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FLAVONOLS AND COUMARINS FROM THE FRUIT OF *MURRAYA OMPHALOCARPA*[*]

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Key Word Index—*Murraya omphalocarpa*; Rutaceae; flavones; murrayanol; 5,4′-dihydroxy-3,6,7,3′,5-pentamethoxyflavone; 3,5,6,7,3′,4′,5′-heptamethoxyflavone; coumarins; coumurrayin; mexoticin; 5,7-dimethoxy-8-(3′-methyl-2′-oxobutyl) coumarin.

Abstract—Separation of the ethanolic extract of the fruit of *Murraya omphalocarpa* afforded a new flavonol, murrayanol, which was characterized as 5,4′-dihydroxy-3,6,7,3′,5′-pentamethoxyflavone, together with the known substances coumurrayin, mexoticin, 3,5,6,7,3′,4′,5′-heptamethoxyflavone, 5,7-dimethoxy-8-(3′-methyl-2′-oxobutyl) coumarin and sitosterol.

INTRODUCTION

During a study of Formosan folk medicines, the constituents of the shrub *Murraya omphalocarpa* were investigated. Ota *et al.* [1] have reported the alkaloid skimmianine from this plant. The present report describes the isolation and characterization of a new flavonol, murrayanol, and the known compounds coumurrayin, mexoticin, 5,7-dimethoxy-8-(3′-methyl-2′-oxobutyl)-coumarin, 3,5,6,7,3′,4′,5′-heptamethoxyflavone and sitosterol.

RESULTS AND DISCUSSION

The ethanolic extract of the fresh fruit of *M. omphalocarpa* was partitioned with ether. Subsequent separation of the ether extract was achieved using Si gel and alumina column chromatography affording six crystalline compounds, **1a**, **1b**, **1c**, **2a**, **2b**, and sitosterol, respectively. Compound **2b**, yellow needles, mp 236–237° and $C_{20}H_{20}O_9$ (M^+ 404 *m/e*), was recrystallized from MeOH. It gave a greyish green colour with $FeCl_3$ and a pale red colour with Mg–HCl, characteristic of a flavonoid. The IR spectrum (KBr) has characteristic absorption bands at 3350 (OH), 1642 (α,β-unsaturated carbonyl), 1619 and 1590 cm^{-1} (C=C, aromatic). The UV spectrum had maxima at 255, 267, 344 and 360 nm. A bathochromic shift with $AlCl_3$ and $AlCl_3$–HCl suggested the presence of a free 5-hydroxyl and a bathochromic shift at band I with NaOMe and NaOAc indicated that the 4-hydroxyl is unsubstituted [2]. The MS fragmentation [3-5] suggested the possibility of a 3-methoxyl, which was confirmed by the dark purple colour of **2b** on paper in UV light (365 nm), indicating that the 3-position is substituted. The NMR spectrum (C_5D_5N) showed three aromatic protons at δ 7.97 (2 H, *s*, C-2′ and C-6′) and 6.94 (1 H, *s*, C-8) and five methoxyl groups at 3.80 (3 H, *s*, OMe), 3.87 (6 H, *s*, 2 × OMe) and 4.01 (6 H, *s*, 2 × OMe). The methylation of **2b** with diazomethane gave colourless crystals, mp 156–157° (MeOH), which were compared with an authentic sample of 3,5,6,7,3′,4′,5′-heptamethoxyflavone (**2a**), by mp, IR and TLC. From the above data, **2b** (murrayanol) is characterized as a new flavonol, 5,4′-dihydroxy-3,6,7,3′,5′-pentamethoxyflavone. The other compounds were identified, by comparison with authentic samples, as coumurrayin (**1a**), mexoticin (**1b**), 5,7-dimethoxy-8-(3′-methyl-2′-oxobutyl) coumarin (**1c**), 3,5,6,7,3′,4′,5′-heptamethoxyflavone (**2a**) and sitosterol by mp, IR and TLC, respectively.

EXPERIMENTAL

All mps were uncorr. UV spectra were determined in EtOH and IR spectra recorded in KBr. NMR spectra were measured at 60 and 100 MHz with TMS as an internal standard. $CDCl_3$ was used as solvent unless otherwise stated. MS spectra were taken with a direct inlet system.

Extraction and isolation. Plant material. Murraya omphalocarpa was collected from Orchid Island, Taiwan, verified by Prof. C. S. Kuoh and a herbarium specimen is deposited at Chia-Nan Junior College of Pharmacy, Tainan, Taiwan, R.O.C. The EtOH extract of the fresh fruits (400 g) of *M. omphalocarpa* was partitioned with Et_2O, the subsequent Et_2O layer was evapd. to dryness and chromatographed on an Al_2O_3 column. The fractions eluted with n-C_6H_{12}, C_6H_6 and $CHCl_3$ afforded compounds **1a**, **1b** and β-sitosterol, respectively. The remaining absorbent was removed from the column, washed with 3% NaOH and the NaOH soln acidified with dil HCl and extracted with Et_2O. The Et_2O layer was evapd to give **2b**. The combined

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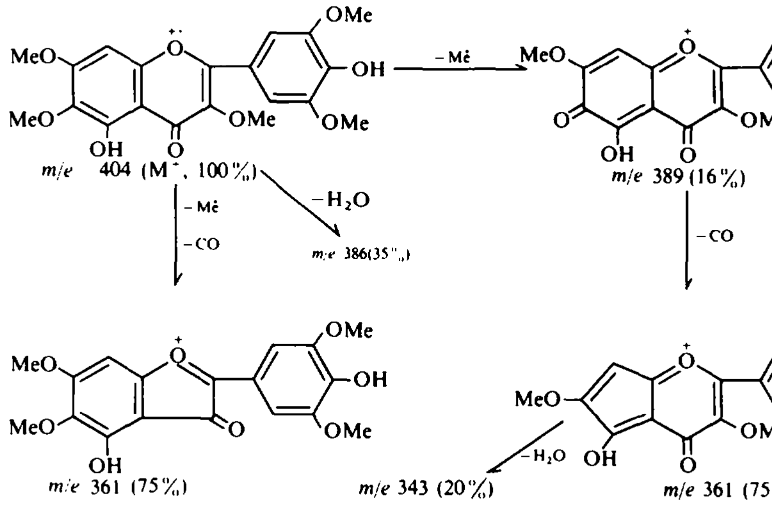
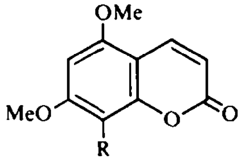
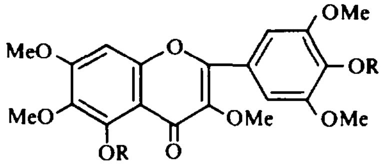
[*] Part V in the series "Studies on the Constituents of Formosan Folk Medicine". For Part IV see Wu, T. S. (1979) *J. Chin. Chem. Soc.* **26**, 25.





1a $R = CH_2CH = CMe_2$
1b $R = CH_2CHOHCOHMe_2$
1c $R = CH_2COCHMe_2$



2a R = Me
2b R = H

mother liquids of fractions **1a**, **1b**, **2b** and β-sitosterol were repeatedly applied to a Si gel column and eluted with *iso*-Pr_2O and *iso*-Pr_2O-Me_2CO (1:1) affording **1c** and **2a**, respectively.

1a (coumurrayin) [7, 10] was cryst. from Me_2CO as colourless needles, mp 155–157°. Found: C, 70.20; H, 6.53. $C_{16}H_{18}O_4$ requires: C, 70.05; H, 6.61%. The IR, NMR, UV and MS spectra agreed with an authentic sample. **1b** (mexoticin) was cryst. from Me_2CO as colourless needles, mp 190–191° (lit. 185°) [8]. Found: C, 62.50; H, 6.48. $C_{16}H_{20}O_6$ requires: C, 62.32; H, 6.54%. The IR, NMR, UV and MS spectra agreed with an authentic sample. **1c** (5,7-dimethoxy-8-(3′-methyl-2′-oxobutyl) coumarin) [9] was cryst. from Me_2CO as colourless needles, mp 129–130°. Found: C, 66.12; H, 6.85. $C_{16}H_{18}O_5$ requires: C, 66.19; H, 6.25%. The IR, NMR, UV and MS spectra agreed with an authentic sample **2a** (3,5,6,7,3′,4′,5′-heptamethoxyflavone) [10] was cryst. from MeOH as colourless needles, mp 156–157°. It gave a pale red color with Mg-HCl. Found: C, 61.12; H, 5.70. $C_{22}H_{24}O_9$ requires: C, 61.10; H, 5.59%. The IR, NMR, UV and MS spectra were superimposable with an authentic sample.

2b (murrayanol). UV: λ_{max} nm (log ε): 255 (4.28), 267 (4.26), 344 (inf 4.29), 360 (4.30); $+AlCl_3$: 263, 275, 366, 420; $+AlCl_3$ + HCl: 263, 275, 367, 420; +NaOMe: 257, 338, 413; +NaOAc: 255, 270 (sh), 335 (sh), 376, 410. IR ν_{max} cm^{-1}: 3350 (OH), 1642 (C=O), 1619, 1580 (C=C). ^1HNMR: (C_5D_5N, 100 MHz): δ 6.94 (1 H, s, C-8), 7.97 (2 H, s, C-2′ and C-6′), 3.80 (3 H, s, OMe), 3.87 (6 H, s, 2 × OMe), 4.01 (6 H, s, 2 × OMe). Found: C, 59.58; H, 4.86. $C_{20}H_{20}O_9$ requires: C, 59.40; H, 4.99%. MS (*m/e*): M^+ 404 (100), 389 (16), 386 (35), 371 (29), 361 (75), 343 (20).

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