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REFERENCES

1. Lanzetta, R., Monaco, P., Previtera, L. and Simaldone, A. (1988) *Phytochemistry*, (in press).
2. Campbell, R. V. M., Crombie, L., Findley, D. A. R., King, R. W., Pattenden, G. and Whiting, D. A. (1975) *J. Chem. Soc. Perkin I* 897.
3. Crombie, L. King, R. W. and Whiting, D. A. (1975) *J. Chem. Soc. Perkin I* 913.
4. Altman, L. J., Ash, L., Kowerski, R. C., Epstein, W. W., Larsen, B. R., Rilling, H. C., Muscio, F. and Gregonis, D. E. (1972) *J. Am. Chem. Soc.* 3257.
5. Altman, L. J., Kowersky, R. C. and Laungani, D. R. (1978) *J. Am. Chem. Soc.* 6174.

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COUMARINS FROM THE LEAVES OF *MURRAYA PANICULATA*

TIAN-SHUNG WU

Department of Applied Chemistry, Providence College of Arts and Science, Taichung, Taiwan 40211, Republic of China

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Key Word Index—*Murraya paniculata* var. *omphalocarpa*; Rutaceae; coumarins; murrayanone; murraculatin.

Abstract—Two new coumarins, murrayanone and murraculatin, together with seven known coumarins have been isolated from the leaves of *Murraya paniculata* var. *omphalocarpa*. The structures of murrayanone and murraculatin were elucidated by spectroscopic methods.

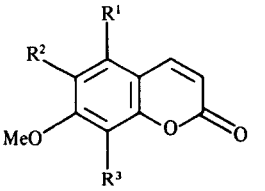
INTRODUCTION

In a previous paper [1], the isolation of a new coumarin, omphamurin, from the leaves of *Murraya paniculata* var. *omphalocarpa Hayata* was reported. Further examination of the leaves of this plant has now resulted in the isolation of 10 further coumarins, two (**1** and **2**) of which are new coumarins.

RESULTS AND DISCUSSION

Murrayanone (**1**), $C_{17}H_{20}O_6$ ($[M]^+$, *m/z* 306), gave IR absorption bands at 1710 (saturated ketone), 1695 (conjugated δ-lactone) and 1590 cm^{-1} (aromatic). Its UV spectrum [λ_{max} 230.5 (sh), 253.5 (sh) and 305.5 nm] was very similar to that of murragleinin [2], i.e. characteristic of a 5,6,7-trioxygenated coumarin (5,6,7-trimethoxycoumarin): λ_{max}^{MeOH} nm: 224 (sh), 253 (sh), 322; λ_{min}^{MeOH} nm: 262. 5,7,8-Trimethoxycoumarin: λ_{max}^{MeOH} nm: 222 (sh), 260, 318; λ_{min}^{MeOH} nm: 236, 273). The ^1H NMR spectrum of **1** had a pair of doublets ($J = 9.7$ Hz) at δ 6.25 and 7.94. The downfield signal (δ 7.94) confirmed the coumarin moiety and the presence of an oxygen in position 5 [3]. Three sharp singlets at δ 3.87, 3.90 and 4.01 due to nine protons suggested the presence of three methoxy groups. A 3-methyl-2-oxobutyl side chain was indicated by the ^1H NMR data [δ 1.23 (6H, *d*, $J = 6.9$ Hz), 2.85 (1H, *hept*, $J = 6.9$ Hz) and 3.96 (2H, *s*)] and mass fragmentation ions at *m/z* 249 $[M-COCH(Me)_2]^+$ and 235 $[M-CH_2COCH(Me)_2]^+$. According to the above data, murrayanone could be formulated as 5,6,7-trimethyoxy-8-(3′-methyl-2′-oxobutyl) coumarin (**1**).

Murraculatin (**2**), $C_{16}H_{18}O_6$, showed the UV absorption characteristics of a 7-alkoxycoumarin [4, 5]. Strong IR absorption bands at 3400 (OH) and 1705 cm^{-1} were indicative of a carboxylic group, and bands at 1690 and 1595 cm^{-1} confirmed the presence of a δ-lactone group



1 $R^1 = R^2 = OMe$, $R^3 = CH_2COCH(Me)_2$
2 $R^1 = OMe$, $R^2 = H$, $R^3 = CH_2C(Me)_2COOH$
3 $R^1 = OMe$, $R^2 = H$, $R^3 = CH_2C(Me)_2COOMe$
7 $R^1 = R^2 = H$, $R^3 = CHCOCH(Me)_2$ | $OCOCH_2CH(Me)_2$

and an aromatic nucleus respectively. The ^{1}H NMR spectrum of **2** displayed characteristic signals for two methyl groups (δ 1.22, 6H, *s*), benzylic methylene protons (δ 3.09, 2H, *s*), two methoxy groups (δ 3.84, 3.92, each 3H, *s*) and the C-3, C-4 protons of the coumarin nucleus (δ6.11 and 7.96, each 1H, *d*, $J = 10$ Hz), and a singlet aromatic proton (δ 6.29, H-6). Since the lone aromatic proton at δ 6.29 was very similar to that of 5,7-dimethoxy-8-alkylcoumarin ($\cong \delta$6.30) [3] and appeared at a higher field than the one in 5,7-dimethoxy-6-alkylcoumarin ($\cong \delta$ 6.50), [13] it had to be located at C-6. The above spectral data, coupled with the mass fragments at *m/z* 306 $[M]^+$ and 219 $[M-C(Me)_2COOH]^+$, and the preparation of the methyl derivative **3** by treatment of **2** with CH_2N_2, led to structure **2** for murraculatin.

In addition to the two new coumarins, coumurrayin (**4**) [6], mexoticin (**5**) [6], seselinal (**6**) [7], (+)-paniculatin (**7**) [8], 5,7-dimethoxy-8-(3′-methyl-2′-oxobutyl) coumarin (**8**) [6], mupanidin (**9**) [9] and (±)-7-methoxy-8-(2′-hydroxy-1′-methoxy-3′-methyl-3′-butyl) coumarin (**10**) [10–12] were isolated and characterized.

EXPERIMENTAL

Mps: uncorr; ^{1}H NMR; $CDCl_3$, except where noted, TMS as int. standard; MS: direct inlet; UV: MeOH; IR: $CHCl_3$, unless otherwise stated.

Plant material. Murraya paniculata var. *omphalocarpa* was collected from Orchid Island (Lan-Yu) in Sept. 1985, and verified by Prof. C.-S. Kuoh. A specimen is deposited in the Herbarium of Cheng-Kung University, Tainan, Taiwan, Republic of China.

Extraction and separation. Air-dried and powdered leaves (1.2 kg) of *M. paniculata* var. *omphalocarpa* were exhaustively extracted (× 3) with MeOH. The MeOH extract was concd and partitioned between $CHCl_3$ and H_2O. The $CHCl_3$ extract was chromatographed on silica gel and eluted exhaustively with gradients of C_6H_6–Me_2CO. Fraction 1–4 was rechromatographed on silica gel and eluted with *n*-hexane–EtOAc (4:1) to afford successively **7** (95 mg), **4** (368 mg) and Mo (52 mg). Fraction 5–9 was repeatedly chromatographed on silica gel with C_6H_6–Me_2CO (9:1) as eluant to give **8** (27 mg) and **1** (7 mg) respectively. Fraction 10–14 was treated similarly to obtain successively **6** (32 mg), **10** (294 mg), **9** (81 mg) and **5** (22 mg). Fraction 15–19 was also subjected to silica gel CC and elution with $CHCl_3$–Me_2CO (9:1) to yield **2** (21 mg).

Murrayanone **(1).** Colourless syrup. Calcd for $C_{17}H_{20}O_6$ $[M]^+ = m/z$ 320.1258; Found: 320.1220. UV λ_{max} nm: 230.5 (sh), 253.3 (sh) and 305.5; IR ν_{max} cm^{-1}: 1710, 1695, 1590, 1130, 1105 and 1035; MS *m/z* (rel. int.): 320 $[M]^+$ (30), 250 (44), 249 (100), 235 (19), 234 (26), 206 (2), 204 (4), 163 (3), 120 (2) and 71 (6).

Murraculatin **(2).** Colourless needles, mp 217–218° (Me_2CO). Calcd for $C_{16}H_{18}O_6$ $[M]^+$ *m/z* 306.1103; Found: 306.1111. UV λ_{max} nm (log ε): 240 (3.78), 253 (3.89), 261.2 (4.00), and 326.9 (4.12); IR ν_{max}^{KBr} cm^{-1}: 3400, 1705, 1690, and 1595; MS *m/z* (rel.int): 306$[M]^+$ (6), 219 (100), 162 (3), 161 (15), and 89 (2).

Methylation of murraculatin **(2).** Murraculatin (10 mg) was treated with excess CH_2N_2 in Et_2O (20 ml), and left overnight. The soln was evaporated to leave a colourless syrup which was crystallized from *n*-hexane to give colourless needles of **3**, mp 149–151°. UV λ_{max} nm: 251, 261.1 and 324.4; IR ν_{max} cm^{-1}: 1720 and 1600; ^{1}H NMR δ: 1.20 (6H, *s*, 2 × Me), 3.03 (2H, *s*, 1′-CH_2), 3.65 (3H, *s*, COOMe), 3.85 (3H, *s*, Ar–OMe), 3.92 (3H,*s*,Ar–OMe), 6.09 (1H, *d*, $J = 10$ Hz, H-3), 6.27 (1H, *s*, H-6), and 7.93 (1H, *d*, $J = 10$ Hz, H-4); MS *m/z*: 320 $[M]^+$, 290, 261, 219 (100%), 189 and 161.

(+)-Paniculatin **(7).** Colourless needles, mp 82–84° (*n*-hexane), $[\alpha]_D$ +70° ($CHCl_3$; *c* 0.86). UV λ_{max} nm: 247.9, 257.1 and 320.2; IR ν_{max} cm^{-1}: 1710 and 1600; ^{1}H NMR δ: 0.97 (6H, *d*, $J = 6.3$ Hz, 4″, 5″-Me), 1.06 and 1.20 (each 3H, *d*, $J = 7$ Hz, 4′, 5′-Me), 1.40–1.90 (1H, *m*, 3″-H), 2.00–2.50 (2H, *m*, 2″-CH_2-), 2.88 (1H, *hept*, $J = 7$Hz, 3′-H), 3.96 (6H, *s*, 2 × OMe), 6.22 (1H, *d*, $J = 10$ Hz, H-3), 6.92 (1H, *d*, $J = 9$ Hz, H-6), 6.94 (1H, *s*, 1′-H), 7.54 (1H, *d*, $J = 9$ Hz, 5-H) and 7.68 (1H, *d*, $J = 10$ Hz, 4-H); MS *m/z*: 360 $[M]^+$, 289, 231, 219, 205 (100%), 190 and 189.

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REFERENCES

1. Wu, T. S. (1981) *Phytochemistry* **20**, 178.
2. Wickramaratne, D. B. M., Kumar, V. and Balasubramaniam, S. (1984) *Phytochemistry* **23**, 2964.
3. Steck, W. and Mazurek, M. (1972) *Lloydia* **35**, 418.
4. Smith, E., Hosanaky, N., Bywater, W. G. and Van Tamelen, E. E. (1975) *J. Am. Chem. Soc.* **79**, 3534.
5. Stanly, W. L., Waiss, A. C., Lundin, R. E., Jr. and Vannier, S. H. (1965) *Tetrahedron* **21**, 89.
6. Wu, T. S., Tien, H. J., Arisawa, M., Shimizu, M. and Morita, N. (1980) *Phytochemistry* **19**, 2227.
7. Banerjee, S. K., Gupta, B. D., Kumar, R. and Atal, C. K. (1980) *Phytochemistry* **19**, 281.
8. Steck, W. (1972) *Can. J. Chem.* **50**, 443.
9. Talapatra, S. K., Dutta, L. N. and Talapatra, B. (1973) *Tetrahedron* **29**, 2811.
10. Manandhar, M. D. (1980) *Indian J. Chem.* **19B**, 1006.
11. Chow, P. W., Duffield, A. M. and Jefferies, P. R. (1966) *Aust. J. Chem.* **19**, 483.
12. Imai, F., Kinoshita, T., Itai, A. and Sankawa, U. (1986) *Chem. Pharm. Bull.* **34**, 3978.
13. Sharma, P. N., Shoeb, A., Kapil, R. S. and Popli, S. P. (1981) *Phytochemistry* **20**, 335.