

STRUCTURE OF MURRAYAQUINONE-B, A NOVEL CARBAZOLE ALKALOID
FROM MURRAYA EUCHRESTIFOLIA HAYATA

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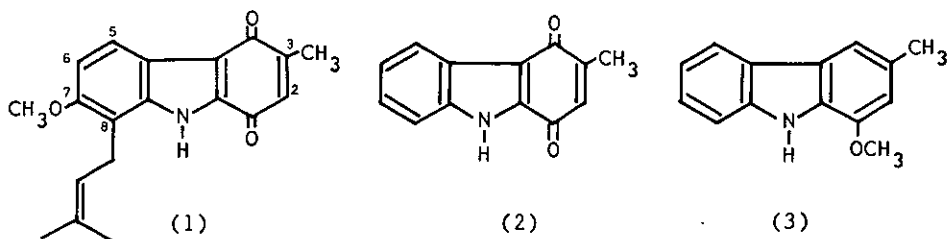
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Abstract — The structure of murrayaquinone-B, a novel carbazole alkaloid isolated from the root bark of Murrraya euchrestifolia Hayata was established as formula 1.

The plants of the genus Murrraya (Rutaceae) growing naturally in southern Asia¹ are shrubs up to 4-5 m high. Extracts of the leaves and bark of this tree have been used as a folk medicine for analgesia and local anesthesia, and for the treatment of eczema, rheumatism, and dropsy. The plants belonging to this genus are also known as a main source of carbazole alkaloids.² We now report here the structural elucidation of a novel carbazolequinone, murrayaquinone-B, which was isolated from the root bark of Murrraya euchrestifolia Hayata collected in Taiwan.

Murrayaquinone-B (1) was obtained as deep purplish needles from acetone, mp 221-223°C (contents: 0.007% from the dried plant material). The molecular formula as C₁₉H₁₉NO₃ was established by high resolution mass spectrometry (Calcd. for C₁₉H₁₉NO₃ 309.1363. Found 309.1360). The presence of a carbazole-1,4-quinone nucleus in the molecule was suggested by the UV [λ_{\max} (MeOH) nm (log ϵ):



210 (sh, 4.28), 231 (4.58), 264 (4.44), 310 (sh, 3.21), and 404 (3.66)] and IR [ν_{\max} (KBr) cm^{-1} : 3280, 1655, 1640, and 1610] spectra^{3,4} together with the appearance of two carbonyl carbon signals at δ 179.8 and 183.7 in the ^{13}C -NMR (CDCl_3) spectrum. This was supported by the remarkable similarity between the UV spectrum of murrayaquinone-B and that of 2⁵ obtained by a photo-oxidation of 3,⁶ considering a bathochromic shift (about 6 nm) in that of murrayaquinone-B. In the ^1H -NMR (CDCl_3) spectrum of murrayaquinone-B, AB type proton signals at δ 7.02 and 7.98 were attributed to mutually ortho-located protons on the aromatic ring, and the lower field signal could be assigned to H-5 which was affected by a deshielding of 4-carbonyl moiety. The presence of a methoxyl and a prenyl group in the molecule was confirmed by NMR and/or mass spectra [OCH_3 : δ_{H} 3.91 (3H, s), δ_{C} 56.7 (q); prenyl: δ_{H} 1.74 (3H, s), 1.85 (3H, s), 3.57 (2H, d, $J=7\text{Hz}$), and 5.23 (1H, br t, $J=7\text{Hz}$); δ_{C} 18.0 (q), 23.7 (t), 25.7 (q), and 121.6 (d); m/z 254 (M^+ - $\text{CH}=\text{C}(\text{CH}_3)_2$), and 241 (M^+ - $\text{CH}_2-\text{CH}=\text{C}(\text{CH}_3)_2 + \text{H}$)]. In addition, the ^1H -NMR spectrum showed a three-proton doublet at δ 2.13 ($J=1.5\text{Hz}$) and a one-proton quartet at δ 6.42 ($J=1.5\text{Hz}$), both having a long range coupling. In an NOE experiment, a 15.2% enhancement of the signal at δ 6.42 was observed on irradiation of the methyl signal at δ 2.13. The chemical shift value (δ 6.42) of the olefinic proton adjacent to the methyl group in murrayaquinone-B, closely related to that of 2 (δ 6.51), suggested that the proton should be located at C-2; since if it was located at C-3, a somewhat more downfield shift would be expected.⁷ The presence of the methyl group at C-3 (not at C-2) of the carbazolequinone nucleus was also indicated by the appearance of the C-2 signal at δ 131.5 in the ^{13}C -NMR spectrum of murrayaquinone-B, almost the same position as that of 2 (δ 131.6), together with biogenetic considerations.^{2,8} Further, the observation of a 15.9% NOE enhancement between H-6 at δ 7.02 and the methoxyl group at δ 3.91 was suggestive of locations of a methoxyl and a prenyl group at C-7 and C-8, respectively. From the results of these spectral data, the structure of murrayaquinone-B should be represented by formula 1. This is the first case of the isolation of the carbazolequinone from natural sources.⁹

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5. Compound 2 was also isolated from the same plant, and named murrayaquinone-A: mp 246-247°C, λ_{\max} (MeOH) nm (log ν): 225 (4.63), 258 (4.51), 293 (sh, 3.85), and 398 (3.93); ν_{\max} (KBr) cm^{-1} : 3200, 1650, and 1595; δ_{H} (CDCl_3): 2.19 (3H, d, J=1.5Hz), 6.51 (1H, q, J=1.5Hz), 7.30-7.60 (3H, m), 8.23 (1H, dt, J=1, 5Hz), and 9.20 (1H, br s); δ_{C} (CDCl_3): 16.0 (q), 113.7 (d), 116.2 (s), 122.2 (d), 123.7 (d), 124.1 (s), 126.1 (d), 131.6 (d), 136.0 (s), 137.8 (s), 148.3 (s), 180.4 (s), and 183.4 (s).
6. The compound 3 was also isolated from the same plant source, and named murrayafoline-A: δ_{H} (CDCl_3): 2.40 (3H, s), 3.76 (3H, s), 6.55 (1H, s), 6.9-7.3 (3H, m), 7.33 (1H, s), 7.87 (1H, d, J=8Hz), and 7.96 (1H, br s). The characterization and reactions of this alkaloid will be reported elsewhere.
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9. The alkaloid, named murrayaquinone-C, having a geranyl moiety instead of the prenyl group in the structure of murrayaquinone-B (1) was also isolated and characterized, δ_{H} (CDCl_3): 1.56 (3H, s), 1.61 (3H, s), 1.85 (3H, s), 2.05 (2H, s), 2.13 (3H, d, J=2Hz), 3.58 (2H, d, J=7Hz), 3.91 (3H, s), 5.03 (1H, m), 5.26 (1H, t, J=7Hz), 6.41 (1H, q, J=2Hz), 7.01 (1H, d, J=9Hz), 7.98 (1H, d, J=9Hz), 9.08 (1H, br d, NH).

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