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VERTINONE AND VERTICILONE, TWO PHENYLBUTENONES FROM *DYSOPHYLA VERTICILLATA*

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Key Word Index—*Dysophyla verticillata*; Labiatae, whole plant; verticilone, phenylbutenones

Abstract—Two novel phenylbutenone derivatives, vertinone and verticilone have been identified from *Dysophyla verticillata*.

INTRODUCTION

In connection with our interest in some bioactive constituents from aquatic Angiosperms [1], we were interested to examine *Dysophyla verticillata* which grows in the marshy tracts of northern part of West Bengal, India. In this communication we report the isolation of two new constituents vertinone **1**, and verticilone **2**

RESULTS AND DISCUSSION

Vertinone **1**, $C_{13}H_{16}O_4$, mp 95° (M^+ 236, optically inactive) was found to be homogeneous by TLC. The positive response to 2:4 DNPH reaction shows the presence of carbonyl function. The IR spectrum of **1** showed the presence of a conjugated carbonyl function (1660 cm^{-1}). The UV spectrum of the compound showed the presence of a phloroacetophenone-like chromophore [2, 3] [λ_{max}^{EtOH} 294 nm, log ε 4 5] while its ^1H NMR spectrum showed the presence of methyl protons (δ 1.90, 3H, *d*, *J* = 8.0 Hz), nine methoxy protons (δ 3.84, 3H, *s* and δ 3.76, 6H, s), *trans*-olefinic protons (δ 6.48, 1H, *d*, *J* = 16.0 Hz and δ 6.72, 1H, *q*, *J* = 15.90 Hz) and two shielded aromatic protons (δ 6.14, 2H, *s*). The IR, UV and ^1H NMR data are consistent with the presence of a trimethoxy phloroglucinol skeleton with a C_4-residue containing *trans*-olefinic protons. The mass spectrum of **1** showed the base peak at *m/z* 195 [M − 41] (100) due to the loss of the fragment [Me_3CH=CH]. The peak at *m/z* 167 [M − 69] (45) could be explained by the loss of the fragment [Me_3CH=CHCO] from **1**. The data are consistent with the structure **1** for vertinone which has also been confirmed from its ^{13}C NMR data (Table 1).

Verticilone **2**, $C_{12}H_{14}O_4$, mp 79° (M^+ 222, optically inactive) was homogeneous by TLC and gave positive ferric reaction The chelated phenolic hydroxyl (ν_{max}^{KBr} 3450 cm^{-1}) group was readily discernible from the ^1H NMR data (δ 12.20, 1H, *br s*). The UV spectrum, the ^1H NMR data of other protons and the mass spectral fragmentation pattern of **2** were almost similar to those of its congener **1** From the data the structure **2** for verticilone is consistent which has further been confirmed by its ^{13}C NMR spectral analysis (Table 1) and its methylation with diazomethane to **1**

EXPERIMENTAL

Plant materials were collected from Malda, West Bengal. Mps uncorr IR KBr, UV EtOH and EtOH + NaOH, ^1H NMR. $CDCl_3$, TMS as int. standard, ^{13}C NMR. 50 MHz, $CDCl_3$, TMS as int standard, EIMS 70 eV

Isolation of vertinone **1** *and verticilone* **2**. *n*-Hexane extract of dried and powdered whole plant of *Dysophyla verticillata* (5 kg), after removal of the solvent, was chromatographed over a column of silica gel (Merk, 60–120 mesh, deactivated with 15% H_2O, 1 kg). From the eluent of a mixture of *n*-hexane and ethylacetate (19 1) fractions (5–10) and (20–30) yielded verticilone **2** and vertinone **1** respectively.

Vertinone **1** [*But-2-en-4(2′,4′,6′-trimethoxyphenyl)-one*] The crude vertinone on recrystallization from *n*-hexane–C_6H_6 (1.1)

Table 1. ^{13}C NMR spectral data of compounds **1** and **2** (50 MHz, $CDCl_3$, TMS as internal standard, chemical shift in δ, ppm)

C	1	2
1	18 13 *q*	18.7 *q*
2	144.6 *d*	145 3 *d*
3	134 3 *d*	134 9 *d*
4	194 35 *s*	196.1 *s*
1′	111 8 *s*	114 8 *s*
3′	90.9 *d*	94 8 *d*
4′	158 5 *s*	159 2 *s*
5′	90 9 *d*	93 5 *d*
6′	162 2 *s**	163.0 *s**
2′	162 2 *s**	163.8 *s**
2′-OMe	55 4 *q**	—
4′-OMe	55.8 *q**	57 0 *q**
6′-OMe	55.4 *q**	56.24 *q**

*Assignments in the same vertical column may be interchanged.

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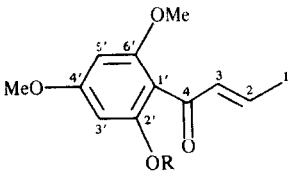

1 R = Me
2 R = H

yielded 30 mg colourless needles, mp 95°, [TLC, R_f 0 54, *n*-hexane–ethylacetate (19 1)], UV λ_{max}^{EtOH} nm (log ε) 294 (4 5), IR ν_{max}^{KBr} cm^{-1}· 1660, 1628, 1590, 1230, 965, 940, ^{1}H NMR (90 MHz, $CDCl_3$, TMS int stand)· δ 1 90 (*d*, J = 8 0 Hz, 3H-1), δ 6 72 (*q*, J = 15.90 Hz, 1H-2), δ 6 48 (*d*, J = 16 0 Hz, 1H-3) δ 6 14 (*s*, 2H-3′,5′), δ 3.76 (*s*, 6H, MeO-2′ and MeO-6′), δ 3 84 (*s* 3H, MeO-6′, EIMS (probe) *m/z* (rel int). 236 $(M)^+$ (80), 221 (35), 206 (20), 195 (100), 181 (20), 167 (45), 69 (30) ^{13}C NMR (50 MHz, $CDCl_3$, TMS int standard) see Table 1.

Verticilone **2**[*But-2-en-4*(*2′-hydroxy-4′,6′-dimethoxyphenyl*)-*one*] The crude verticilone was recrystallized to homogeneity from *n*-hexane [TLC, 0.81, *n*-hexane–EtOAc (19 1)] (20 mg), yellow needles, mp 79°, UV λ_{max}^{EtOH} nm (log ε) 296 (4 25), UV $\lambda_{max}^{EtOH+NaOH}$ nm 296, 310 (infl), IR ν_{max}^{KBr} cm^{-1} 3450, 1655, 1630, 1590, 1210, 1120, 1060, 960, ^{1}H NMR (90 MHz, $CDCl_3$, TMS int stand). δ 1 93 (*d*, J = 7.8 Hz, 3H-1), δ 6 75 (*q*, J = 16 0 Hz, 1H-2) δ 6 51 (*d*, J = 16 0 Hz, 1H-3), δ 6 17 (*d*, J = 3 0 Hz, 1H-3′), δ 6 20 (*d*, J = 3 0 Hz, 1H-5′), δ 3 90 (*s*, 3H, MeO-4′), δ 3 83 (*s*, 3H, Meo-6′), δ 12 20 (*br s*, 1H, disappeared on D_2O exchange), EIMS (probe) *m/z* (rel int) 222 $(M)^+$ (75), 207 (25), 192 (20), 181 (100), 153 (40), 69 (30), ^{13}C NMR (50 MHz, $CDCl_3$, TMS int standard), see Table 1

Methylation of **2** *to* **1** Verticilone **2** (10 mg) in ethereal solution (15 ml) was methylated with diazomethane in the usual way On removal of the solvent and chromatography over alumina yielded a colourless compound which after recrystallization from *n*-hexane–benzene (1 1) yielded vertinone **1** (6 mg) was identified by mmp, IR and UV

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ARYLNAPHTHALENE LIGNAN FROM *JATROPHA GOSSYPIFOLIA*

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Key Word Index—*Jatropha gossypifolia*, Euphorbiaceae, arylnaphthalene lignan, 2,3-*bis*-(hydroxymethyl)-6,7-methylenedioxy-1-(3′,4′-dimethoxyphenyl)-naphthalene

Abstract—2,3-Bis-(hydroxymethyl)-6,7-methylenedioxy-1-(3′,4′-dimethoxyphenyl)-naphthalene has been isolated from *Jatropha gossypifolia* This is the first report of the isolation of this arylnaphthalene lignan from a natural source.

INTRODUCTION

In continuation of our work [1–5] on the lignan constituents of *Jatropha gossypifolia*, we report the isolation of 2,3-bis-hydroxymethyl)-6,7-methylenedioxy-1-(3′,4′-dimethoxyphenyl)-naphthalene from the petrol extract of the plant. This arylnaphthalene lignan has not previously been encountered in nature.

RESULT AND DISCUSSION

2,3-Bis-(hydroxymethyl)-6,7-methylenedioxy-1-(3′,4′-dimethoxyphenyl) naphthalene (**1**), $C_{21}H_{20}O_6$ ($[M]^+$ *m/z* 368), mp 184°, was isolated as colourless needles The UV spectrum of **1** with λ_{max}^{EtOH} nm (log ε). 247 (4 74), 290 (3.92) and 332 (3 43) was consistent with an 1-arylnaphthalene lignan system [6] while the IR spectrum showed the