Pergamon

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ACETYLENIC THIOPHENES FROM *BLUMEA OBLIQUA*

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Key Word Index—*Blumea obliqua*; Asteraceae; Acetylenic thiophenes.

Abstract—The acetylenic thiophene constituents from the aerial parts of *Blumea obliqua* yielded a novel dithienyl acetylene, 5′-Methylene-bis-[5-(3-butene-1-ynyl)]-2,2′-bithiophene, along with 5′-Hydroxymethyl-5-(3-butene-1-ynyl)-2,2′-bithiophene and 5′-Carboxaldehyde-5-(3-butene-1-ynyl)-2,2′-bithiophene. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

Acetylenic thiophenes have been found to possess very interesting biological activities. They have been found to show nematocidal [1], insecticidal [2], antibacterial [3], antifungal [4] and antiviral [5] activity.

In our previous papers [6–7], we have dealt with the phytochemical study of the hexane-soluble part of the methanolic extract of *Blumea obliqua*, which led to the isolation of six acetylenic thiophenes. We have now reinvestigated the same plant for thiophenic constituents and isolated three more acetylenic thiophenes (**1**, **2** and **4**).

RESULTS AND DISCUSSION

Compound **1** was obtained as needle like crystals. The EI-mass spectrum showed a molecular ion peak [M$^+$] at *m/z* 444.2. A strong [M + 2]$^+$ peak (14.8% of [M$^+$] indicated the presence of sulfur in the compound. HREI mass spectroscopy of the molecular ion peak resulted in the exact value of 444.0146 which was analyzed for the molecular formula $C_{25}H_{16}S_4$, suggesting eighteen degrees of unsaturation. The UV spectrum showed absorption maxima at 347.6 and 242.2 nm. This indicated the presence of a dithienyl acetylenic chromophore [8]. The IR spectrum displayed intense absorption peaks at 2900 (C—H) and 2175 cm^{-1} (C≡C). The ^{1}H NMR spectrum exhibited signals for two thiophenes, a vinyl group and a CH_2 group.

These findings suggested that **1** was a dimer of **2** and **3**, which were also found abundantly in Asteraceae. The compound **1** may have been formed as a result of an enzyme catalyzed condensation reaction of **2** with **3** or it may be an artifact. As the plant material was not subjected to acid or base and was not exposed to heat, it must be concluded that **1** was not an artifact. Dimeric compounds have also been reported in *Echinops bonnaticus* and *E. ritrol* [9] and in *Cardopatium corymbosum* [10].

The structure of compound **2** was established by comparing its ^{1}H NMR and EI mass spectral values with the literature values [12] and its ^{13}C NMR data is presented in Table 1. Compound **4** was isolated previously from *Dyssodia acerosa* [13], but no structural data is available in the literature. We report here its UV, EIMS and ^{1}H NMR data in the Experimental.

EXPERIMENTAL

The NMR spectra were recorded on 400 and 500 MHz instruments and measured in $CDCl_3$, using TMS as an internal standard. Silica gel (Merck 70–230 mesh) was used for CC and silica gel 60 F_{254}, 0.25 mm precoated plates (Merck) were used for TLC and prep. TLC.

Plant Material

Aerial parts (60 kg fr. wt.) of *B. obliqua* were collected from Karachi in July 1995. A voucher specimen is stored in the herbarium at the Botany Department, University of Karachi (voucher No. 63484).

Extraction and Isolation

The air dried plant was chopped and macerated × 2 in MeOH for a 7 day period each time. The extract was filtered and evaporated under red. pres. to a viscous mass (1132 g) which was partitioned between MeOH–H_2O (9:1) and C_6H_{14}. The C_6H_{14} soluble portion was evaporated under red. pres. to an oily paste

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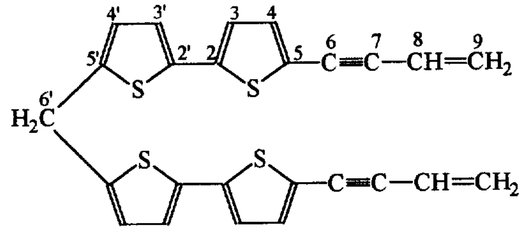

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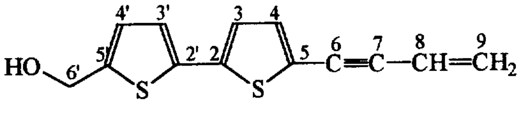

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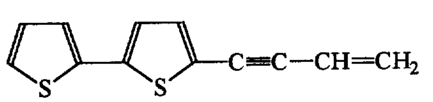

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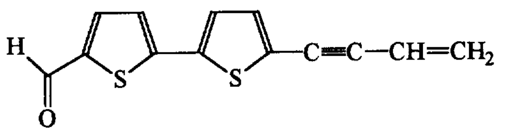

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(51 g). This was loaded onto a silica gel column and eluted with C_6H_{14}, C_6H_{14}–$CHCl_3$ and $CHCl_3$. The fractions obtained with 10% $CHCl_3$ in C_6H_{14} were combined and rechromatographed repeatedly on a silica gel column. Finally, elution with 3% $CHCl_3$ in C_6H_{14} yielded **1**. Prep. TLC of another fraction from 20% $CHCl_3$ in C_6H_{14} elution yielded **2** and **4**.

5′-Methylene-bis-[5-(3-butene-1-ynyl)-2,2′-bithiophene (*1*). Colorless needle like crystals (10 mg); UV λ_{max}^{MeOH} nm; 347.6, 242.2; IR $\nu_{max}^{CHCl_3}$ cm^{-1}; 2900 (C—H), 2150 (C≡C); EIMS *m/z* (rel. int.); 444.2 [M^+] (78.1), 229.1 (19.5), 57 (100); HREIMS *m/z* 444.0146 ($C_{25}H_{16}S_4$, requires 444.0134); ^1H and ^{13}C NMR ($CDCl_3$, 400 and 125 MHz); see Table 1.

5′-Hydroxymethyl-5-(3-butene-1-ynyl)-2,2′-bithiophene (**2**). Purified as yellow crystals (6 mg) by prep. TLC using C_6H_{14}:Et_2O (4:1, $R_f = 0.4$); UV $\lambda_{max}^{Et_2O}$ nm 347.2, 249.6; EIMS *m/z* (rel. int.): 245.7 (94.6), 228.8 (70), 216.8 (100); HREIMS *m/z* 246.0155 ($C_{13}H_{10}OS_2$, requires 246.0173), ^1H NMR and ^{13}C NMR ($CDCl_3$, 400 and 100 MHz); see Table 1.

5′-Carboxaldehyde-5-(3-butene-1-ynyl)-2,2′-bithiophene (*4*). Purified as yellow amorphous solid (4 mg) by prep. TLC using C_6H_{14}:Et_2O (4:1, $R_f = 0.3$); UV $\lambda_{max}^{Et_2O}$ nm : 370.2, 201.8; EIMS *m/z* (rel. int.) 243.7 (100), 214.7 (5.3); Peak matching *m/z* 243.9994 ($C_{13}H_8OS_2$, requires 244.0016), ^1H NMR ($CDCl_3$, 500 MHz): δ 5.58 (1H, *dd*, *J* = 1.9, 11.2 Hz, H-9 *cis*), 5.72 (1H, *dd*, *J* = 1.9, 17.5 Hz, H-9 *trans*), 6.04 (1H, *dd*, *J* = 11.2, 17.5 Hz, H-8) 7.13 (1H, *d*, *J* = 3.8 Hz, H-4)[a], 7.21 (1H, *d*, *J* = 3.8 Hz, H-3)[a], 7.24 (1H, *d*, *J* = 3.8 Hz, H-3′)[a], 7.65 (1H, *d*, *J* = 3.8 Hz, H-4′)[a], and 9.85 (1H, *s*, H-6′) (a = assignments may be interchanged).

Table 1. ^{13}C NMR data and $^1H/^{13}C$ connectivities (HMQC) for **1** and **2**

	Compound **1**		Compound **2**	
Position	Chemical Shift (δ)	$^1H/^{13}C$ Connectivity (*J* = Hz)	Chemical Shift (δ)	$^1H/^{13}C$ Connectivity (*J* = Hz)
2	139.1	—	138.5	—
3	124.0	6.95 (*d*, *J* = 3.8)	123.4	6.99 (*d*, *J* = 3.8)
4	132.7	7.06 (*d*, *J* = 3.8)	132.8	7.07 (*d*, *J* = 3.8)
5	121.6	—	121.9	—
6	83.2	—	83.1	—
7	92.9	—	93.0	—
8	116.9	6.01 (*dd*, *J* = 11.2, 17.5)	116.8	6.01 (*dd*, *J* = 11.0, 17.5)
9	126.8	5.52 (*dd*, *J* = 1.9, 11.2) *cis*	126.9	5.52 (*dd*, *J* = 1.9, 11.0) *cis*
9	126.8	5.72 (*dd*, *J* = 1.9, 17.5) *trans*	126.9	5.72 (*dd*, *J* = 1.9, 17.5) *trans*
2′	135.8	—	138.9	—
3′	123.2	7.00 (*d*, *J* = 3.6)	123.8	7.02 (*d*, *J* = 3.6)
4′	126.3	6.80 (*d*, *J* = 3.6)	126.1	6.89 (*d*, *J* = 3.6)
5′	142.5	—	143.8	—
6′	30.7	4.27 (*s*)	60.1	4.80 (*s*)

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