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INDOLE ALKALOIDS AND COUMARINS FROM THE ROOT BARK OF *MURRAYA PANICULATA* VAR. *OMPHALOCARPA*

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Key Word Index—*Murraya paniculata* var *omphalocarpa*, Rutaceae, indole alkaloids, murrayacarine, coumarins.

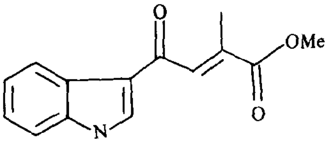
Abstract—A new indole alkaloid, murrayacarine together with 13 known compounds, 3-formylindole, omphalocarpin, 5,7-dimethoxy-8-(3′-methyl-2′-oxobutyl) coumarin, coumurrayin, murragleimin, omphamurin, murraol, (−)-murracarpin, (±)-murracarpin, mupanidin, mexoticin, murrangatin, and ferulyl esters were isolated from the root bark of *Murraya paniculata* var *omphalocarpa*. Their structures were characterized on the basis of the spectral analysis.

INTRODUCTION

In continuation of our investigation on the constituents of *Murraya paniculata* var. *omphalocarpa* Hayata, [1–4] we now report the isolation and structural elucidation of a new indole alkaloid, murrayacarine (**1**) together with 13 known compounds from the root bark of the same plant collected at Orchid island, Taiwan.

Murrayacarine (**1**) was isolated as pale yellow needles, mp 146–148°.The molecular formulae $C_{14}H_{13}NO_3$ was established by high resolution mass sectrometry. The presence of an indole nucleus of **1** were suggested by UV absorption maxima at 208.3, 246.7, 268.4, 275.4(sh) and 321.2 nm [5, 6], coupled with IR bands at 3350 (NH), 1595 and 1520 (aromatic C=C) cm^{-1}. This assumption was substantiated by ^{1}H NMR spectrum of **1**, in which the following characteristic signals were observed: (i) four mutually coupling aromatic protons at δ7.32 (2H, *m*, H-5,6), 7 42 (1H, *m*, H-7), and 8.42 (1H, *m*, H-4); (ii) a one proton doublet at δ7.82 ($J = 3$ Hz, H-2); (iii) a NH proton at δ8.62 (*br s*, exchangeable with D_2O) This ^{1}H NMR spectral pattern was similar to that of 3-formylindole (**2**) [7], indicating that the C-3 position of the indole moiety was substituted. On the other hand, a singlet signal at δ3.74 (3H, OMe) in the ^{1}H NMR spectrum together with IR bands at 1650 and 1720 cm^{-1}, indicated the presence of a α,β-unsaturated carbonyl group and a carbomethoxy group in the side chain. In addition, the ^{1}H NMR spectrum showed a three-proton doublet at δ2.15 ($J = 1.5$ Hz) and a one proton quartet at δ6.70 ($J = 1.5$ Hz), both having a long range coupling. The above data was in excellent accord with 3′-carbomethoxy-1′-oxo-2′-butene for the side chain which was also supported by the mass fragmentation ions at m/z 184 $[M-COOMe]^+$, 144 $[M-CH=C(Me)-COOMe]^+$, and 116 $[M-COCH=C(Me)COOMe]^+$. On the basis of the above results we assign structure **1** to murrayacarine.*

In addition to the new indole alkaloid, 3-formylindole (**2**)[7], omphalocarpin (**3**)[4], 5,7-dimethoxy-8-(3′-methyl-2′-oxobutyl) coumarin (**4**)[1, 3, 4], coumurrayin (**5**)[1, 4], murragleimin (**6**) [8], omphamurin (**7**) [2], murraol (**8**) [10], (−)-murracarpin (**9**) [4], (±)-murracarpin (**10**)[4], mupanidin (**11**)[10], mexoticin (**12**)[1, 3], murrangatin (**13**)[4] and ferulyl esters (**14**)[9] were also isolated and characterized.



1

EXPERIMENTAL

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

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. The fresh root bark (1 06 kg) of *M. paniculata* var. *omphalocarpa* were exhaustively extracted ×3 with hot MeOH The MeOH extract was concd and partitioned between $CHCl_3$ and H_2O The $CHCl_3$ extract was subjected to chromatography on a silica gel column and eluted with gradients of C_6H_6–Me_2CO to afford 6 fractions Fraction 1 was rechromatographed on silica gel and eluted with *n*-hexane–EtOAc (4 1) to give ferulyl esters (**14**, C number of ester = 18 ~ 26, 35 mg) and **5** (10 mg), respectively. Fraction 2 was also rechromatographed on a silica gel column and eluted with gradients of $CHCl_3$–Me_2CO to afford unknown **A** (1 mg), **4** (6 mg), **6** (1 mg), **7** (2 6 mg), **1** (1 mg), **8** (1 mg) and **12** (5 mg), successively The fraction 3 was repeatedly chromatographed on silica gel with $CHCl_3$–Me_2CO (30 1) as eluant to obtain unknown **B** (20 mg), unknown **C** (10 mg) and **13** (2 mg), respectively. Fraction 5 was chromatographed on 10% $AgNO_3$ silica gel column with C_6H_6–Me_2CO (9:1) as eluant to afford **2** (3 mg), **3** (35 mg), **10** (50 mg) and **9** (6 9 mg), successively Compound **11** (20 mg) was obtained from fraction 6

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*The geometric structure of the side chain was undetermined

Murrayacarine (1) Pale yellow needles, mp 146–148° ($CHCl_3$). HRMS. Calcd for $C_{14}H_{13}NO_3$ $[M]^+$ 243.0894, Found 243.0894 UV λ_{max} nm (log ε). 208.3 (4.17), 246.7 (3.73), 268.4 (3.68), 275.4 (3.65, sh) and 321.2 (3.74), IR ν_{max} cm^{-1} 3350, 1720, 1650, 1595, 1520 EIMS m/z (rel int) 243 (M^+, 48), 211 (24), 184 (24), 144 (100), 116 (33), 98 (29)

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