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

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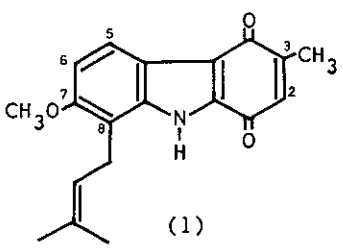
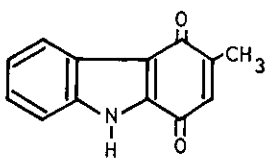
Abstract —— The structure of murrayaquinone-B, a novel carbazole alkaloid isolated from the root bark of Murraya euchrestifolia Hayata was established as formula 1.

The plants of the genus Murraya (Rutaceae) growing naturally in southern Asia[1] 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 Murraya euchrestifolia Hayata collected in Taiwan.

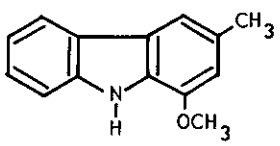
Murrayaquinone-B (1) was obtained as deep purplish needles from acetone, mp 221-223°C (contents: 0.007% from the dried plant material). The molecular formula as $C_{19}H_{19}NO_3$ was established by high resolution mass spectrometry (Calcd. for $C_{19}H_{19}NO_3$ 309.1363. Found 309.1360). The presence of a carbazole-1,4-quinone nucleus in the molecule was suggested by the UV [λ_{max} (MeOH) nm (log ε):



(1)



(2)



(3)

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 2[5] obtained by a photo-oxidation of 3,[6] considering a bathochromic shift (about 6 nm) in that of murrayaquinone-B. In the ^{1}H-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=7Hz), and 5.23 (1H, br t, J=7Hz); δ_C 18.0 (q), 23.7 (t), 25.7 (q), and 121.6 (d); m/z 254 (M^+- $CH=C(CH_3)_2$), and 241 (M^+- CH_2-$CH=C(CH_3)_2$ + H)]. In addition, the ^{1}H-NMR spectrum showed a three-proton doublet at δ 2.13 (J=1.5Hz) and a one-proton quartet at δ 6.42 (J=1.5Hz), 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 ε): 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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