Photoactivated Insecticidal Thiophene Derivatives from *Xanthopappus subacaulis*

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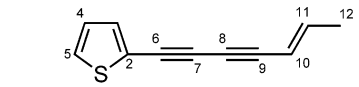
Three new photoactivated insecticidal thiophene derivatives, xanthopappins A−C (**1**−**3**), were isolated from *Xanthopappus subacaulis*, along with three known thiophene acetylenes, 5-hydroxymethyl-2-(*E*)-hept-5-ene-1,3-diynylthiophene (**4**), 5-(1,2-dihydroxyethyl)-2-(*E*)-hept-5-ene-1,3-diynylthiophene (**5**), and 5-(1,2-diacetoxyethyl)-2-(*E*)-hept-5-ene-1,3-diynylthiophene (**6**). The structures of **1**−**3** were elucidated by spectroscopic methods. Compounds **1**−**6** exhibited significant photoactivated insecticidal activity against the fourth-instar larvae of the Asian tiger mosquito.

Phototoxic phytochemicals have attracted considerable attention for more than 30 years because of their potent biocidal activities and widespread occurrence among plants.[1] These compounds are characterized by the great enhancement of their activities after absorption of light energy and have diverse biological effects including insecticidal, fungicidal, bactericidal, nematicidal,[2] and herbicidal[3] activities. A large number of compounds possessing photoactivated insecticidal activities have been isolated from plants since 1978, when the photoinduced toxicity of a plant-derived furanocoumarin, xanthotoxin, toward larvae of the armyworm, *Spodoptera eridania*, was reported.[4,5] More than 15 structural classes of plant-derived phototoxins have been described, among which thiophene derivatives represent one of the most thoroughly investigated groups of phototoxic phytochemicals.[6]

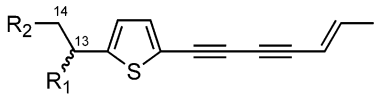
Xanthopappus subacaulis C. Winkl. (Asteraceae) is an endemic plant in mainland China. During screening for photoactivated insecticidal plants growing in northwest China, we found that a methanol extract of its stems and roots exhibited potent photoactivated insecticidal activity against the fourth-instar larvae of the Asian tiger mosquito, *Aedes albopictus* (Skuse). This prompted us to investigate the active constituents of *X. subacaulis*. Three new photoactivated insecticidal thiophene derivatives, xanthopappins A−C (**1**−**3**), were isolated along with three known thiophenes, 5-hydroxymethyl-2-(*E*)-hept-5-ene-1,3-diynylthiophene (**4**), 5-(1,2-dihydroxyethyl)-2-(*E*)-hept-5-ene-1,3-diynylthiophene (**5**), and 5-(1,2-diacetoxyethyl)-2-(*E*)-hept-5-ene-1,3-diynylthiophene (**6**),[7] by activity-directed fractionation. The structures of **1**−**3** were established by spectroscopic means. Herein we report the isolation, structure elucidation, and photoactivated insecticidal activity of these compounds.

The methanol extract of the plant was fractionated by successive extraction with petroleum ether, $CHCl_3$, and ethyl acetate. The photoactivated insecticidal fractions, the petroleum ether-soluble and $CHCl_3$-soluble fractions, were individually separated by column chromatography over silica gel and Sephadex LH-20, followed by preparative thin-layer chromatography (TLC) over silica gel, to afford **1**−**6**.

Xanthopappin A (**1**) gave the molecular formula $C_{11}H_8S$ by combined analysis of its HRTOFMS, ^{13}C NMR, and DEPT data. The ^1H NMR spectrum exhibited signals at δ 5.61 (1H, dq, J = 15.8, 1.8 Hz), 6.35 (1H, dq, J = 15.8, 6.9 Hz), and 1.84 (3H, dd, J = 6.9, 1.8 Hz) for a *trans*-propenyl group, and a group of double doublets at δ 7.29 (1H, J = 3.7, 1.1 Hz), 6.96 (1H, J = 5.1, 3.7 Hz), and 7.27 (1H, J = 5.1, 1.1 Hz) for a 2-thienyl group.[8,9] The ^{13}C NMR and DEPT spectra showed signals for a methyl carbon, six olefinic carbons, of which five were methines and one was quaternary, and four alkynyl quaternary carbons (δ 72.2, 73.5, 78.3, and 82.9). Analysis of the $^1H-^1H$ COSY, HSQC, and HMBC data furnished the assignments of all ^1H and ^{13}C NMR signals (Table 1). The HMBC correlations (Table 1) from H-11 to C-9, from H-10 to C-9 and C-8, and from H-3 to C-6 indicated a connectivity between the thienyl group and the *trans*-propenyl group through a butadiyne chain. Thus, the structure of **1** was established as 2-(*E*)-hept-5-ene-1,3-diynylthiophene.



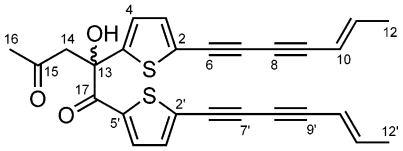
1



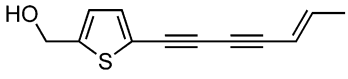
2 R_1 = OH, R_2 = Cl

5 R_1 = R_2 = OH

6 R_1 = R_2 = OAc



3



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Xanthopappin B (**2**) was shown to have a molecular formula of $C_{13}H_{11}OSCl$, by analysis of its HRTOFMS,^{13}C NMR, and DEPT spectra (Table 1). The presence of a chlorine atom in the molecule of **2** was clearly indicated by the ion peak intensity ratio between $[M + 2]^+$ and $[M + 1]^+$ in the EIMS. The ^1H and ^{13}C NMR spectra of **2** (Table 1) showed the same signals indicating the presence of a (*E*)-hept-5-ene-1,3-diynyl group as those in **1**. The presence of a pair of doublets at δ 7.17 (1H, J = 3.7 Hz) and 6.89 (1H, J = 3.7 Hz) in the ^1H NMR spectrum and two quaternary carbon signals at δ 146.3 and 122.4 in the ^{13}C NMR spectrum of **2** indicated that the thiophene ring is disubstituted in **2**, [10] rather than monosubstituted in **1**. Moreover, the proton signals at δ 5.10 (1H, dd, J = 7.9, 3.7 Hz), 3.79 (1H, dd, J = 11.3, 3.7 Hz), and 3.70 (1H, dd, J = 11.3, 7.9 Hz) and the EIMS fragment ions at m/z 201 $[M - CH_2Cl]^+$

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Table 1. ^{1}H and ^{13}C NMR Spectroscopic Data and HMBC Correlations for **1** and **2** in $CDCl_3$[a]

	1			**2**		
position	^{1}H	^{13}C	HMBC	^{1}H	^{13}C	HMBC
2		122.4 s			122.4 s	
3	7.29 dd (3.7, 1.1)	133.9 d	C-2, C-4, C-5, C-6	7.17 d (3.7)	133.9 d	C-2, C-4, C-5, C-6
4	6.96 dd (5.1, 3.7)	127.1 d	C-2, C-3, C-5	6.89 d (3.7)	124.6 d	C-2, C-3, C-5
5	7.27 dd (5.1, 1.1)	128.4 d	C-2, C-3, C-4		146.3 s	C-2, C-3, C-4
6		73.5 s			73.1 s	
7		78.3 s			78.7 s	
8		72.2 s			72.1 s	
9		82.9 s			83.3 s	
10	5.61 dq (15.8, 1.8)	109.9 d	C-8, C-9, C-11, C-12	5.62 dq (15.8, 1.6)	109.8 d	C-8, C-9, C-11, C-12
11	6.35 dq (15.8, 6.9)	143.9 d	C-9, C-10, C-12	6.37 dq (15.8, 6.9)	144.3 d	C-9, C-10, C-12
12	1.84 dd (6.9, 1.8)	18.9 q	C-10, C-11	1.84 dd (6.9, 1.6)	19.0 q	C-10, C-11
13				5.10 dd (7.9, 3.7)	70.4 d	C-4, C-5, C-14
14				3.79 dd (11.3, 3.7)	50.1 t	C-5, C-13
				3.70 dd (11.3, 7.9)		C-5, C-13

[a] Chemical shifts (δ) in ppm; coupling constants (parentheses) given in Hz.

(100) and 171 [M − $CH_2ClCH(OH)$]$^+$ (18) revealed the presence of a 2-chloro-1-hydroxyethyl group in the molecule.[11,12] This was further supported by the ^{13}C NMR signals at δ 70.4 and 50.1 (Table 1). The HMBC correlations (Table 1) from H-13 to the thiophene quaternary carbon at δ 146.3 and the thiophene methine carbon at δ 124.6 were present, while the correlations from H-13 to other thiophene carbons were not observed. This, in combination with the coupling constant (J = 3.7 Hz)[10] between two thiophene protons, indicated the attachment of the 2-chloro-1-hydroxyethyl group to C-5. Therefore, **2** was determined as 5-(2-chloro-1-hydroxyethyl)-2-(*E*)-hept-5-ene-1,3-diynylthiophene.

Xanthopappin C (**3**) was determined to have a molecular formula of $C_{27}H_{20}O_3S_2$, according to its HRTOFMS,^{13}C NMR, and DEPT spectra. The ^{1}H NMR spectra of **3** (Table 2) gave four doublets at δ 7.08, 6.73, 7.16, and 7.91 (each 1H, J = 3.8 Hz) for four thiophene protons. In the ^{13}C NMR and DEPT spectra, the signals for olefinic, thiophene, and alkynyl carbons were coupled (Table 2). Such evidence was indicative of a structure for **3** with two 5-substituted 2-(*E*)-hept-5-ene-1,3-diynylthiophene moieties. In addition, the ^{1}H and ^{13}C NMR spectra indicated the presence of a methyl group [δ_H 2.28 (3H, s, H-16); δ_C 30.9 (q, C-16)], a methylene [δ_H 3.74 and 2.86 (each 1H, d, J = 17.5 Hz, H-14); δ_C 52.2 (t, C-14)], an oxygenated quaternary carbon [δ_C 82.1 (s, C-13)], and two ketone carbonyl carbons [δ_C 210.9 (s, C-15) and 190.4 (s, C-17)]. The connectivities among the groups, carbons, and structural moieties of **3** were deduced from the correlations in the HMBC spectrum (Table 2). The HMBC correlations from H-16 to C-15 and C-14, from H-14 to C-15, C-13, and C-17, and from OH-13 to C-13, C-14, and C-17 revealed a 2-hydroxypentane-1,4-dione moiety. The HMBC correlations from H-14 to C-5, from H-4 to C-13, from H-4′ to C-17, and from OH-13 to C-5 suggested linkages between C-5 and C-14 and between C-5′ and C-17. Therefore, the structure of **3** was assigned as 1,2-bis[5-(*E*)-hept-5-ene-1,3-diynylthiophen-2-yl]-2-hydroxypentane-1,4-dione.

The spectroscopic data of compounds **4**−**6** were coincident with the known thiophene acetylenes,[7] 5-hydroxymethyl-2-(*E*)-hept-5-ene-1,3-diynylthiophene, 5-(1,2-dihydroxyethyl)-2-(*E*)-hept-5-ene-1,3-diynylthiophene, and 5-(1,2-diacetoxyethyl)-2-(*E*)-hept-5-ene-1,3-diynylthiophene, respectively. The previously unreported ^{13}C NMR data for **4** and **6** are given in the Experimental Section.

The optical rotations ($[\alpha]_D$) of compounds **2**, **3**, **5**, and **6** were found to be 0, which suggested they are racemates. Mosher esterifications of **2** and **5** with (*R*)-α-methoxy-α-trifluoromethylphenylacetic acid (MTPA) in the presence of 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC-HCl)[13] afforded a mixture of two isomeric esters in approximately 1:1 ratio for each reaction, which was estimated from the intensity of methyl proton (H-12) signals in the ^{1}H NMR spectra. Thus, **2** and **5** were both confirmed to be an equimolar racemic mixture.[14−16] Since the structure of **3** is closely related to those of **2** and **5**, and its optical rotation was 0, it was assumed that **3** is also an equimolar racemic mixture. These findings cast doubt on the occurrence of these racemates as natural products, but they are unlikely to be isolation artifacts because compounds **2** and **5**, two major racemates, could be detected from the $CHCl_3$-soluble extract by co-TLC [Merck Kieselgel 60G, developed with petroleum ether−EtOAc (2:1) and $CHCl_3$−MeOH (20:1), detection effected by fluorescent light (365 nm)] with the authenticated compound samples.

Table 2. ^{1}H and ^{13}C NMR Spectroscopic Data and HMBC Correlations for **3** in $CDCl_3$[a,b]

position	^{1}H	^{13}C	HMBC
2		123.0 s	
3	7.08 d (3.8)	134.3 d	C-2, C-4, C-5, C-6
4	6.73 d (3.8)	123.8 d	C-2, C-3, C-5, C-13
5		147.0 s	
6		73.0 s	
7		79.1 s[c]	
8		72.1 s	
9		83.5 s	
10	5.63 dq (15.8, 1.6)	109.9 d	C-8, C-9, C-11, C-12
11	6.38 dq (15.8, 6.9)	144.2 d	C-9, C-10, C-12
12	1.84 dd (6.9, 1.6)	18.9 q	C-10, C-11
13		82.1 s	
14	3.74 d (17.5), 2.86 d (17.5)	52.2 t	C-5, C-13, C-15, C-16, C-17
15		210.9 s	
16	2.28 s	30.9 q	C-14, C-15
17		190.4 s	
2′		131.5 s	
3′	7.16 d (3.8)	133.9 d	C-2′, C-4′, C-5′, C-6′
4′	7.91 d (3.8)	136.0 d	C-2′, C-3′, C-5′, C-17
5′		139.0 s	
6′		72.7 s	
7′		81.9 s[c]	
8′		71.9 s	
9′		85.0 s	
10′	5.61 dq (15.8, 1.6)	109.7 d	C-8′, C-9′, C-11′, C-12′
11′	6.38 dq (15.8, 6.9)	145.0 d	C-9′, C-10′, C-12′
12′	1.84 dd (6.9, 1.6)	19.0 q	C-10′, C-11′
OH-13	5.74 br s		C-5, C-13, C-14, C-17

[a] Chemical shifts (δ) in ppm; coupling constants (parentheses) given in Hz. [b] Assignments interchangeable between positions 8−12 and 8′−12′ as a whole. [c] Assignments interchangeable.

The photoactivated insecticidal activity of compounds **1**−**6** against the fourth-instar larvae of the Asian tiger mosquito at 24 h was evaluated by incubating the larvae in water containing the test compounds. The LC_{50} values of **1**−**6** under UV light were 0.71, 0.53, 0.95, 0.30, 4.2, and 0.66 μg/mL, respectively, while in the

dark, those of **1** and **3**−**6** were more than 10 μg/mL and that of **2** was 5.1 μg/mL. The irradiation-generated enhancement in the activity of **1** and **3**−**6** was more than 14.1-, 10.5-, 33.3-, 2.4-, and 15.2-fold, respectively, and that of **2** was 9.6-fold. Because the light-dependent toxicity results from photooxidation of various substrates leading to membrane damage, enzyme inactivation, cell death, and other biological function losses,[17] it could be predicted that weeds, bacteria, fungi, nematodes, and other organisms would also be sensitive to these compounds in the presence of light due to their common targets.

Experimental Section

General Experimental Procedures. Optical rotations were obtained on a Perkin-Elmer 343 polarimeter with acetone as solvent. The ^{1}H (500 MHz), ^{13}C (125 MHz), and 2D NMR spectra were recorded in $CDCl_3$ on a Bruker AV-500 instrument using TMS as an internal reference. HRTOFMS data were obtained on an API QSTAR TOF mass spectrometer in the positive-ion mode. EIMS were collected on a VG Auto Spec-3000 mass spectrometer by direct inlet. For column chromatography, silica gel (100−200 and 200−300 mesh, Qingdao Marine Chemical Ltd., Qingdao, People's Republic of China) and Sephadex LH-20 were used. Preparative TLC was performed on precoated silica gel plates (GF_{254}, Qingdao Marine Chemical Ltd., Qingdao, People's Republic of China, 0.25 mm thickness) with detection under fluorescent (λ = 254 nm) light.

Plant Material. The stems and roots of *Xanthopappus subacaulis* C. Winkl. were collected at Tianzhu County, Gansu Province, People's Republic of China, in July 2004. An authenticated voucher specimen (No. NW040706) was deposited at the herbarium of the College of Forestry, South China Agriculture University, Guangzhou, People's Republic of China.

Extraction and Isolation. The powdered dry plant material (10 kg) was extracted with MeOH three times at room temperature, and the MeOH solutions were combined and concentrated in vacuo. The residue (588 g) was suspended in H_2O and then sequentially extracted three times each with petroleum ether, $CHCl_3$, and EtOAc, to afford dried petroleum ether- (117 g), $CHCl_3$- (38 g), EtOAc- (35 g), and H_2O-soluble (382 g) extracts. These extracts together with the crude MeOH extract were evaluated for photoactivated insecticidal activity against the larvae of the Asian tiger mosquito. The LC_{50} (μg/mL) values of crude MeOH-, petroleum ether-, and $CHCl_3$-soluble extracts under UV light were 115.7, 5.3, and 4.1, respectively. The other extracts under UV light and all extracts in the dark did not cause the test insects to die at 500 μg/mL.

The petroleum ether-soluble extract was subjected to passage over a silica gel column, eluted with petroleum ether−acetone mixtures of increasing polarities (100:0−90:10), to obtain 19 fractions (PI−PXIX), which were evaluated for photoactivated insecticidal activity against the larvae of the Asian tiger mosquito. The mortalities of fractions PIV and PXIII at the concentration of 50 μg/mL were 100% under UV light, and those of others were 0−45% at the same concentration. Thus, the most active fractions, PIV and PXIII, were chosen for further detailed purification.

Fraction PIV, obtained on elution with petroleum ether−acetone (95:5), was applied to a silica gel column, eluted with petroleum ether−EtOAc (25:1−4:1), to afford 14 subfractions (PIV-1−PIV-14). Subfraction PIV-5 was further separated by Sephadex LH-20 column chromatography eluted with acetone followed by preparative TLC developed with petroleum ether−acetone (8:1) to give compound **1** (26.3 mg; R_f 0.75). Fraction PXIII, obtained on elution with petroleum ether−acetone (10:1), was subjected to silica gel column chromatography, eluted with petroleum ether−acetone (15:1−10:1), to afford nine subfractions (PXIII-1−PXIII-9). Subfraction PXIII-7 was further separated by Sephadex LH-20 column chromatography, eluted with acetone, and then preparative TLC developed with petroleum ether−EtOAc (4:1) to give compound **6** (13.1 mg; R_f 0.43).

The $CHCl_3$-soluble extract was chromatographed over a silica gel column, eluted with $CHCl_3$−MeOH mixtures of increasing polarities (100:0−20:3), to yield 17 fractions (CI−CXVII), which were also evaluated for photoactivated insecticidal activity. The mortalities of fractions CI, CII, CIII, and CXIII at the concentration of 50 μg/mL were all 100% under UV light, and those of others were 0−42% at the same concentration. The fractions CI, CII, CIII, and CXIII were therefore applied for further purification.

Fraction CI, obtained on elution with $CHCl_3$, was separated by silica gel column chromatography eluted with petroleum ether−acetone (18:1−12:1) to afford 12 subfractions (CI-1−CI-12). Subfraction CI-11 was further separated by Sephadex LH-20 column chromatography eluted with acetone and then purified by preparative TLC developed with petroleum ether−EtOAc (3:1) to give compound **3** (6.4 mg; R_f 0.44). Fraction CII, obtained on elution with $CHCl_3$, was separated by silica gel column chromatography eluted with petroleum ether−acetone (6:1−2:1) to afford 13 subfractions (CII-1−CII-13). Subfraction CII-6 was further applied to a Sephadex LH-20 column, eluted with acetone, followed by preparative TLC developed with petroleum ether−EtOAc (2:1) to give **2** (22.1 mg; R_f 0.79). Fraction CIII, obtained on elution with $CHCl_3$, was separated by silica gel column chromatography eluted with petroleum ether−acetone (6:1−2:1) to afford 12 subfractions (CIII-1−CIII-12). Subfraction CIII-9 was further separated on a Sephadex LH-20 column eluted with acetone and purified by preparative TLC developed with petroleum ether−EtOAc (5:2) to give **4** (22.3 mg; R_f 0.51). Fraction CXIII, obtained on elution with $CHCl_3$−MeOH (40:3), was separated by silica gel column chromatography eluted with $CHCl_3$−MeOH (40:1−20:3) to afford 12 subfractions (CXIII-1−CXIII-12). Subfraction CXIII-5 was further separated by Sephadex LH-20 column chromatography eluted with acetone followed by preparative TLC developed with $CHCl_3$−MeOH (40:3) to give compound **5** (24.1 mg; R_f 0.62).

Xanthopappin A (1): brown oil; UV (MeCN) λ_{max} (log ϵ) 206 (4.31), 252 (4.22), 313 (4.08) nm; ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$), see Table 1; EIMS *m*/*z* 172 $[M]^+$ (47), 171 $[M - H]^+$ (34), 144 $[M - C_2H_4]^+$ (32); HRTOFMS *m*/*z* 173.0428 $[M + H]^+$ (calcd for $C_{11}H_9S$, 173.0424).

Xanthopappin B (2): brown oil; $[\alpha]^{20}_D$ 0 (*c* 0.377, acetone); UV (MeCN) λ_{max} (log ϵ) 209 (4.37), 268 (4.44) nm; ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$), see Table 1; EIMS *m*/*z* 252 $[M + 2]^+$ (14), 251 $[M + 1]^+$ (6), 250 $[M]^+$ (38), 201 $[M - CH_2Cl]^+$ (100), 171 $[M - CH_2ClCH(OH)]^+$ (18); HRTOFMS *m*/*z* 273.0112 $[M + Na]^+$ (calcd for $C_{13}H_{11}ONaSCl$, 273.0116).

Xanthopappin C (3): brown oil; $[\alpha]^{20}_D$ 0 (*c* 0.085, acetone); UV (MeCN) λ_{max} (log ϵ) 215 (4.72), 269 (4.83), 353 (4.52) nm; ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$), see Table 2; EIMS *m*/*z* 456 $[M]^+$ (4), 398 $[M - CH_3COCH_3]^+$ (17), 370 $[M - CH_3COCH_3 - H_2O]^+$ (9), 257 $[M - HCOC_4H_2SC{\equiv}CC{\equiv}CCH{=}CHCH_3]^+$ (25), 200 $[HCOC_4H_2SC{\equiv}CC{\equiv}CCH{=}CHCH_3]^+$ (18), 199 $[HCOC_4H_2SC{\equiv}CC{\equiv}CCH{=}CHCH_3 - H]^+$ (100), 171 (6); HRTOFMS *m*/*z* 479.0737 $[M + Na]^+$ (calcd for $C_{27}H_{20}O_3NaS_2$, 479.0751).

5-Hydroxymethyl-2-(*E*)-hept-5-ene-1,3-diynylthiophene (4): brown oil; UV (MeCN) λ_{max} (log ϵ) 214 (4.55), 257 (4.46), 268 (4.45), 318 (4.33) nm; ^{1}H NMR (500 MHz, $CDCl_3$), identical with those reported;[7] ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.2 (C-5), 144.1 (C-11), 134.0 (C-3), 125.1 (C-4), 122.4 (C-2), 109.9 (C-10), 83.2 (C-9), 78.4 (C-7), 73.5 (C-6), 72.1 (C-8), 60.2 (C-13), 18.9 (C-12); EIMS *m*/*z* 202 $[M]^+$ (100), 185 $[M - OH]^+$ (31), 171 $[M - CH_2OH]^+$ (14); HRTOFMS *m*/*z* 203.0525 $[M + H]^+$ (calcd for $C_{12}H_{11}OS$, 203.0530).

5-(1,2-Dihydroxyethyl)-2-(*E*)-hept-5-ene-1,3-diynylthiophene (5): white solid; $[\alpha]^{20}_D$ 0 (*c* 0.083, acetone); UV (MeCN) λ_{max} (log ϵ) 209 (4.43), 259 (4.45), 268 (4.47) nm; ^{1}H NMR (500 MHz, $CDCl_3$) and ^{13}C NMR (125 MHz, $CDCl_3$), identical with those reported;[7,18] EIMS *m*/*z* 232 $[M]^+$ (40), 201 $[M - CH_2OH]^+$ (100), 171 $[M - CH_2(OH)CH(OH)]^+$ (20); HRTOFMS *m*/*z* 255.0458 $[M + Na]^+$ (calcd for $C_{13}H_{12}O_2NaS$, 255.0455).

5-(1,2-Diacetoxyethyl)-2-(*E*)-hept-5-ene-1,3-diynylthiophene (6): brown oil; $[\alpha]^{20}_D$ 0 (*c* 0.218, acetone); UV (MeCN) λ_{max} (log ϵ) 209 (4.43), 258 (sh), 268 (4.62) nm; ^{1}H NMR (500 MHz, $CDCl_3$), identical with those reported;[7] ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4 (CH_3CO_2-14), 20.7 (CH_3CO_2-14), 169.7 (CH_3CO_2-13), 20.9 (CH_3CO_2-13), 144.3 (C-11), 141.5 (C-5), 133.6 (C-3), 126.5 (C-4), 123.2 (C-2), 109.8 (C-10), 83.4 (C-9), 78.9 (C-7), 72.9 (C-6), 72.0 (C-8), 68.8 (C-13), 65.4 (C-14), 19.0 (C-12); EIMS *m*/*z* 316 $[M]^+$ (34), 256 $[M - AcOH]^+$ (63), 214 $[M - AcOH - Ac]^+$ (100), 201 $[M - CH_2(OAc)CH(OAc)]^+$ (77); HRTOFMS *m*/*z* 339.0663 $[M + Na]^+$ (calcd for $C_{17}H_{16}O_4NaS$, 339.0667).

Preparation of Mosher's Esters. A solution of compound **2** (4.0 mg, 0.016 mmol) in CH_2Cl_2 (1.0 mL) was treated with (*R*)-MTPA (51.1 mg, 0.22 mmol) in the presence of EDC−HCl (41.9 mg, 0.22 mmol) and 4-DMAP (18.0 mg, 0.15 mmol), and the mixture was stirred at

room temperature (20 °C) under an N_2 atmosphere for 8 h. It was poured into ice−water, and the whole was extracted with EtOAc. The EtOAc extract was successively washed with 5% aqueous HCl, aqueous saturated $NaHCO_3$, and brine, then dried over $MgSO_4$ and filtered. Evaporation of the solvent from the filtrate under reduced pressure furnished a residue, which was purified on a silica gel column (0.6 g, *n*-hexane−EtOAc, 20:1) to give a mixture of a pair of (*R*)-MTPA esters (3.2 mg). Through a similar procedure, **5** (3.7 mg) yielded a pair of (*R*)-Mosher's esters (3.1 mg) by reacting with (*R*)-MTPA. Each pair of Mosher's esters was obtained in a ca. 1:1 ratio according to the ^{1}H NMR spectra.

(*R*)-MTPA Esters of 2. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42−7.33 (10H, m, Ar−H), 7.15 (1H, d, J = 3.8 Hz, H-3), 7.14 (1H, d, J = 3.8 Hz, H-3), 6.92 (1H, d, J = 3.8 Hz, H-4), 6.91 (1H, d, J = 3.8 Hz, H-4), 6.39 (1H, m, H-11), 6.32 (1H, dd, J = 10.5, 3.9 Hz, H-13), 6.31 (1H, dd, J = 10.5, 3.9 Hz, H-13), 6.23 (1H, m, H-11), 5.63 (1H, br d, J = 15.8 Hz, H-10), 5.62 (1H, br d, J = 15.8 Hz, H-10), 3.90 (1H, dd, J = 12.0, 3.8 Hz, H-14), 3.88 (1H, dd, J = 12.0, 3.8 Hz, H-14), 3.80−3.84 (2H, m, H-14), 1.97 (3H, dd, J = 7.0, 1.6 Hz, H-12), 1.87 (3H, dd, J = 7.0, 1.6 Hz, H-12).

(*R*)-MTPA Esters of 5. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53−7.40 (10H, m, Ar−H), 7.14 (1H, d, J = 3.8 Hz, H-3), 7.12 (1H, d, J = 3.8 Hz, H-3), 6.98 (1H, d, J = 3.8 Hz, H-4), 6.97 (1H, d, J = 3.8 Hz, H-4), 6.48−6.46 (2H, m, H-13), 6.42 (1H, m, H-11), 6.24 (1H, m, H-11), 5.63 (1H, br d, J = 15.8 Hz, H-10), 5.62 (1H, br d, J = 15.8 Hz, H-10), 4.74−4.70 (2H, m, H-14), 4.50−4.46 (2H, m, H-14), 1.98 (3H, dd, J = 7.0, 1.6 Hz, H-12), 1.87 (3H, dd, J = 7.0, 1.6 Hz, H-12).

Photoactivated Insecticidal Activity. Photoactivated insecticidal activity was determined as described previously.[19,20] The test insects were the fourth-instar larvae of *Aedes albopictus* (Skuse), from a laboratory colony maintained in Guangdong Center for Disease Control and Prevention, Guangzhou, People's Republic of China. The extracts and compounds were individually dissolved and serially diluted with acetone. Each resultant solution (0.4 mL) was added to a beaker containing 20 mL of dechlorinated water, and then 30 larvae were transferred into the beaker. Two sets of experiments were performed for each test sample, one of which was for ultraviolet-treated trials, and another was held in the dark throughout the trials. After 3 h of incubation in a dark room, the ultraviolet-treated groups were irradiated for 1.5 h, receiving 2074 μW/cm^2 under a light source emitting at 300−400 nm with a maximum at 365 nm, and then returned to darkness for a 24 h incubation. The average mortality of three replications at each concentration was calculated, and the LC_{50} value, which was defined as the concentration causing 50% mortality, was determined. For the activity of the chromatographic fractions, the mortalities only at the final concentration of 50 μg/mL were determined.

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