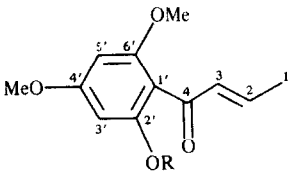

1 R = Me
2 R = H

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

Acknowledgement—We thank Prof B B Biswas (Director of Bose Institute) and Prof. P Chakrabarti (Chair-Person of the Department of Chemistry) for their interest Thanks are also due to Mr Kamal Chakraborty and Mr N K Das for experimental assistance

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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

presence of an hydroxyl group (3420 cm^{-1}). In the 300 MHz ^1H NMR spectrum of **1** in $CDCl_3$ the aromatic region clearly showed the presence of two types of aromatic nuclei. The two singlets at δ7.06 (1H, *s*, H-5) and 6.69 (1H, *s*, H-8) confirmed the presence of two *para* protons while an ABX system was evident from the signals at δ6.78 (1H, *d*, J=2 Hz, H-2'), 6.86 (1H, *dd*, J=8 and 2 Hz, H-6') and 6.85 (1H, *d*, J=8 Hz, H-5'). Two hydroxyls appeared as broad signals at δ3.05 (exchangeable with D_2O) The methylene protons at C-2α and C-3α resonated comparatively downfield at δ4.55 (2H, *s*) and 4 85 (2H, *s*) indicating their association with the hydroxyls as $-CH_2OH$ One methylenedioxy appeared at δ5.93 (2H, *s*) and two methoxyl signals at δ3.90 and 3.78 (3H, *s* each). The methylenedioxy group was reasonably placed in ring A at C-6, C-7 and the two methoxyls in ring C at C-3' and C-4'. The alternative location of the substituents in the aromatic rings was ruled out on the basis of the observation [7] that $\Delta\delta$ for A-ring methoxyls would be >0.2 ppm. The substitution pattern was further confirmed from the mass spectral analysis of **1** which showed the presence of the dimethoxyphenyl fragment ion at *m/z* 137. This was obviously obtained by fragmentation [8] of ring C of the lignan. Other important peaks in the mass spectrum were observed at *m/z* 368 $[M]^+$, 353 $[M-Me]^+$, 350 $[M-H_2O]^+$, 339 $[M-CHO]^+$, 338 $[M-CH_2O]^+$, 321 $[M-H_2O-CHO]^+$, 320 $[M-H_2O-CH_2O]^+$, 231 $[M-C_8H_9O_2]^+$ and 216 $[M-C_8H_9O_2-H_2O]^+$

The structure of **1** was unambiguously assigned from the study of its 75 MHz ^{13}C NMR spectrum in $CDCl_3$ (Table 1). The signals were assigned from the DEPT experiment and the data compared with the reported values [9] of the corresponding signals of known arylnaphthalene lignans.

Table 1. ^{13}C NMR spectral data of lignan **1** (75 MHz, $CDCl_3$)

C	Chemical shift (δ in ppm)
1	135 76
2	131 33
2α	60 71
3	139 73
3α	65 25
4	127 85
5	103 63
6	147 96
7	147.71
8	102.47
9	130 00
10	133 33
1'	130 02
2'	113 31
3'	148 82
4'	148 38
5'	111.02
6'	122 27
$-OCH_2O$	101 05
$-OMe$	55 89

Although lignan **1** has previously been reported as an intermediate [10–11] in the synthesis of chinensin and retrochinensin no data were available on this compound. This is the first report of the natural occurrence of **1** and a detailed study of both its ^1H and ^{13}C NMR data. As the compound was present in the original petrol extract of *J. gossypifolia* (indicated from TLC) it is unlikely to be an artefact.

EXPERIMENTAL

Mp. uncorr Specific rotation was measured in $CHCl_3$, UV spectra in EtOH and IR spectra in KBr ^1H NMR spectra at 300 MHz was recorded in $CDCl_3$ using TMS as int. std, ^{13}C NMR spectra at 75 MHz in $CDCl_3$. The MS was determined at 75 eV

Plant material. Seeds, roots and stem of *J. gossypifolia* L. were collected from Nadia District, West Bengal, India. Voucher specimens, JG (Se), JG (r) and JG (st), have been preserved in our laboratory

Isolation of 2,3-*bis*(*hydroxymethyl*)-6,7-*methylenedioxy*-1-(3',4'-*dimethoxyphenyl*)-*naphthalene* (**1**) Air-dried and finely milled stems, roots and seeds (30 kg) of *J. gossypifolia* were exhaustively extd with petrol (60–80°) in a Soxhlet apparatus for 72 hr. The ext was concd and chromatographed over silica gel, the column being eluted with solvents of increasing polarity The EtOAc eluate afforded **1** which was crystallized from petrol–C_6H_6, mp 184°, yield 6 mg (Found. C, 68.62; H, 5.32. $C_{21}H_{20}O_6$ requires. C, 68 46; H, 5.43%), IR ν_{max}^{KBr} cm^{-1} 3420, 1628, 1605, 1505, 1255, 1180, 1025, 945

Acknowledgements—The authors express their sincere thanks to A. K Acharya, J. Ghosh and P Ghosh of the Organic Instrumentation Laboratory, Department of Chemistry, Calcutta University for recording the spectra and to UGC, New Delhi, for financial assistance.

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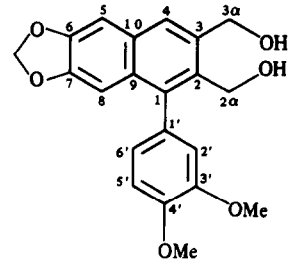

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A PHENOL FROM THE BROWN ALGA *PERITHALIA CAUDATA*

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Key Word Index—*Peritholia caudata*, Phaeophyta, Sporochnaceae, phenol, 2,4-bis(3-methylbut-2-enyl)phenol

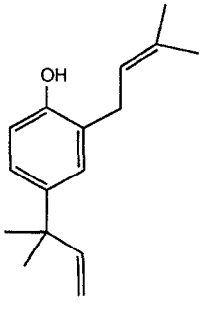
Abstract—The diprenylated phenol 2,4-bis(3-methylbut-2-enyl)phenol as well as the previously described isomeric 4-(1,1-dimethylprop-2-enyl)-2-(3-methylbut-2-enyl)phenol have been isolated from the brown alga *Peritholia caudata*. The relative proportions of these two phenols varies considerably between individual plants.

INTRODUCTION

In an earlier paper we reported that the main secondary metabolite from *Peritholia caudata* (Lab.), a brown seaweed (order Sporochnales) which is common around the coast of southern Australia, was 4-(1,1-dimethylprop-2-enyl)-2-(3-methylbut-2-enyl)phenol (**1**), a diprenylphenol containing a 'reverse' isoprene unit at the 4-position as well as a 'normal' unit at the 2-position [1] The phenol was isolated from a combined collection of the alga A number of plants had been collected, combined and processed to give an oil (1 8% dry weight) consisting of a mixture of **1** (90%) and a second component (9%), which at the time could not be separated This second component has now been obtained pure and identified as 2,4-bis(3-methylbut-2-enyl)phenol (**2**)

RESULTS AND DISCUSSION

Analysis of individual plants, collected at the same location as those in the previous study, has now revealed that there is a considerable variation in the distribution of compounds **1** and **2** in *Peritholia caudata*. Five plants were freeze-dried and powdered Representative samples of each were analysed by GC-MS; relative amounts of **1** and **2**, based on total ion chromatogram measurements, varied from 7.3 . 1 to 0 37 : 1 No other isomeric phenols were detected. The plant extract richest in the second component was subjected to preparative gas chromatography allowing **2** to be obtained in a pure state The molecular formula of **2** was established as $C_{16}H_{22}O$ by high resolution mass spectroscopy, showing that **2** was isomeric with **1**. The low field region of the ^1H NMR spectrum of **2** was quite similar to that of **1**; the three aromatic protons formed an ABX system revealing that **2** was also a 2,4-disubstituted phenol Differences in the rest of the spectrum indicated that the substituents were two nonequivalent 3-methylbut-2-enyl groups, so both of the isoprene units were attached in the normal manner rather than one of them being reversed as in **1** This is the first report of **2** as a natural product although it has previously been synthesized [2, 3]



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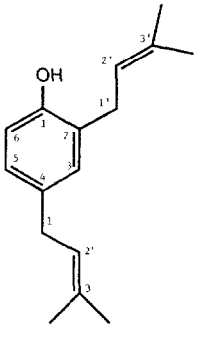

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