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Acampaquinone a Novel Phenanthraquinone Isolated from the Whole Plant of *Acampae praemorsa*

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Abstract

From the whole plant of *Acampae praemorsa* belonging to the family *Orchidaceae*, a novel phenanthra- quinone derivative was isolated. Its structure was elucidated as 2-hydroxy- 6-methoxy – 1, 4 – phenanthra- quinone on the basis of spectroscopic data. This is the first report of phenanthraquinone from*Acampae praemorsa*.

Keywords:*Acampae praemorsa*, *Orchidaceae*, Phenanthraquinone

1. Introduction

In In the course of our investigation on the chemical constituents of some south Indian orchids we reported the isolation and characterization of a numberof pyrans[1-6], pyrones[7-11], quinones[12], bibenzyls[13], phenantherene carboxylic acids[14] and a novel pyrene[15]. In this paper we report the structural elucidation of a new phenanthraquinone derivative Acampaquinone from *Acampae praemorsa*.

1.2 Experimental:

The plant material of *Acampae praemorsa* was collected in Araku Valley during Nov 2009.

$_{Mpsuncorr}$. IR, ν_{max}^{KBr}, UV λ_{max}^{EtoH}, ^{1} HNMR δ ppm

90MHz $CDCl_3$, CC and TLC on silicagel

1.2.1 Extraction and isolation:

The air dried whole plant of *Acampae praemorsa* was extracted with hexane and methanol. Each extract was impregnated on minimum amount of silicagel and washed with hexane, benzene, acetone and methanol. The washes of the two extracts were compared on TLC and similar fractions were mixed.

The benzene elute of methanol extract was subjected to column chromatography using hexane, benzene, acetone and methanol. The combined chromatographic benzene elute (21-30) (2gms)

was rechromatographed over a column of silicagel (30gm) using hexane + benzene, benzene + acetone. The hexane + benzene (8:2) elute upon recrystallisation from benzene yielded violet solid. Further purification was carried out by preparative TLC. The compound was visible as a violet band and was purified using PTLC. The compound was eluted with acetone, dried under vacuum and recrystallised using benzene. On crystallisation the compound was separated as violet needles.

Yield = 7mg; m.p. 232^0C

It gave a positive ferric chloride reaction characteristic of a phenol. It gave a pink colour with methanolic magnesium acetate indicating it to be a hydroxy quinone.

(found C, 71%, H, 4.0%)

($C_{14}H_{10}O_4$ requires C 70.80%, H 3.91%)

UV $\left[\lambda_{max}^{EtoH}\right]$ nm 220, 270, 300,450 and 520 nm

$\left[\lambda_{max}^{NaoMe}\right]$ nm 220, 280, 350 and 440 nm

^{1}HNMR [($CDCl_3$)] (ppm) 12.2 (1H,S, - OH), 8.17(2H,S, H-9, H-10) , 6.30(S, 1H, H-3), 4.00 (3H,S-OCH_3), 7.55 (d,1H,J = 9Hz, H-8), 7.45 (dd,1H,J=9, 2.5Hz,H-7), 7.20 (d,1H,J=2.5Hz, H-5)

The compound was identified as 2 – hydroxy, 6-methoxy-1, 4-phenanthraquinone.

1.2.2 **Acetylation of compound**

4 gm of compound was dissolved in 0.5ml of pyridine and 1ml of acetic anhydride. The mixture was kept at room temperature for about 36 hours. Excess pyridine was removed under vacuum. The acetate formed was dissolved in $CHCl_3$ and washed with 0.5% HCl to remove excess pyridine. Then washed with water, dried overanhydrous sodium sulphate and concentrated under vacuum. The residue obtained was recrystallised by using methanol.

Yield = 3mg, m.p. 180-182^0C

(Found, C, 69%, H, 4.1%)

$C_{17}H_{12}O_5$, requires,C, 68.9%, H, 4.05%)

1.3 Results and discussion

The Compound melted at 232^0C and analyzed for $C_{15}H_{12}O_4$ ([M^+] m/z=254). Compound gave a positive ferric chloride reaction for the presence of phenolic hydroxyl groups and Shibata's test yielding a pink colour with methanolic magnesium acetate for a hydroxy quinone.

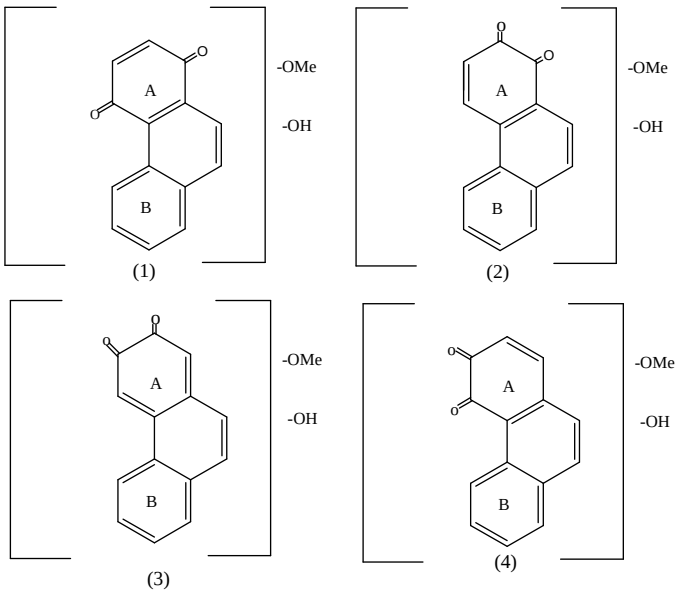
The IR absorption bands at $\nu_{\max}^{KBr} 1620,1637 cm^{-1}$ indicated the presence of quinone carbonyls.

UV spectrum exhibited absorption bands at $\lambda_{\max}^{EtoH}$ 220, 270, 300, 450 and 520nm supported the presence of a phenanthraquinone system. Alkali induced bathochromic shift from $270 \Rightarrow 280$ and $300 \Rightarrow 350$ nm indicated phenolic nature.

Compound formed an acetate (low melting; analyzed for $C_{17}H_{14}O_6$) on treatment with acetic anhydride and pyridine for 24hrs at room temperature supported the presence of hydroxyl group. The molecular formula indicated that it might be a monoacetate.

The 90MHz ^{1}HNMR spectrum of compound showed the presence of one methoxyl at $\delta 4.00(3H, s)\, ppm$ and one hydroxyl at δ 12.2 (1H, s) ppm. Thus, compound might be a mono-methoxy-mono-hydroxy-phenanthraquinone.

The singlet signal integrating for two protons at δ 8.17 suggested the presence of 9, 10-dehydro-phenanthrene skeleton. Hence, the partial structures 1,2,3 and 4 might be proposed for compound.



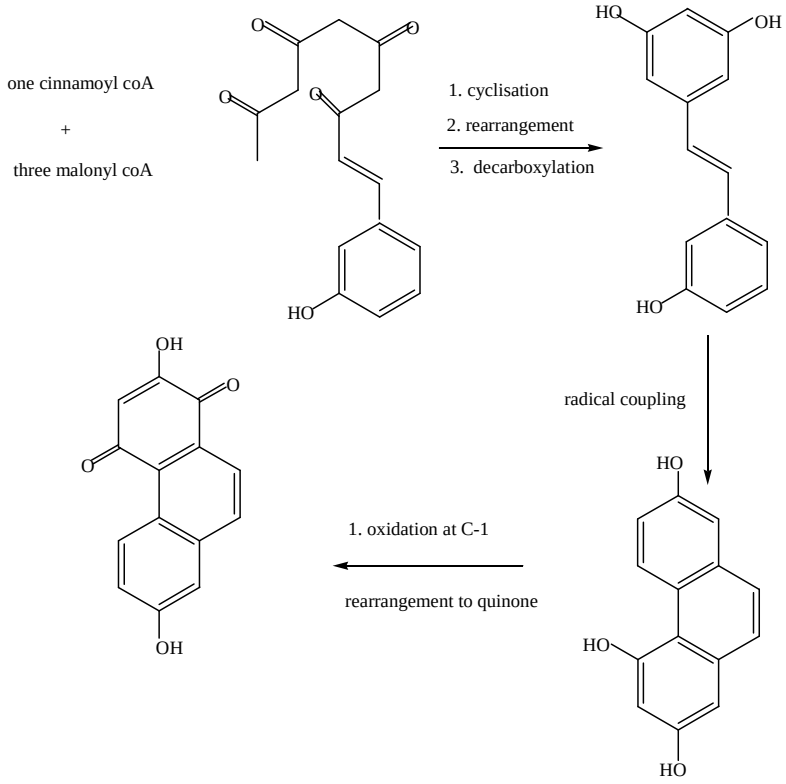
The UV absorption bands at $\lambda_{\max}^{EtoH}$ 220, 270 300, 450 and 520nm supported the *para*-quinone structure for compound and ruled out the *ortho*-quinone structures (2 to 4) as a long wave length band beyond $\lambda_{\max}^{EtoH}$ 520nm was expected for *ortho*-quinone type of compounds which is not seen in the present compound.

The positions of methoxyl and hydroxyl groups were assigned based on the ^{1}HNMR data and mass spectral

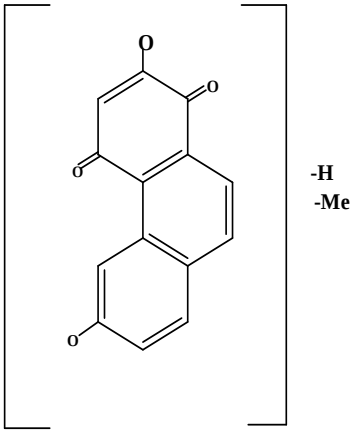
data and on biogenetic considerations.

The characteristic one proton singlet at δ 6.30 ppm due to α protons in quinones indicated that one of the carbons C-3 or C-2 were substituted. The signal at δ 6.30 might be assigned to H-2 or H-3. The biogenetic consideration[16](Scheme) indicated that the oxy-substituent might be assigned to C-2 and not C-3. Hence, the above signal was assigned to H-3.

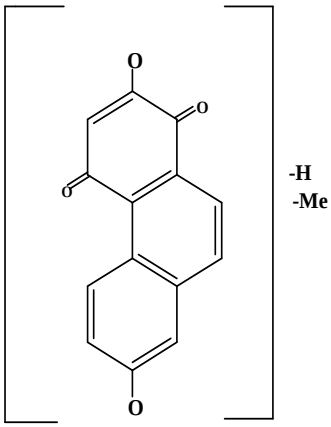
Biogenetic pathway



The three aromatic signals appeared at δ 7.20 (d, 1H, J= 2.5Hz), 7.45 (dd, 1H, J=2.5, 9Hz) and 7.55 (d, 1H, J=9Hz) ppm indicated ABX pattern of protons in B-ring, Thus, the two possible structures (5 and 6) were proposed for compound.

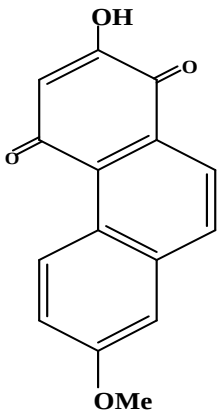


(5)

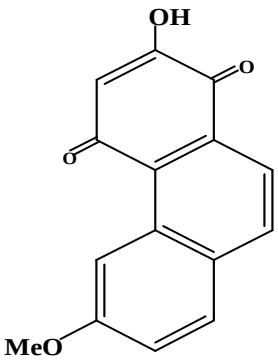


(6)

The hydroxyl group at δ 12.2ppm suggested that the hydroxyl was in close proximity to the carbonyl carbon. Thus, hydroxyl was allocated to C-2. the allocation of hydroxyl to C-2 was further supported by the mass spectrum of compound. Thus, the two possible structures for compound were (8) and (7).

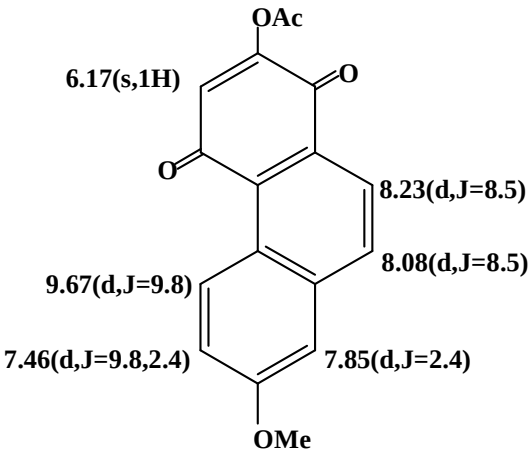


(7)

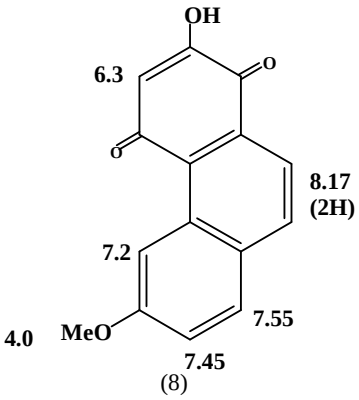


(8)

7 was an already reported quinone, ochrone-B isolated and reported as ochrone-B acetate from *Coelogyne ochracea*. The signals assigned for ochrone-B acetate were as shown in 7



(7A)



(8)

The most downfield signal in the aromatic ABX pattern of protons of compound was observed at δ 7.55ppm. The most down field signal in ochrone acetate (7A) was at δ 9.67ppm and was allocated to H-5. The absence of a down field signal in compound and the absence of any co-relation in the aromatic regions between the chemical shifts of ochrone acetate (7A) and compound indicated that compound might not be ochrone. This was further supported by the non-super imposable IR and co-TLC of compound acetate and ochrone acetate. However, as there is no hydroxyl in ring-B, much chemical shift difference in ring- B protons were not expected between compound and its acetate.

The above discussion suggested the structure 8 for compound which was further supported by the mass spectrum of compound. Thus, the methoxyl was assigned to C-6 and the signals at δ 7.20 (d, 1H, J=2.5Hz), 7.45(dd, 1H, J=9,, 2.5 Hz) and 7.55(d, 1H, J=9Hz) were respectively allocated to H-5, H-7 and H-8 protons based on their coupling constants.

. The allocation was further supported by the fragment ions at m/z239 and m/z169 in the mass spectrum of compound. The other peaks at m/z197 (10) and m/z183 (40) were due to cleavage a.

The peak at m/z155 might be attributed to [m/z183-CO]. The other significant peaks at m/z223[M^+-OCH_3], 211[M^+-CH_3-CO], 195[M^+-OCH_3-2CO], 183[M^+-CH_3-2CO], 167[M^+-OCH_3-2CO], 155[M^+-CH_3-3CO or M^+-OCH_3-68], 142[M^+-CH_3-CO-69] strongly supported the allocation of methoxyl at C-6 and hydroxyl at C-2. The peaks at m/z114 and m/z127 were due to 142-CO and 155-CO respectively which further supported the above allocation.

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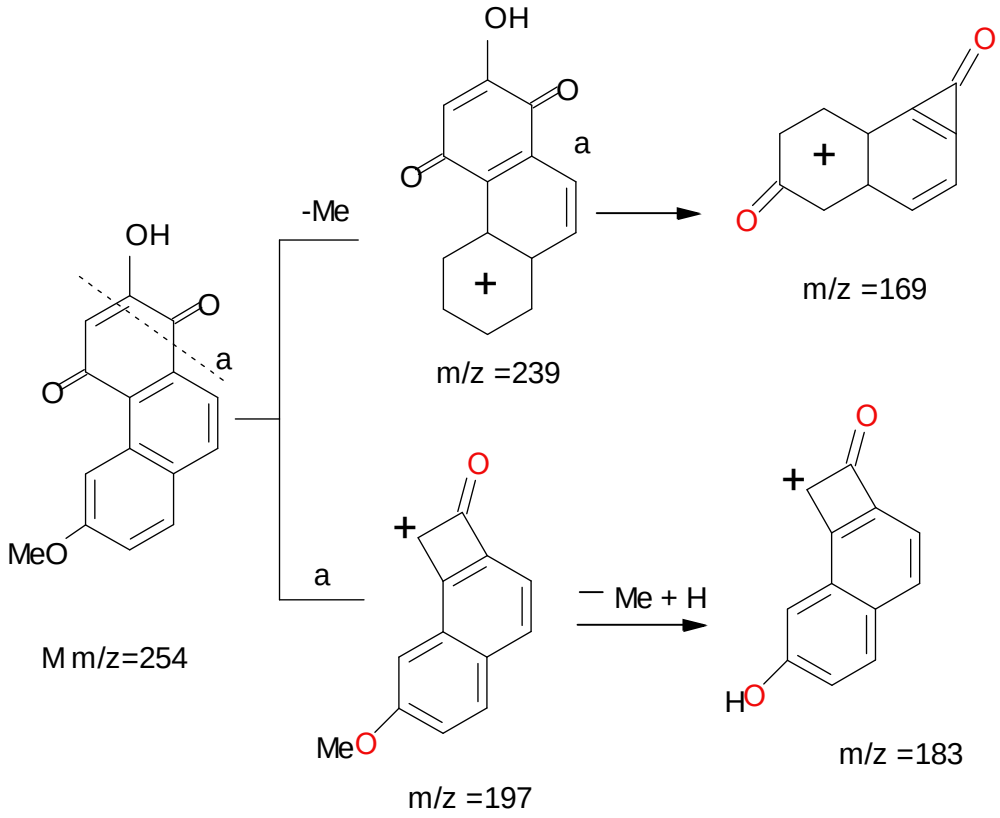

1.4 Conclusion

Thus, compound was assigned the structure 2-hydroxy-6-methoxy-phenanthraquinone and named as acampaquinone. This is a first report from nature and from *Acampae praemorsa*

1.5 Acknowledgements

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1.6 References

1. Veerraju, P., Prakasarao, N.S., Jagan MohanRao , L., Jagannada Rao, K.V.J., and Mohan Rao, P.R. (1989) *Phytochemistry*, 28:950.
2. Anuradha, V. and Prakasa Rao, N.S. (1994) *Phytochemistry*, 35(1):273.
3. Anuradha V. and Prakasa Rao, N.S. (1994) *Phytochemistry*, 37(3):909.
4. Anuradha, V. and Prakasa Rao. N.S. (1998) *Phytochemistry*, 48(1):181-182.
5. Anuradha, V. and Prakasa Rao. N.S., (1998) *Phytochemistry*, 48(1):(183-184).
6. Anuradha, V. and Prakasa Rao. N.S. (1998) *Phytochemistry*, 48(1):(185-186).
7. Uday Bhaskr, M., Jaganmohanrao, L., Prakasa Rao, N.S., JaganadhaRao, K.V.J., and Mohan Rao, P.R. (1989) *Phytochemistry* 28:3435.
8. Uday Bhaskr, M., Jaganmohanrao, L., Prakasa Rao, N.S., JaganadhaRao, K.V.J., and Mohan Rao, P.R. (1991) *J. Nat. Prod*., 54:386.
9. Veerraju, P., Prakasa Rao, N.S., Jaganmohan Rao,L., Jagannadha Rao,K.V.J., and Mohan Rao, P.R. (1989) *Phytochemistry*, 28:3031.
10. Anuradha,V., Prakasa Rao N.S., and Uday Bhaskar, M., *Phytochemistry*, (1994) 36(6):1515.
11. Anuradha, V. L. Kalyani and B. Srikanth. (2011) *Asian J. Research Chem* (4), 8 1221-24
12. Anuradha,V., Prakasa Rao N.S., and Uday Bhaskar, M. (1995) *Phytochemistry*, 39(6):429.
13. Uday Bhaskar, M., Jaganmohan Rao,L. And Prakash Rao N.S. (1993) *Ind.J. of Chemistry*, 32B:975-977.
14. Anuradha,V., Prakasa Rao N.S., and Uday Bhaskar, M. (1994) *Phytochemistry*, 36(6):1515-1517.
15. Anuradha,V., Prakasa Rao N.S., and Uday Bhaskar, M. (1994) *Phytochemistry*, 39(6):1429-1431.
16. R.H. Thomson and Chapman & Hall(1987) London:*Naturally Occuring Quinones///*, 567