were collected from Pontian, Johor, Malaysia in July 2002.

Extraction and Isolation

The dried and powdered leaves of *Melastoma malabathricum* (377.0 g) was extracted by soxhlet extractor using hexane, EtOAc and MeOH successively. Evaporation of the solvent gave a green gum (15.5 g) for hexane extract, a green gum (14.0 g) for EtOAc extract and a brown gum (40.1 g) for MeOH extract.

The MeOH extract was fractionated by VLC over silica gel 230-400 mesh using EtOAc with increasing polarity of MeOH to afford five fractions (1-5).

Fraction 1 was purified by CC using EtOAc-MeOH (9:1 to 2:8) to give compounds **1** (58.8 mg) and **2** (7.1 mg).

Quercetin 3-*O*-α-D-rhamnoside **1**. Yellowish needles, m.p. 174-176 °C; R_f 0.44 (EtOAc:MEOH/ 9:1); UV λ_{max} (MeOH) nm: 347, 305, 261, 200: +NaOMe, 391, 328, 269, 203: +NaOAc, 357, 266, 200: +NaOAc/H_3BO_3, 361, 260, 200: +$AlCl_3$, 414, 337, 321, 271, 195: +$AlCl_3$/HCl, 388, 345, 267, 198; IR (KBr) ν_{max} cm^{-1}: 3279, 1657 1600 1497, 1062, 999, 963; ^1H NMR (CD_3OD): δ 6.19 (d, 1H, J = 2.13 Hz, H-6),

6.36 (d, 1H, J = 2.13 Hz, H-8), 7.33 (d, 1H, J = 2.13 Hz, H-2'), 7.30 (dd, 1H, J = 2.13 Hz and 8.24 Hz, H-6'), 6.90 (d, 1H, J = 8.24 Hz, H-5'), 5.34 (d, 1H, J = 1.53 Hz, H-1"), 4.20 (m, 1H, H-2"), 3.7 (dd, 1H, J = 3.36 Hz and 9.46 Hz, H-3"), 3.32-3.33 (m, 2H, H-4" and H-5"), 0.93 (d, 3H, J = 5.10 Hz, H-6"); ^{13}C NMR (CD_3OD): δ 159.32 (C-2), 136.25 (C-3) 179.66 (C-4), 163.24 (C-5), 99.88 (C-6), 166.09 (C-7), 94.76 (C-8), 105.88 (C-8a), 123.01 (C-1'), 122.86 (C-2'), 149.83 (C-3'), 146.45 (C-4'), 116.39 (C-5'), 116.95 (C-6'), 103.57 (C-1"), 71.5 (C-2"), 72.04 (C-3"), 73.28 (C-4"), 71.92 (C-5"), 17.65 (C-6").

Quercetin **2**. Yellowish needles, m.p. 289-291°C dec.; R_f 0.7 (EtOAc); UV λ_{max} (MeOH) nm: 370, 359 255: +NaOMe 423 321, 277: +NaOAc 380, 359, 325, 270, 257: +NaOAc/H_3BO_3, 383, 325 314, 259: +$AlCl_3$, 440, 359, 332, 329, 306, 268: +$AlCl_3$/HCl, 418, 356, 353, 306, 264; IR (KBr) ν_{max} cm^{-1}: 3409, 1666, 1612, 1519, 1265; ^{1}H NMR (CD_3OD): δ 6.25 (d, 1H, J = 2.13 Hz, H-6), 6.51 (d, 1H, J = 2.13 Hz, H-8), 7.82 (d, 1H, J = 2.21 Hz, H-2'), 6.98 (d, 1H, J = 8.31 Hz, H-5'), 7.69 (dd, 1H, J = 2.21 Hz and 8.31 Hz, H-6'); ^{13}C NMR (CD_3OD): δ 176.79 (C-4), 162.22 (C-5), 99.11 (C-6), 164.90 (C-7), 94.42 (C-8), 157.76 (C-4a), 123.76 (C-1'), 115.75 (C-2'), 145.77 (C-3'), 148.29 (C-4'), 116.19 (C-5'), 121.43 (C-6').

RESULTS AND DISCUSSION

Dried leaves of *M. malabathricum* L. were extracted successively with hexane, ethyl acetate (EtOAc) and methanol (MeOH) by using soxhlet apparatus. The MeOH extract was subjected to several chromatographic techniques (vacuum liquid chromatography and column chromatography) to yield two flavonoids (**1-2**).

Ultraviolet spectrum of **1** in methanol showed absorption of 261 (band II) and 461 nm (band I) indicated that **1** is a flavonol [3]. A bathochromic shift (44 nm) was observed for band I after an addition of NaOMe indicating the presence of a free hydroxyl group at 4' position. A bathochromic shift (10 nm) in the presence of NaOAc showed the existence of a free hydroxyl group at 7 position. Addition of H_3BO_3 resulted in 10 nm bathochromic shift suggesting an existence of a free *ortho*-dihydroxyl group in ring B. Addition of $AlCl_3$/HCl gave a bathochromic shift of 41 nm for band I revealed a 5'-hydroxyl group.

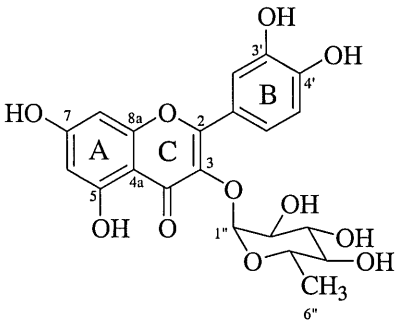
Infrared spectrum of compound **1** showed strong absorption bands at 3279 (OH), 1657 (C=O), 1600 (C=C aromatic) and a broad band at 1143-999 cm^{-1} indicating for glycosidic nature.

^{1}H NMR spectrum showed five aromatic signals at δ 6.19 (d, 1H, J = 2.13 Hz), 6.36 (d, 1H, J = 2.13 Hz), 7.33 (d, 1H, J = 2.13 Hz), 7.30 (dd, 1H, J = 2.13 Hz and 8.24 Hz) and 6.90 (d, 1H, J = 8.24 Hz) which were assigned to H-6, H-8, H-2', H-6' and H-5' respectively. These data were confirmed by ^{1}H-^{1}H COSY correlation. A multiplet signal at (0.93 – 5.34 ppm) was assigned to a sugar moiety. The methyl group appeared at δ 0.93 (d, 3H, J = 5.1 Hz) and an anomeric proton H-1" at δ 5.34 (d, 1H, J = 1.53 Hz) were suggested to an α-rhamnoside unit. The total assignment of the sugar protons, were carried out by ^{1}H-^{1}H COSY experiment.

The sugar moiety was confirmed by ^{13}C NMR spectrum, by the presence of an anomeric carbon at δ 103.5, four sugar carbons at δ 71.9-73.2 and a methyl group at δ 17.6. Beside the sugar signals, 15 carbons from δ 94.7 to 179.6 were assigned to the tetrahydroxylated flavonol unit. Based on its physical properties and comparison with the spectroscopic data in literature [4], compound **1** was identified as quercitrin (quercetin 3-*O*-α-D-rhamnoside).

The UV spectrum of flavonoid **2** showed an almost identical pattern to that of flavonoid **1**, except the presence of a peak in the region of 370 nm showed that flavonoid **2** has a free hydroxyl at C-3.

The ^{1}H NMR spectrum showed five aromatic signals at δ 7.82 (d, 1H, J = 2.21 Hz), 7.69 (dd, 1H, J = 2.21 Hz and 8.31 Hz), 6.98 (d, 1H, J = 8.31 Hz), 6.51 (d, 1H, J = 2.1 Hz) and 6.25 (d, 1H, J = 2.1 Hz) which were assigned to H-2', H-6', H-5', H-8, and H-6 respectively. Flavonoid **2** was identified as quercetin based on its physical properties and comparison of spectroscopic data of isolated compound from the leaves of *Leea guinensis* [4].



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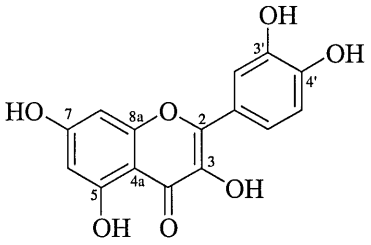

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REFERENCES

1. Burkill, I. H. (1966). *A Dictionary of the Economic Products of the Malay Peninsula.* Kuala Lumpur, Singapore: Government of Malaysia and Singapore by the Ministry of Agriculture and Co-Operatives, p. 1462-1464.
2. Corner, E. J. H. *Wayside Trees of Malaya.* (1951). **1**: 445-453.
3. Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970). *The Systematic Identification of Flavonoids.* Springer-Verlag. New York, Heidelberg, Berlin.
4. Beck, P. O. D., Dijoux, M. G., Cartier, G. and Mariote, A. M. (1998). *Phytochemistry.* **47**: 1171-1173