

## Oxo-tessallatin , a novel phenanthrapyrene isolated from *Vanda tessalata*

V. ANURADHA\*, MANDAVA V. BASAVESWARA RAO<sup>1</sup> and ANAND S. ASWAR<sup>2</sup>

\* Department of Chemistry, Vignan School of PG Studies,

Vignan School of P.G. Studies, Vignan Degree College, Guntur (India).

<sup>1</sup>Department of Chemistry, GITAM University, Visakhapatnam - 530 045 (India).

<sup>2</sup>Department Of Chemistry, S.G.B. Amaravati University, Amaravati - 444 602 (India).

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### ABSTRACT

From the whole plant of *Vanda tessalata* a new phenanthrapyrene derivative was isolated. Its structure was elucidated as 3,7-dihydroxy-2-methoxy-9,10-dihydrophenanthrapyrene on the basis of spectroscopic data. This is the first report of phenanthrapyrene from *Vanda tessalata*.

**Key word:** *Vanda tessalata*, *Orchidaceae*, oxo-tessallatin, phenanthrene-9,10-dihydro-phenanthrapyrene.

### INTRODUCTION

In the course of our investigations on the chemical constituents of different orchids we reported the isolation and characterization of pyrans<sup>1-6</sup>, pyrone<sup>7,8</sup>, quinones<sup>9</sup>, bibenzyls<sup>10</sup>, a phenanthrene carboxylic acid<sup>11</sup> and a novel pyrene<sup>12</sup>. In this paper we report the structural elucidation of a novel phenanthrapyrene derivative oxo-tessallatin [1] from *Vanda tessalata*.

### EXPERIMENTAL

The plant material of *Vanda tessalata* was collected in Tirumala hills during November 2001.

#### Extraction and Isolation

The air dried whole plant of *Vanda tessalata* was extracted with hexane acetone and methanol. Each extract was impregnated with minimum amount of silica gel and washed with

hexane, benzene, acetone and methanol. The washes of all the three extracts were compared on TLC and similar fractions were mixed. The benzene elute of acetone extract was subjected to column chromatography using hexane, benzene, acetone and methanol. The benzene:acetone 8:2 elute was subjected to phenolic and non-phenolic separation and phenolic part was concentrated and rechromatographed on a small length column using benzene+acetone mixtures. Benzene+acetone (8:2) mixture was subjected to PTLC using HF254 silica gel. The fluorescent band was eluted with dichloromethane concentrated and recrystallised using benzene to yield tessallatin. Benzene+acetone 7:3 fraction was subjected to PTLC using benzene+chloroform9:1 mixture when two bands were separated. Lower Rf value fraction was identified to be coelogenin and the higher Rf value one as a new phenanthrapyrene, oxo-tessallatin. Oxo-tessallatin (I) m.p. 168-169°C, analysed for C<sub>16</sub>H<sub>12</sub>O<sub>5</sub>

UV  $\lambda_{\text{max}}^{\text{EtOH}}$  256, 287, 289 and 366 nm

$\lambda_{\text{max}}^{\text{EtOH} + \text{NaOH}}$  225, 267, 298, 375 and 415 nm

IR  $\nu_{\text{max}}^{\text{KBr}}$  3450, 1695, 1453 and 1426  $\text{cm}^{-1}$

$^1\text{HNMR}$  ( $\text{CDCl}_3$ )  $\delta$ ppm: 2.92 (4Hs, H-9 and H-10), 3.78 (3H, s, -OMe), 8.90, 9.02 (each 1H, s,  $\text{D}_2\text{O}$  exchangeable, ArOH), 6.65 (1H, d,  $J=2.5$  Hz, H-6) and 6.54 (d, 1H,  $J=2.5$  Hz, H-8), 6.25(s, 1H, H-1). Mass  $[\text{M}^+]$   $m/z$  284, 269, 241, 242, 240, 239, 212, 171 & 117

Oxotessallatin diacetate (II) m.p.  $138^\circ\text{C}$ , analysed for  $\text{C}_{20}\text{H}_{16}\text{O}_7$

$^1\text{HNMR}$  ( $\text{CDCl}_3$ )  $\delta$ ppm: 2.52 (3Hs, -OCOMe), 2.67 (3H, s, -OCOMe), 2.89 (4H, s, H-9 and H-10), 3.80 (3H, s, ArOMe), 6.82 (2H brs, H-6 and H-8), 6.26(s, 1H, H-1)

#### DDQ reaction of tessallatin diacetate

Tessallatin diacetate was refluxed with three mole equivalents of DDQ in dry benzene and the reaction was continued till the disappearance of the aeridin diacetate on TLC. Reaction period was about 12hrs. The reaction mixture was filtered and the residue thoroughly washed with dry benzene. The filtrate was evaporated to dryness under vacuum and the residue was rechromatographed and then crystallized from methanol. m.p. U.V.,  $^1\text{HNMR}$  was found to be similar to oxo-tessallatin diacetate.

### RESULTS AND DISCUSSION

Oxotessallatin (I) gave positive ferric chloride reaction characteristic of a phenolic hydroxyl group (m.p.  $168-169^\circ\text{C}$ . analysed for  $\text{C}_{16}\text{H}_{12}\text{O}_5$   $[\text{M}^+]$   $m/z = 284$ ). It showed UV maxima at  $\lambda_{\text{max}}^{\text{EtOH}}$  256, 287, 289 and 366nm characteristic of a 9,10 dihydro-phenanthrene skeleton,  $\lambda_{\text{max}}^{\text{EtOH}}$  366nm suggested continued conjugation in the molecule. The bathochromic shift in all the absorption bands on addition of alkali indicated phenolic nature of the compound ( $\lambda_{\text{max}}^{\text{EtOH} + \text{NaOH}}$  225, 267, 298, 375, 415nm). The IR absorption band at  $\nu_{\text{max}}^{\text{KBr}}$   $1695\text{cm}^{-1}$  besides  $3450\text{cm}^{-1}$  supported the presence of a non-chelated carbonyl and hydroxyl group in oxo-tessallatin.

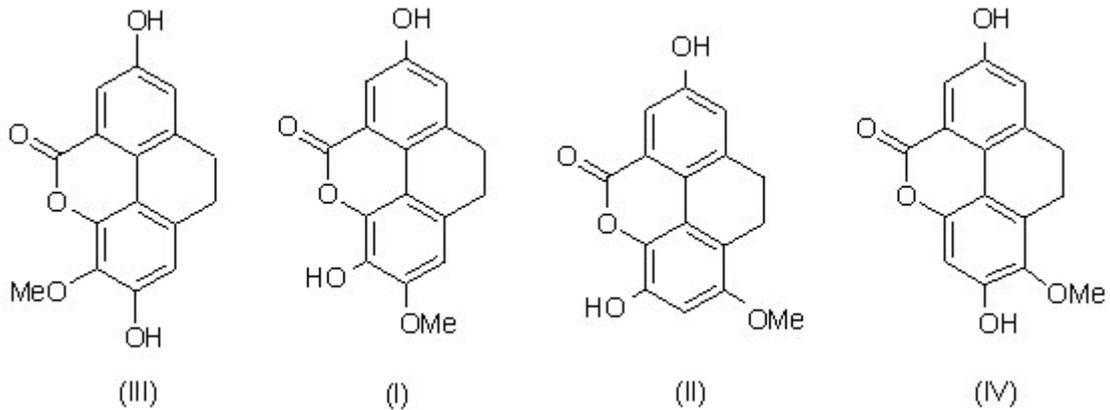
The  $^1\text{HNMR}$  spectrum of (I) showed an aromatic methoxyl group at  $\delta 3.78$ (s, 3H)ppm. Two  $\text{D}_2\text{O}$  exchangeable hydroxyl groups at  $\delta 8.90$  and  $\delta 9.02$ ppm accounting for the three of the oxygen atoms in the molecular formula. Absence of downfield signals corresponding to bay protons of 4 and 5 positions of phenanthrene nucleus and absence of a signal at  $\delta 5.1-5.3$ ppm corresponding to 5H protons of a phenanthrapyran suggested the presence of phenanthrapyron nucleus which is further confirmed by the presence of  $\nu_{\text{max}}^{\text{KBr}}$   $1695\text{cm}^{-1}$  corresponding to a carbonyl group. Thus, the compound is a dihydroxy-monomethoxy-phenanthrapyron and accounted for the five oxygen atoms in the molecular formula. (I) formed a diacetate (VI) (m.p.  $138^\circ\text{C}$ . analysed for  $\text{C}_{20}\text{H}_{16}\text{O}_7$   $[\text{M}^+]$   $m/z = 368$  with acetic anhydride and pyridine supporting the presence of two hydroxyl groups. The two acetoxyl signals in  $^1\text{HNMR}$  of (VI) at  $\delta 2.52$ (s, 3H) and  $\delta 2.67$  (s, 3H) ppm further supported the presence of two hydroxyl groups.

The singlet signal at  $\delta 2.92$  (brs, 4H) ppm in (I) is allocated to the 9 and 10 methylene protons indicating it to be a 9,10-dihydrophenanthrapyron derivative.

The two doublets at  $\delta 6.65$  ( $\delta$ , 1H,  $J=2.5\text{Hz}$ )ppm and  $\delta 6.54$  (d, 1H,  $J=2.5\text{Hz}$ )ppm in (I) shifted to down field and appeared as a singlet at  $\delta 6.82$  (brs, 2H) ppm in (VI) indicating the two protons to be meta coupled to each other and ortho to phenolic hydroxyl group. The signals may be assigned to either H-1 and H-3 with a hydroxyl at C-2, or, to H-6 and H-8 with a hydroxyl at C-7. The comparatively downfield signals indicated the presence of the protons in close proximity of a carbonyl group. Hence, the two protons were assigned to H-6 and H-8 with a hydroxyl at C-7 respectively.

The remaining one hydroxyl and a methoxyls were at C-1, C-2 and C-3. There was no downfield shift in 9 and 10 protons in the compound acetate (VI). Thus, the position of hydroxyl at C-1 is ruled out.

There were four possibilities for the structure of the compound 2,7-dihydroxy-,3-

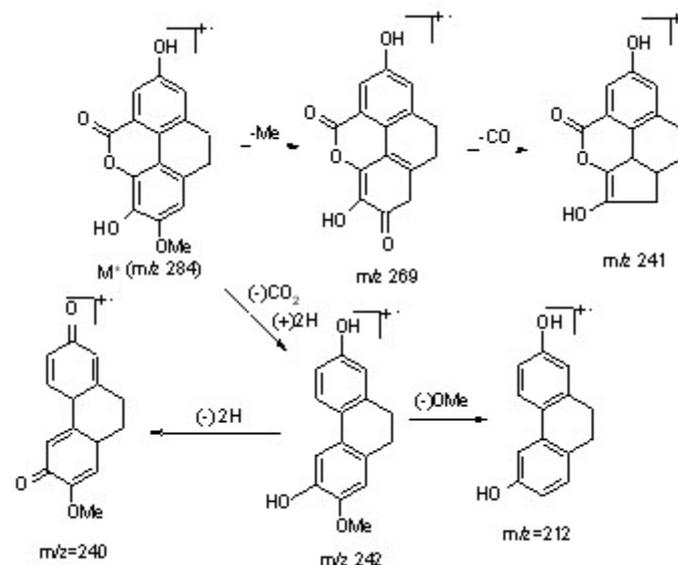
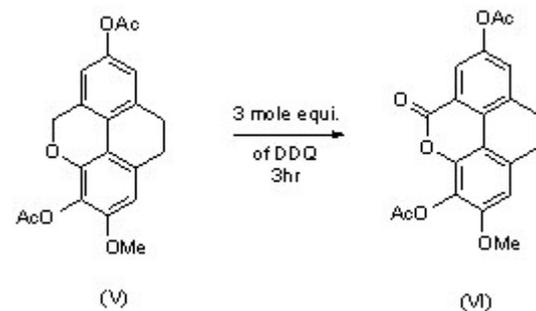


methoxy (III) or 3,7-dihydroxy- 2-methoxy- (I) or 2,7 dihydroxy-1 methoxy (IV) or 3,7-dihydroxy-1 methoxy (II) 9,10 dihydrophenanthra-pyrone.

Since there is no downfield shift of the singlet proton  $\delta$  6.25 (s, 1H) in the diacetate (II)  $\delta$  6.26 (s, 1H) the proton is not adjacent to a hydroxyl group in (I). Thus this rules out the possibility of 2,7-dihydroxy-3-methoxy, 2,7-dihydroxy-1-methoxy, 3,7-dihydroxy-1-methoxy substitution and 3,7-dihydroxy-2-methoxy is the only possible substitution.

3,7-dihydroxy-2-methoxy-9,10-dihydrophenanthrapyran is tessallatin<sup>(5)</sup> reported from the same plant.

Tessallatin diacetate (V) was taken and subjected to DDQ reaction<sup>12</sup> for 3 hrs. The resultant compound was purified and crystallized in benzene-methanol mixtures. The compound was chromatographed along with the diacetate of the isolated compound



and it was found that the Rf value of the compound is super imposable with the diacetate (VI) of the isolated phenanthrapyrone (I). The spectral data of the two compounds are also super imposible Thus, the 3,7-dihydroxy-2-methoxy was the only possible structure.

The methoxyl groups are allocated to C-2 and hydroxyls to C-3 and C-7 assigning the structure of oxo-tessalatin (I) as 2-methoxy-3,7-dihydroxy-9,10 dihydro phenanthrapyrone

The mass spectral data of (I) as depicted in (scheme-I) further supported the assigned structure.

The ions at m/z 269 ( $M^+ - CH_3$ ), 242 ( $M^+ - CO_2 + 2H$ ) and 241 ( $M^+ - CH_3 - CO$ ) correlates the assigned structure. Thus (I) is 2-methoxy-3,7-dihydroxy-9,10-dihydro-phenanthrapyrone

This is the first report of the compound from nature and from *Vanda tessalata*

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