Phytochemistry, 1981, Vol. 20, pp. 178–179. © Pergamon Press Ltd. Printed in England. 0031-9422/81/0101-0178 $02.00/0

OMPHAMURIN—A NEW COUMARIN FROM *MURRAYA OMPHALOCARPA**

TIAN-SHUNG WU

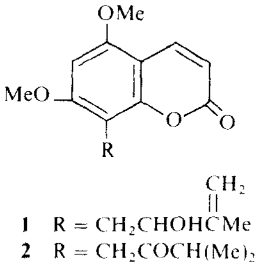
Chia-Nan Junior College of Pharmacy, Tainan, Taiwan, Republic of China

(*Received* 28 *February* 1980)

Key Word Index—*Murraya omphalocarpa*; Rutaceae; coumarin; omphamurin, 5,7-dimethoxy-8-(2′-hydroxy-3′-methyl-3′-butenyl) coumarin.

Abstract—A new coumarin, omphamurin, isolated from the *n*-hexane extract of the leaves of *Murraya omphalocarpa*, was characterized as 5,7-dimethoxy-8-(2′-hydroxy-3′-methyl-3′-butenyl) coumarin by chemical evidence and spectral data.

In a previous paper [1], we reported that the fruit of *Murraya omphalocarpa* contains flavonoids and coumarins. This paper reports a new coumarin, named omphamurin (**1**), obtained from the *n*-hexane extract of the leaves of the same plant. Omphamurin gave colourless needle crystals which were insoluble in dilute NaOH solution, with mp 131–132° (acetone), $[\alpha]_D^{20}$ −22° ($CHCl_3$, $c = 0.405$) and $C_{16}H_{18}O_5$ (*m/e* 290). The UV spectrum in methanol had maxima at 239, 254, 262 and 327 nm and there was no bathochromic shift by adding NaOH solution. The above properties of **1** suggested that it was a non-phenolic and 7-*O*-substituted coumarin [2–5]. This fact was confirmed by the ^{1}H NMR spectrum of **1** in $CDCl_3$. The characteristic coumarin C-3/C-4 doublet pair appeared at δ6.13 (1H, *d*, $J = 10$ Hz) and 7.99 (1H, *d*, $J = 10$ Hz). The latter doublet signal corresponding to C-4 suggested that there was an oxygen function at the C-5 position [6, 7]. The terminal vinylic protons appeared at δ4.88 and 4.79 and the methyl group at δ1.87. The tertiary hydrogen C-2′ proton, occurred as the X portion of an ABX system at δ4.30. The benzylic protons appeared at 2.99–3.10 showing the expected AB pattern of an ABX system. The δ2.04 peak was assigned to the OH group since it disappeared after addition of D_2O to the solution. A signal at 3.94 (6 H, *s*) was assigned to both C-5 and C-7 methoxyl groups, and the C-6 proton signal appeared at 6.33 as singlet. In the IR spectrum of omphamurin there were characteristic peaks at 3480 (broad, OH), 1695 (C=O) and 900 cm^{-1} (terminal >C=CH$_2$). In the mass spectrum of omphamurin, there were characteristic or intensive fragments at *m/e* (rel. int.) 290 (1, M$^+$), 220 (56), 219 (100) and 205 (6). When omphamurin was heated with 20 % H_2SO_4 for 3 hr it gave a colourless crystalline compound with mp 129–130° whose mp, TLC properties and IR (KBr) spectrum were all identical with those of authentic 5,7-dimethoxy-8-(3′-methyl-2′-oxobutyl)coumarin (**2**) [1]. From the above chemical evidence and spectral data, omphamurin was assigned as 5,7-dimethoxy-8-(2′-hydroxy-3′-methyl-3′-butenyl)coumarin (**1**).



1 $R = CH_2CHOH\overset{\overset{\displaystyle CH_2}{\|}}{C}Me$

2 $R = CH_2COCH(Me)_2$

EXPERIMENTAL

All mps were uncorr., IR spectra were recorded in KBr. The ^{1}H NMR spectrum was measured at 100 MHz with TMS as an internal standard, $CDCl_3$ was used as solvent. MS spectra were taken with a direct inlet system.

Plant material. Murraya omphalocarpa was collected from Orchid Island, Taiwan and verified by Professor C.-S. Kuoh and the herbarium specimen is deposited at Chia-Nan Junior College of Pharmacy, Tainan, Taiwan, R.O.C.

The *n*-hexane extract of the dried powdered leaves (1 kg) of *Murraya omphalocarpa* was dissolved in Me_2CO and filtered. The Me_2CO soluble portion was evaporated to dryness. When the residue was chromatographed on Si gel using C_6H_6–Me_2CO (9:1) as eluent and recrystallized from Me_2CO, omphamurin with mp 131–132° was obtained as colourless needle crystals (0.005 %), $[\alpha]_D^{20}$ −22° ($CHCl_3$, $c = 0.405$), UV λ_{max}^{MeOH} nm (log ε): 239 (3.59), 254 (3.74), 262 (3.79), 327 (3.91). IR ν_{max} cm^{-1}: 3480 (OH), 1695 (C=O), 1600, 1500 (C=C) and 895 (>C=CH$_2$). ^{1}H NMR: δ7.99 (1H, *d*, $J = 10$ Hz, C-4), 6.33 (1H, *s*, C-6), 6.13 (1H, *d*, $J = 10$ Hz, C-3), 4.88 and 4.79 (2H, >C=CH$_2$), 4.30 (1H, *m*, C-2′), 3.94 (6H, *s*, 2 × OMe), 2.99–3.10 (2H, *m*, C-1′), 2.04 (1H, *br*, OH), 1.87 (3H, *s*, Me): MS *m/e* (rel. int.): M$^+$ 290 (1.0), 220 (56), 219 (100), 205 (6), 161 (27). Found: C 66.02 H 6.47. Calc. for $C_{16}H_{18}O_5$, C 66.19 H 6.25 %.

Omphamurin (**1**), 20 mg, was heated gently to reflux in 6 ml 20 % H_2SO_4 for 3 hr. The product was extracted with Et_2O. After the Et_2O extract was washed with 5 % $NaHCO_3$ and H_2O, it was

---

*Part VI in the series. 'Studies on the Constituents of Formosan Folk Medicine.' For Part V see ref. [1].

dried (Na_2SO_4), and the solvent removed to yield a slightly coloured oily residue consisting of two compounds: colourless needle crystals with mp 131–132° and colourless needle crystals with mp 129–130°. The separation of these compounds was achieved by TLC (Si gel, thickness 0.5 mm; solvent C_6H_6–Me_2CO, 9:1). The former compound was identified with anthentic omphamurin and the latter compound with mp 129–130°, UV λ_{max}^{EtOH} nm: 252, 261, 324, IR ν_{max} cm^{-1}: 1720 and 1710 (C=O); MS m/e: 290 (M^+), was identified with an authentic sample of 5,7-dimethoxy-8-(3′-methyl-2′-oxobutyl)-coumarin (**2**) [1] by mmp and comparisons of TLC properties and IR spectra.

Acknowledgments—The author thanks Professor N. Morita (Toyama Medical and Pharmaceutical University) for the measurement of ^{1}H NMR, MS and elemental analysis and Professor C-S. Kuoh for the identification of the plant.

REFERENCES

1. Wu T-S, Tien H-J,. Arisawa M., Shimizu M. and Morita N. (1980) *Phytochemistry* **19**, 2227.
2. Chakraborty D. P., Chowdhury B. K. and Das B. C. (1967) *Tetrahedron Letters* 3471.
3. Dreyer D. L. (1967) *Tetrahedron* **23**, 4613.
4. Dreyer D. L. (1968) *J. Org. Chem.* **33**, 3574.
5. Austin P. W., Seshadri T. R., Sood M. S. and Vishwapanl (1968) *Tetrahedron* **24**, 3247.
6. Reisch J., Novak I., Szendrei and Minker E. (1967) *Die Pharm.* **22**, 205.
7. Steck W. and Mazurek M. (1972) *Lloydia* **35**, 418.