Communications to the Editor

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NEW CARBAZOLEQUINONES HAVING DIMETHYLPYRAN RING SYSTEM, FROM MURRAYA EUCHRESTIFOLIA

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The structures of pyrayaquinone-A (1) and -B (2), the first naturally occurring carbazolequinone alkaloids having a dimethylpyran ring system from Murraya euchrestifolia Hayata (Rutaceae), have been determined by spectral and synthetic experiments.

KEYWORDS — pyrayaquinone-A; pyrayaquinone-B; Murraya euchrestifolia; Rutaceae; carbazole alkaloid; carbazolequinone; palladium(II) acetate; dimethylchromene

The plants of the genus Murraya (Rutaceae) are known as a rich source of carbazole alkaloids.[1] Our current studies on the chemical components of Murraya euchrestifolia Hayata, have led us to the isolation of carbazoles, carbazolequinones, and dimeric carbazole alkaloids.[2-5] In continuing our investigation of the constituents of the same plant, we now describe the first isolation and structure elucidation of two new carbazolequinones, namely, pyrayaquinone-A (1) and -B (2), having dimethylpyran ring system in the molecule.

The acetone extract of the root bark of the plant collected in Taiwan in December was subjected to silica gel column chromatography with successive elution with hexane, benzene, and benzene-acetone (9:1). The benzene eluant was repeatedly chromatographed on silica gel to afford two new carbazolequinones, pyrayaquinone-A (1) and -B (2) (0.0002 and 0.0003% yields from the dried bark, respectively).

Pyrayaquinone-A (1), mp 222°C (dec.), and pyrayaquinone-B (2), mp 244°C (dec.), were found to have the same molecular formula, $C_{18}H_{15}NO_3$, by high resolution mass spectral analysis (Calcd for $C_{18}H_{15}NO_3$ 293.1051, Found 293.1053 and 293.1052, respectively) and gave the following spectral data.

Pyrayaquinone-A (1): UV λ_{max} (EtOH) 220sh, 252, 308sh, and 460 nm; IR ν_{max} ($CHCl_3$) 1660, 1640, 1630, and 1610 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 1.48 (6H, s), 2.16 (3H, d, J=1.5 Hz), 5.72 (1H, d, J=10 Hz), 6.46 (1H, q, J=1.5 Hz), 6.48 (1H, d, J=10 Hz), 6.83 (1H, s), 7.79 (1H, s), and 9.02 (1H, br s); MS m/z 293 (M^+), 278 (100%), 250, 236, and 222.

Pyrayaquinone-B (2): UV λ_{max} (EtOH) 229sh, 248, 295sh, 320, and 410 nm; IR ν_{max} (KBr) 1650, 1640, 1635, and 1605 cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ: 1.48 (6H, s), 2.14 (3H, d,

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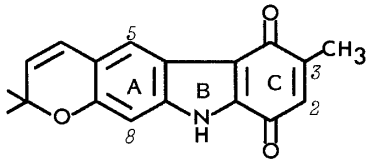
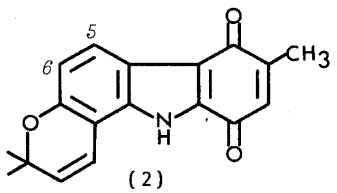
J=1.5 Hz), 5.70 (1H, d, J=10 Hz), 6.44 (1H, q, J=1.5 Hz), 6.60 (1H, d, J=10 Hz), 6.86 (1H, d, J=9 Hz), 7.94 (1H, d, J=9 Hz), and 9.32 (1H, br s); MS m/z 293 (M^+), 278 (100%), 250, 222, and 210.

The UV spectra and the fine structures of IR bands in the region of carbonyl absorptions which were similar in pyrayaquinone-A and -B suggested that they possessed the same basic carbazolequinone structure.[6,7] In the ^{1}H-NMR spectra of these alkaloids, the AB-type signals at δ 5.72 and 6.48 (each 1H, d, J=10 Hz) in the spectrum of 1, and at δ 5.70 and 6.60 (each 1H, d, J=10 Hz) in that of 2, together with a six-proton singlet at δ 1.48 in those of both alkaloids revealed the presence of a dimethylpyran ring system. Furthermore, a three-proton doublet at δ 2.16 and a one-proton quartet at δ 6.46, both having a long range coupling (J=1.5 Hz) in the spectrum of 1, and at δ 2.14 (3H, d) and 6.44 (1H, q) in that of 2 reflect the partial structure of ring C.[8] The major differences were the spectral features derived from aromatic ring A. In pyrayaquinone-A, two singlets at δ 6.83 and 7.79 were assigned to H-8 and H-5,[2] respectively, located para each other. On the other hand, in pyrayaquinone-B, ortho-coupled AB-type proton signals at δ 6.86 and 7.94 (each 1H, d, J=9 Hz) were observed. The lower signal at δ 7.94 is characteristic of H-5, which affected the deshielding with C-4 carbonyl moiety in a carbazolequinone nucleus.[2]

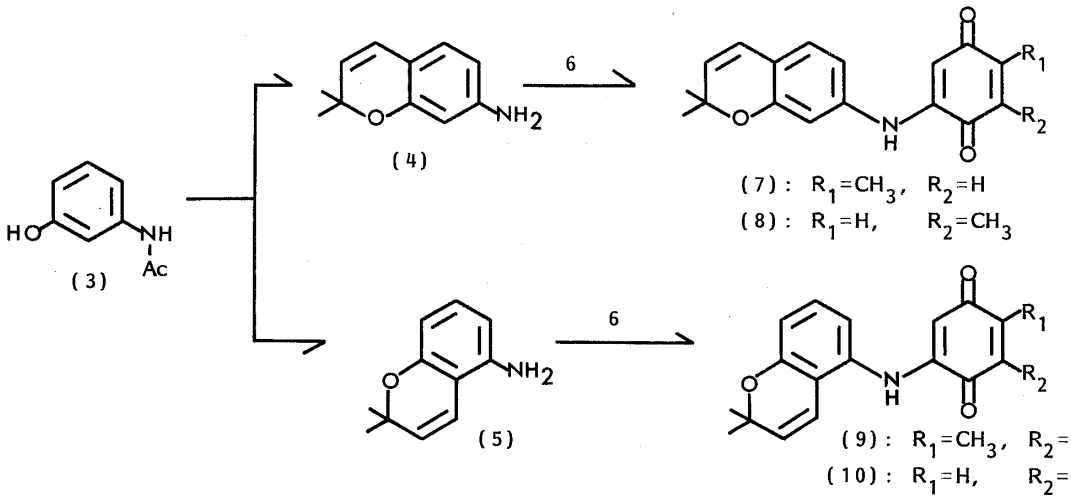
On the results of these data coupled with biogenetic considerations, the structures of pyrayaquinone-A and -B were proposed as formulae 1 and 2, respectively.



(1)



(2)



In order to confirm the structures of these alkaloids, we have carried out their syntheses. First, 7-amino-2,2-dimethylchromene (4)[9] prepared from m-acetamidophenol (3) was condensed with 2-methyl-1,4-benzoquinone (6)[11] to afford 7, mp 134-135°C, as a major product (14%), along with the corresponding regio isomer (8).[12-14] Treatment of 7 with palladium(II) acetate in acetic acid for 4 min at

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refluxing temperature, gave 1, mp 228°C (dec.), in 78% yield.[15,16] This compound was found to be identical with pyrayaquinone-A by comparison of the ^{1}H-NMR, IR, and mass spectra and TLC.

Synthesis of pyrayaquinone-B (2) was also achieved the same way: Condensation of 5-amino-2,2-dimethylchromene (5)[9] with 6 gave 9, mp 114-116°C, in 18% yield.[12, 13] Then, cyclization of 9 in acetic acid in the presence of $Pd(OAc)_2$ furnished the carbazolequinone (2),[15] which was identical to the natural pyrayaquinone-B (^{1}H-NMR, IR, MS, and TLC comparisons).

Consequently, the structures of pyrayaquinone-A and -B were established as formulae 1 and 2, respectively.

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9) 1,1-Dimethylpropargyl ether of m-acetamidophenol (3) was heated in N,N-diethylaniline[10] to give two isomeric chromenes according to the direction of the cyclization, and then treatment of each isomer with diluted aqueous HCl led to aminochromenes (4) and (5). The structures of these isomers were easily deduced by the ^{1}H-NMR ($CDCl_3$) spectra as follows: (4): mp 35-36°C, δ 1.38 (6H, s), 3.42 (2H, br s), 5.38 (1H, d, J=10 Hz), 6.10 (1H, d, J=1.5 Hz), 6.14 (1H, dd, J=1.5 & 8 Hz), 6.22 (1H, d, J=10 Hz), and 6.74 (1H, d, J=8 Hz). (5): oil, δ 1.38 (6H, s), 3.60 (2H, br s), 5.56 (1H, d, J=10 Hz), 6.20 (1H, dd, J=1.5 & 8 Hz), 6.24 (1H, dt, J=1.5 & 8 Hz), 6.33 (1H, d, J=10 Hz), and 6.88 (1H, t, J=8 Hz).
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13) Structure assignments of the reaction products could be confirmed by the analysis of signals due to the substituted methylbenzoquinone moiety in the ^{1}H-NMR ($CDCl_3$) spectra. (7): δ 2.10 (3H, d, J=1.5 Hz), 6.24 (1H, s), and 6.54 (1H, q, J=1.5 Hz). (8): δ 2.08 (3H, d, J=1.5 Hz), 6.18 (1H, d, J=2.5 Hz), and 6.50 (1H, sextet, J=1.5 & 2.5 Hz). (9): δ 2.08 (3H, d, J=1.5 Hz), 5.72 (1H, s), and 6.55 (1H, q, J=1.5 Hz). (10): δ 2.08 (3H, d, J=1.5 Hz), 5.68 (1H, d, J=2.5 Hz), and 6.48 (1H, sextet, J=1.5 & 2.5 Hz).
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