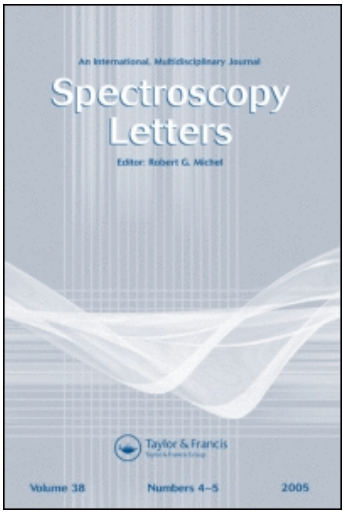

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Structural Elucidation: IR, ^{1}H-NMR and Mass Spectroscopic Study of Novel 4-Amino-6-oxo,4a,5,12,12a-tetrahydro(7*H*),benzopyrano[3,2-*c*]quinoline

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Structural Elucidation: IR, ^{1}H-NMR and Mass Spectroscopic Study of Novel 4-Amino-6-oxo,4a,5,12,12a-tetrahydro(7*H*), benzopyrano[3,2-*c*]quinoline

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ABSTRACT

1-methyl-3-methylene-2,4(1*H*,3*H*)-quinolinedione, prepared from 4-hydroxy-1,3-dimethyl-2(1*H*)-quinoline with aniline and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone in dry benzene for 48 hr, gave the Diels–Alder cycloaddition products. Elucidation of hitherto unknown 4-amino-6-oxo,4a,5,12,12a-tetrahydro-(7*H*),benzopyrano[3,2-*c*]quinoline by IR, NMR, and mass spectroscopic methods is reported.

Key Words: 4-Amino-6-oxo4a,5,12,12a-tetrahydro(7*H*)benzopyrano [3,2-*c*]-quinoline; Structural elucidation; ^{1}H-NMR; IR; Mass spectroscopy.

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INTRODUCTION

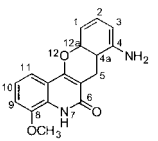
The *O*-quinone methides are fascinating intermediates in organic synthesis, as many reactions involving them invariably yield novel heterocyclic ring systems.[1–6] However, the Diels–Alder reactions of heterocyclic quinone methides in general and quinolone quinone methide in particular, have received only subdued attention.[7–11] In the context of our general interest in the cycloaddition chemistry[12,13] of *o*-quinones with anilines and with a hope to develop novel naphthyridine heterocyclic ring systems, our investigations have ended up with the titled compounds.

RESULTS AND DISCUSSIONS

As a one-pot synthesis, 4-hydroxy-3-methyl-2(1*H*)-quinolinone, aniline, and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) were refluxed in dry benzene for 48 hr. The solution was cooled, filtered, and dried. Then extracted with ethyl acetate. The residue was then triturated with petroleum ether–ethyl acetate (80 : 20), and the solid obtained was recrystalized from chloroform. Further examination of the reaction gave no trace of the dimer product. These methylene-substituted quinones are generated from 4-hydroxy-3-methyl-(2*H*)quinolinone in the presence of DDQ and benzene.[5] They are more reactive because of the additional driving force of aromatization after conjugative addition when compared to α, β-unsaturated ketones. But these reactions can be regarded as the electron deficient enone, and in the presence of electron rich aniline it preferentially undergoes an inverse electron demand cycloaddition reaction[1,5] leading to a Diels–Alder cycloaddition product (pyrano quinolines).

The IR spectrum of all the compounds **4a–f** showed its absorption between 3175 and 3300 cm^{-1} confirming the presence of the amino group in the product. The ^{1}H-NMR spectrum revealed a broad singlet at δ 2.4 indicating the amino group. The quartet at δ 3.4 for the C_{4a} methine proton with a J value of 7.14 Hz supplements the amine protons that are at C_4 ring system and thus ruling out alternate possibility at C_1. The triplet at δ 6.75 for C_{12a} methine proton further advocates the earlier mentiond. The other peaks observed are as follows:

δ 1.7(d, 2H, -CH_2-, J=7.16 Hz)
δ 3.90(s, 3H, OCH_3)
δ 6.69(d, 1H, C_3-H, J= 7.84 Hz)
δ 6.88(d, 1H, C_9-H, J=8.0 Hz)
δ 6.96(t, 1H, C_1-H, J=7.48Hz)
δ 7.05(t, 1H, C_2-H, J=7.28)
δ 7.15(t, 1H, C_{10}-H, J=7.74 Hz)
δ 8.30(d, 1H, C_{11}-H, J=7.60 Hz)
δ 9.80(s, 1H, NH).

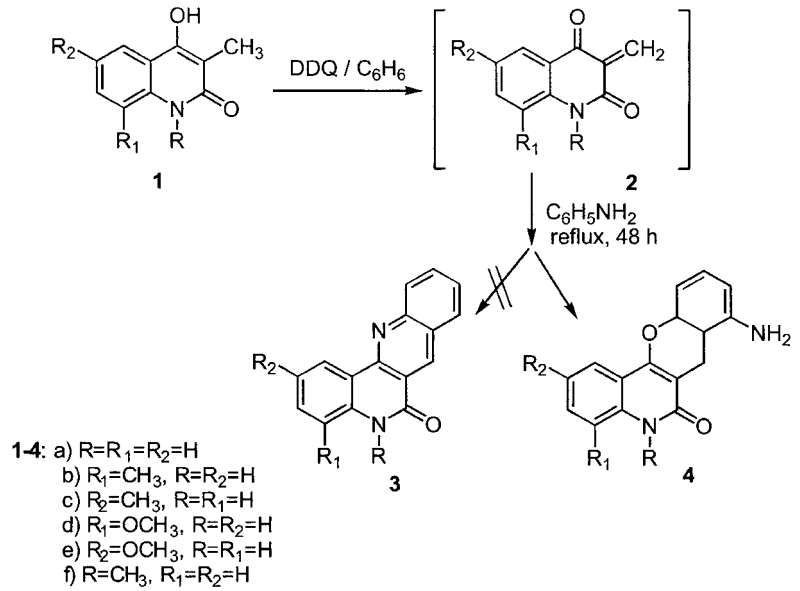


These details are further corroborated by its mass spectra, as its molecular ion peak is observed at [M^+] 296 and base peak 93 (100%), and CHN analysis endorsed it. The above values accredited the compound as 4-amino-8-methoxy-6-oxo,4a,5,12,12a-tetrahydro(7*H*),benzopyrano[3,2-*c*]-quinoline (**4d**). The exclusive products **4(a–c, e, f)** have been characterized by analytical and spectroscopic data (Sch. 1).

EXPERIMENTAL

Reagent grade ethylacetoacetate, aniline, diphenyl ether, and DDQ were used after the usual purification methods. Similarly, solvents such as petroleum ether, ethyl acetate, and benzene were purified by standard reported procedures. The reactions are performed under dry condition at 100°C for the stipulated period of time. Reaction sequences were inferred through thin layer chromatography techniques.

Thin layer chromatography was used to assess the reactions and purity of products. Melting points were determined on a Boetius Microheating Table and Mettler-FP5 Melting apparatus and are uncorrected. IR spectra were recorded on Shimadzu-8201 FT instrument in KBr disc and only noteworthy absorption levels are listed. ^{1}H-NMR spectra were recorded



Scheme 1.

in an AMX-400 MHz spectrometer in $CDCl_3$ solution; chemical shifts are expressed in ppm (δ) relative TMS, and coupling constants (J) in Hz.

Mass spectra were recorded on a Jeol-300 mass spectrometer. 4-Hydroxy-3-methyl-2(1*H*)-quinolinones were prepared according to literature procedures.[5]

4a: IR (KBr) [υmax]: 3250–3350 cm^{-1}, 1676 cm^{-1}; ^{1}H-NMR ($CDCl_3$) [δ ppm]: 1.7 (d, 2H, $-CH_2-$, $J = 7.08$ Hz), 3.0 (bs, 2H, $-NH_2$), 3.6 (q, 1H, $-C_{4a}-H-$, $J = 7.16$ Hz), 6.6 (d, 1H, C_3-H, $J = 7.92$ Hz), 6.8 (t, 1H, $C_{12a}-H$), 7.0–7.7 (m, 5H, Ar-H), 9.5 (s, 1H, NH). MS (EI, 70 eV) m/z 266 (M^+).

4b: IR (KBr) [υmax]: 3175–3225 cm^{-1}, 1675 cm^{-1}; ^{1}H-NMR ($CDCl_3$) [δ ppm]: 1.6 (d, 2H, $-CH_2-$, $J = 7.12$ Hz), 2.2 (s, 3H, CH_3), 2.6 (bs, 2H, $-NH_2$), 3.47 (q, 1H, $-C_{4a}-H-$, $J = 7.06$ Hz), 6.75 (d, 1H, C_3-H, $J = 7.96$ Hz), 6.81 (t, 1H, $C_{12a}-H$), 7.0–7.6 (m, 5H, Ar-H), 9.5 (s, 1H, NH); MS (EI, 70 eV) m/z 280 (M^+).

4c: IR (KBr) [υmax]: 3200–3350 cm^{-1}, 1676 cm^{-1}; ^{1}H-NMR ($CDCl_3$) [δ ppm]: 1.7 (d, 2H, $-CH_2-$, $J = 7.44$ Hz), 3.58 (q, 1H, $-C_{4a}-H-$, $J = 7.28$ Hz), 2.4 (s, 3H, CH_3), 2.8 (bs, 2H, $-NH_2$), 6.8–7.6 (m, 7H, Ar-H & $C_{12a}-H$), 9.6 (s, 1H, NH); MS (EI, 70 eV) m/z 280 (M^+).

4d: IR (KBr) [υmax]: 3225–3350 cm^{-1}, 1680 cm^{-1}; ^{1}H-NMR and MS: see in the text.

4e: IR (KBr) [υmax]: 3150–3300 cm^{-1}, 1685 cm^{-1}; ^{1}H-NMR ($CDCl_3$) [δ ppm]: 1.8 (d, 2H, $-CH_2-$, $J = 7.24$ Hz), 3.64 (q, 1H, $-C_{4a}-H-$, $J = 7.18$ Hz), 3.1 (bs, 2H, $-NH_2$), 4.0 (s, 3H, OCH_3), 6.7–7.5 (m, 7H, Ar-H & $C_{12a}-H$), 9.7 (s, 1H, NH); MS (EI, 70 eV) m/z 296 (M^+).

4f: IR (KBr) [υmax]: 3100–3300 cm^{-1}, 1680 cm^{-1}; ^{1}H-NMR ($CDCl_3$) [δ ppm]: 1.7 (d, 2H, $-CH_2-$, $J = 7.12$ Hz), 3.0 (bs, 2H, $-NH_2$), 3.52 (q, 1H, $-C_{4a}-H-$, $J = 7.14$ Hz), 3.6 (s, 3H, $N-CH_3$), 6.9–7.8 (m, 7H, Ar-H & C_{12a} H); MS (EI, 70 eV) m/z 280 (M^+).

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REFERENCES

1. Ryan, W.; Van, W.D.; Thomas, R.R.P. *o*-Quinone methides: intermediates underdeveloped and underutilized in organic synthesis. Tetrahedron **2002**, *58*, 5367.

2. Wagner, H.U.; Gompper, H. In *The Chemistry of Quinonoid Compounds*; Patai, S., Ed.; Wiley: New York, 1974; Vol. 2, 1145.
3. Desimoni, G.; Tacconi, G. Heterodiene syntheses with α,β-unsaturated carbonyl compounds. Chem. Rev. **1975**, *75*, 651.
4. Kumaraswami, K.; Shanmugam, P. Synthesis of 3,4-dihydro-4-methyl-2-(quinolin-3-yl)-2H-pyrano[3,2-c]quinolines. Tetrahedron Lett. **1988**, *29*, 2235.
5. Chauncey, A.M.; Grundon, M.F. Reactions of heterocyclic quinone methides: 1-methyl-3-methylene-2,4(1*H*,3*H*)-quinolinedione. Synthesis **1990**, *11*, 1005.
6. Nair, V.; Jayan, C.N.; Treesa, P.M.; Swaroop Mathen, J.; Luxmi Varma. A facile generation of quinoline quinine methide and its [4 + 2] cycloaddition pentafulvenes: Synthesis of novel pyranoquinolinone derivatives. Ind. J. Chem. **2001**, *40B*, 1108.
7. Asherson, J.L.; Young, W.D. A general and practicable synthesis of polycyclic heteroaromatic compounds. Part 1. Use of a putative quinolone-quinone-methide in the synthesis of polycyclic heteroaromatic compounds. J. Chem. Soc. Perkin Trans-I **1980**, 512.
8. Ye, J.H.; Ling, K.Q.; Zhang, Y.; Li, N.; Xu-j, H.J. Syntheses of 2-hydroxypyrano[3,2-*c*]quinolin-5-ones from 4-hydroxyquinolin-2-ones by tandem Knoevenagel condensation with aldehyde and Michael addition of enamine with the quinone methide-thermo- and photochemical approaches. J. Chem. Soc. Perkin Trans-I **1999**, *14*, 2017.
9. Grundon, M.F.; Ramachandran, V.N.; Sloan, B.M. Tetrahedron **1981**, *22*, 3105.
10. Nair, V.; Kumar, S. [4π+2π]Cycloaddition reactions of *o*-benzoquinones with symmetrical 6,6-dialkyl and cycloalkylfulvenes: Formation of bicycle [2.2.2] octane diones and cyclopenta[*b*][1,4]benzodioxins. Some novel observations. Tetrahedron **1996**, *52*, 4029.
11. Nair, V.; Kumar, S.; Anil Kumar, G.; Nair, J.S. Tetrahedron **1995**, *51*, 9155.
12. Balasubraminian, C.; Kumaraswami, K.; Dharmaraj, N.; Mohan, P.S. Quinone methide reactions: synthesis of novel pyranodiquinolines. Ind. J. Chem. **1993**, *32B*, 460.
13. Nandha Kumar, R.; Suresh, T.; Thamarai Selvi, S.; Mohan, P.S. Reactions of heterocyclic quinone methides: a facile entry to synthesize the alkaloid, flindersine and its analogues. Ind. J Chem. **2003**, *42B*, 187.

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