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Synthesis and Investigation of Mass Spectra of 3-[5'-(2'-Substituent)thienyl]benzo[5,6]coumarins

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SYNTHESIS AND INVESTIGATION OF MASS SPECTRA OF 3-[5'-(2'-SUBSTITUENT)-THIENYL]BENZO[5,6]COUMARINS

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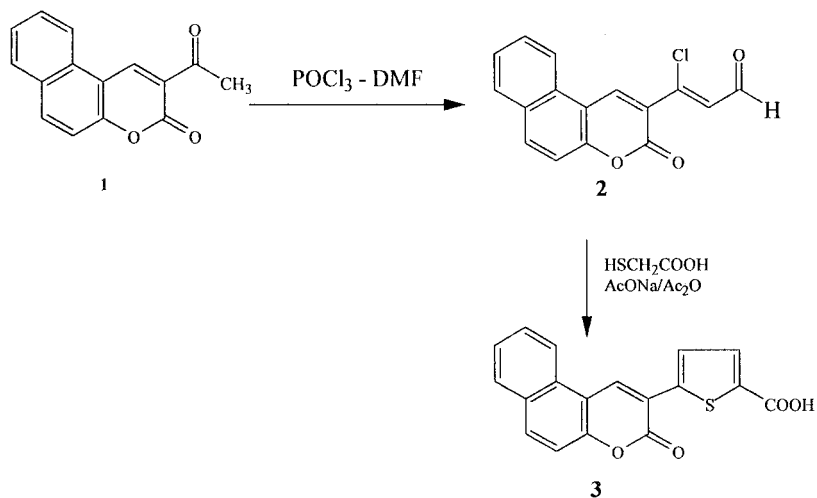
(Received December 13, 2002; accepted January 8, 2003)

3-[5'-(2'-Hydroxycarbonyl)thienyl]benzo[5,6]coumarin (3) was prepared via condensation of 2 with thioglycolic acid in the presence of AcONa and Ac₂O. Esterification of 3 with alcohols gave 3-[5'-(2'-alkoxycarbonyl)thienyl]benzo[5,6]-coumarins (4a,b). The chemical behavior of 4 toward nucleophilic reagents (such as ammonia, hydroxylamine, and hydrazine derivatives) is described. The electron impact ionization mass spectra of compounds 4b, 5, and 8a,b show a weak molecular ion peak and a base peak of m/z 278 resulting from a cleavage fragmentation. In contrast compounds 3 and 4a show a base peak of m/z 250 and m/z 74 resulting from fragmentation. Compounds 9 and 10 give a characteristic fragmentation pattern with a very stable fragment of m/z 305.

Keywords: Coumarins; mass spectra

Benzo[5,6]coumarin derivatives show antimicrobial,¹ antiinflammatory,² and anticancer³ activities. According to our previous work,^{4,5} 3-acetylbenzo[5,6]coumarin (1) reacted with POCl₃-DMF affording 3-(2'-formyl-1'-chlorovinyl)benzo[5,6]-coumarin (2). As an extension of our previous work,⁴⁻¹² the present work describes the synthesis and investigation of mass spectra of 3-[5'-(2'-substituent)thienyl]benzo[5,6]-coumarins using 2 as a key starting material. The reactions studied and the products obtained are depicted in Schemes 1 and 2.

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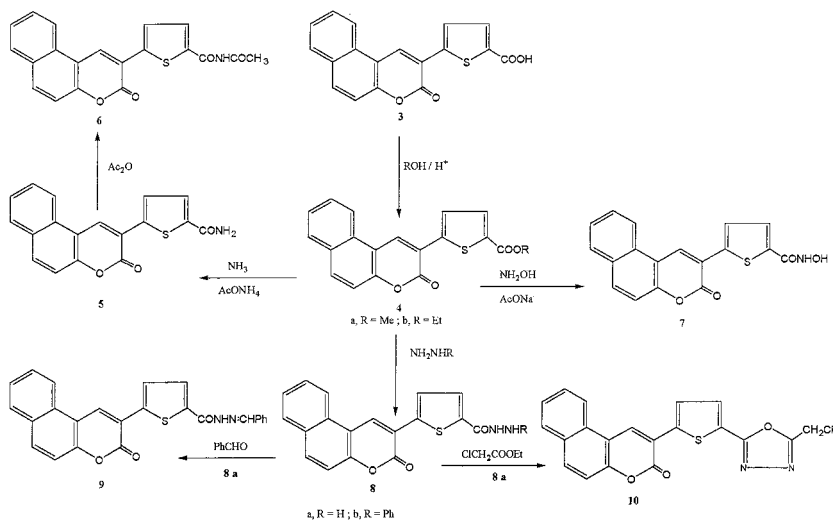


SCHEME 1

RESULTS AND DISCUSSION

Chemistry

3-(2'-Formyl-1'-chlorovinyl)benzo[5,6]coumarin (**2**) was prepared from 3-acetylbenzo[5,6]coumarin (**1**) and DMF-POCl₃, according to literature



SCHEME 2

procedure.¹³ Treatment of compound **2** with thioglycolic acid in the presence of fused sodium acetate and acetic anhydride in acetic acid under reflux, gave the corresponding 3-[5'-(2'-hydroxycarbonyl)-thienyl]benzo[5,6]coumarin (**3**) (Scheme 1).

Esterification of compound **3** with alcohols (such as methanol and ethanol) in the presence of sulphuric acid in benzene to afford the corresponding 3-[5'-(2'-alkoxycarbonyl)thienyl]benzo[5,6]coumarins (**4a,b**). Aminolysis of compound **4** with ammonia from ammonium acetate or formamide by fusion at 100°C in oil-bath yielded the corresponding 3-[5'-(2'-aminocarbonyl)thienyl]benzo[5,6]coumarin (**5**).

3-[5'-(2'-Acetylaminocarbonyl)thienyl]benzo[5,6]coumarin (**6**) was prepared by refluxing **5** with acetic anhydride.

The reaction of 3-[5'-(2'-alkoxycarbonyl)thienyl]benzo[5,6]coumarins (**4a,b**) with hydroxyl amine and hydrazine derivatives (such as phenylhydrazine sulphate and hydrazine sulphate) in ethanol under reflux gave the corresponding 3-[5'-(2'-hydroxyaminocarbonyl)-thienyl]benzo[5,6]coumarin (**7**) and 3-[5'-(2'-alkylhydrazinylcarbonyl)thienyl]benzo[5,6]coumarins (**8a,b**) respectively.

Condensation of compound **8a** with benzaldehyde in boiling acetic led to the formation of 3-[5'-(2'-benzylidenehydrazinylcarbonyl)-thienyl]benzo[5,6]coumarin (**6**). Treatment of **8a** with ethyl chloroacetate in the presence of triethylamine in ethanol under reflux, yielded the corresponding 3-[2'-(2''-chloromethyl-1'',3'',4''-oxadiazol-5''-yl)thien-5'-yl]benzo[5,6]coumarin (**10**) (Scheme 2).

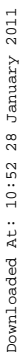
Mass Spectroscopy

Table I lists the $\underline{m/z}$ (relative abundance, %) values of the principle fragment of the synthesized compounds, while Figures 1, 2, 3, and 4 illustrate, the mass spectra of compounds **3**, **4b**, **8a**, and **10** respectively.

Compounds 3-8

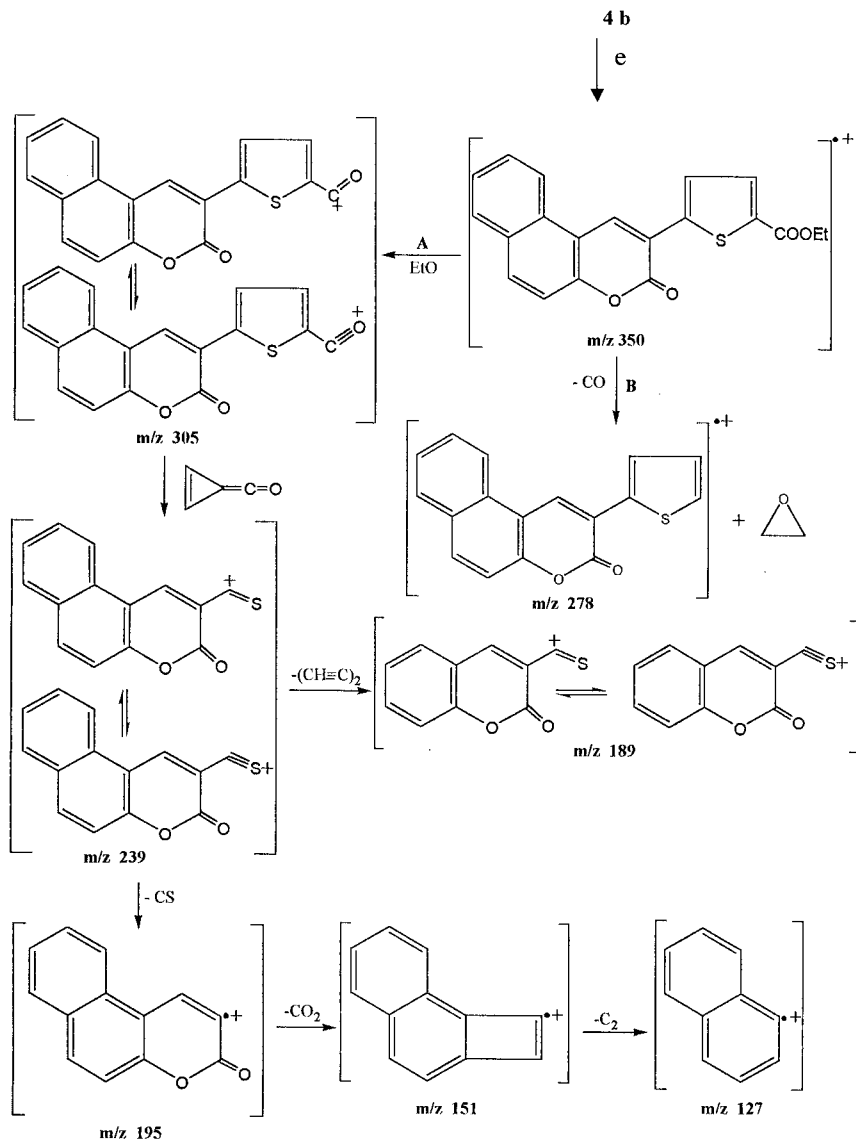
The mass spectra (Table I) of compound **3-8** show relatively small molecular ions and peaks typical of a cleavage or rearrangement type fragmentation. From study the mass spectra of the compound **3-8**, it was found that the molecular ion for all these compounds had fragmented to ion $\underline{m/z}$ 278. This ion of $\underline{m/z}$ 278 fragmented further and involved four various pathways as illustrated by Schemes 3 and 4 as a representative examples.

The ion of $\underline{m/z}$ 278 fragmented via the pathway A and gave a fragmented ion of $\underline{m/z}$ 239 which further fragmented and gave a fragmented ion of $\underline{m/z}$ 194 by losing HCS or gave a fragmented ion of $\underline{m/z}$ 189 by losing $\text{CH}=\text{C}-\text{C}=\text{CH}$.



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SCHEME 4

via the pathway C by losing $\text{CH}=\text{C}=\text{S}$ to give an ion of m/z 221 which lost COOH to give an ion of m/z 176. Finally, the ion of m/z 278 was broken via pathway D to give an ion of m/z 196 which lost CO or CO_2 . This fragmentation led to m/z 168 and m/z 152, respectively.

TABLE I EI Mass Spectra (70 eV) of Compound 2-10 m/z (Relative Intensity, %)

Compound	M ⁺	M ⁻	m/z	Other important ions
2	[C ₁₆ H ₉ ClO ₃] ⁺ 284 (6.30)	CO	[C ₁₅ H ₈ ClO ₂] ⁺ 256 (78.01)	286 (M ⁺ + 2, 2.30), 257(22.10), 249(52.30), 222(16.40), 194(7.10),
		Cl	[C ₁₅ H ₉ O ₂] ⁺ 221 (100)	192(21.50), 165(46.40), 164(29.6), 162(10.20), 140(5.00),
		CO	[C ₁₄ H ₈ O] ⁺ 193 (35.02)	96(12.00), 87(10.90), 82(28.00), 81(22.70), 75(8.60), 74(8.10),
		CH ₂ O	[C ₁₃ H ₇] ⁺ 163 (63.80)	63(15.90), 62(8.60), 51(10.50), 50(9.00).
3	[C ₁₈ H ₁₀ O ₄ S] ⁺ 322 (7.26)	CO ₂	[C ₁₇ H ₁₀ O ₃ S] ⁺ 278 (46.73)	304(12.83), 279(11.86), 277(11.14), 276(13.32), 251(23.24),
		CO	[C ₁₆ H ₁₀ OS] ⁺ 250 (100)	249 19.37, 239(10.41), 223(24.21), 222(17.19), 221(82.81),
		—C ₄ H ₂ S	[C ₁₂ H ₈ O] ⁺ 168 (19.85)	220(10.17), 196(11.62), 195(20.34), 189(29.06), 187(16.95),
		C ₄ H ₄	[C ₈ H ₄ O] ⁺ 116 (36.50)	176 46.73, 173(26.88), 171(15.74), 164(10.41), 163(30.51),
				152(17.68) 150(20.58), 140(18.64), 139(81.11), 137(15.50),
				128(27.36), 127(2.03), 126(24.70), 115(61.74), 114(18.64).
4a	[C ₁₉ H ₁₂ O ₄ S] ⁺ 336 (20.41)	CH ₂ O	[C ₁₈ H ₁₀ O ₃ S] ⁺ 306 (10.11)	337(M ⁺ + 1, 5.00), 279(12.46), 251(8.00), 239(9.55), 238(9.43)
		CO	[C ₁₇ H ₁₀ O ₂ S] ⁺ 278 (44.72)	223(8.43), 196(17.03), 195(15.05) 188(11.27), 187(15.34),
		CO	[C ₁₆ H ₁₀ OS] ⁺ 250 (34.52)	176(16.01), 171(13.05), 168(49.15), 139(48.57), 115(53.37),
				113(13.07), 109(51.73), 75(30.21), 74(100), 73(17.55).
4b	[C ₂₀ H ₁₄ O ₄ S] ⁺ 350 (3.48)	C ₂ H ₄ O	[C ₁₈ H ₁₀ O ₃ S] ⁺ 306 (13.63)	279(20.81), 277(19.17), 271(21.31), 270(42.02), 251(14.37),
		CO	[C ₁₇ H ₁₀ O ₂ S] ⁺ 278 (100)	250(61.58), 249(17.95), 242(21.90), 241(20.30), 239(18.03),
		C ₂ HS	[C ₁₅ H ₈ O ₂] ⁺ 221 (34.25)	189(15.24), 187(10.32), 176(17.81), 171(11.72), 163(13.53),
		C ₂ H	[C ₁₃ H ₈ O ₂] ⁺ 196 (20.75)	152(15.99), 151(14.70), 150(12.02), 140(12.30), 128(14.01),
		CO	[C ₁₂ H ₈ O] ⁺ 168 (13.83)	127(19.49), 126(16.54), 113(11.70), 89(12.91), 88(12.49),
		CHO	[C ₁₁ H ₇] ⁺ 139 (37.46)	87(13.90), 77(15.05), 76(10.08), 75(14.93), 74(14.03), 63(23.05).
		C ₂	[C ₉ H ₇] ⁺ 115(24.42)	
		O=C=NH	[C ₁₇ H ₁₀ O ₂ S] ⁺ 278 (100)	332(M ⁺ + 1, 7.00), 306(10.30), 280(17.03), 279(20.01), 277(19.17),
		CH=C=S	[C ₁₅ H ₈ O ₂] ⁺ 221 (42.75)	257(17.01), 256(10.75), 251(14.37), 250(61.58), 249(17.85),
		CH=C ⁺	[C ₁₃ H ₈ O ₂] ⁺ 196 (20.01)	242(21.99), 241(20.30), 239(10.03), 238(5.13), 230(15.12),
5	[C ₁₈ H ₁₁ NO ₃ S] ⁺ 321 (4.83)	CO	[C ₁₂ H ₈ O ₂] ⁺ 168 (13.01)	222(9.60), 220(8.91), 205(14.81), 197(20.14), 195(13.05),
		CHO	[C ₁₁ H ₇] ⁺ 139 (36.86)	189(15.21), 187(10.32), 176(17.01), 171(11.72), 169(7.65),
		C ₂	[C ₉ H ₇] ⁺ 115 (24.42)	152(15.88), 151(14.70), 150(12.02), 140(12.30), 138(7.33),
				113(11.70), 89(12.01), 88(12.49), 87(13.90), 77(15.05),

6	$[\text{C}_{20}\text{H}_{13}\text{NO}_4\text{S}]^+ 363 (4.83)$	$\text{CH}_2=\text{C}=\text{O}$ $\text{O}=\text{C}=\text{NH}$ CO $\text{C}_4\text{H}_2\text{S}$ C_4H_4	$[\text{C}_{18}\text{H}_{13}\text{NO}_3\text{S}]^+ 321 (6.78)$ $[\text{C}_{17}\text{H}_{10}\text{O}_2\text{S}]^+ 278 (100)$ $[\text{C}_{16}\text{H}_{10}\text{OS}]^+ 250 (11.65)$ $[\text{C}_{12}\text{H}_5\text{O}]^+ 168 (9.21)$ $[\text{C}_8\text{H}_4\text{O}]^+ 116 (31.37)$	351(24.30), 350(80.21), 337(7.10), 335(7.18), 336(11.47), 335(7.18), 322(14.65), 320(5.20), 318(13.04), 244(10.70), 291(15.17), 282(10.50), 81(19.90), 279(35.00), 277(10.40), 252(2.14), 187(30.13), 185(13.25), 184(32.25), 183(34.17), 177(18.60), 176(60.45), 170(16.64), 152(13.67), 150(13.07), 55(10.50).
7	$[\text{C}_{18}\text{H}_{11}\text{NO}_4\text{S}]^+ 337 (39.70)$	H^+ 2CO, NO	$[\text{C}_{18}\text{H}_{10}\text{NO}_4\text{S}]^+ 336 (63.82)$ $[\text{C}_{16}\text{H}_{10}\text{OS}]^+ 250 (50.72)$	281(37.60), 239(46.30), 176(63.77), 150(52.17), 139(100), 127(50.42), 117(31.08), 113(42.03), 88(31.00), 87(34.78), 77(47.83), 75(48.20).
8a	$[\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3\text{S}]^+ 336 (48.27)$	$\text{HN}=\text{NH}$ CO $\text{HC}^+=\text{C}=\text{S}$ COOH C ₂	$[\text{C}_{18}\text{H}_{10}\text{O}_3\text{S}]^+ 306 (17.98)$ $[\text{C}_{17}\text{H}_{10}\text{O}_2\text{S}]^+ 278 (100)$ $[\text{C}_{15}\text{H}_9\text{O}_2\text{S}]^+ 221 (54.10)$ $[\text{C}_{14}\text{H}_8\text{S}]^+ 176 (24.10)$ $[\text{C}_{12}\text{H}_8\text{S}]^+ 152 (23.11)$	337($\text{M}^+ + 1$), 13.68), 308(11.41), 279(21.22), 277(15.17), 251(18.85), 250(78.05), 249(16.70), 205(10.07), 197(19.20), 196(11.06), 144(28.10), 139(20.10), 126(19.35), 125(21.24), 115(41.08), 110(21.55), 98(14.01); 97(10.54), 88(22.71), 87(10.30), 77(21.00), 74(23.11), 69(2.16), 63(32.12), 51(25.05).
8b	$[\text{C}_{24}\text{H}_{16}\text{N}_2\text{O}_3\text{S}]^+ 412 (8.05)$	C_6H_4 $\text{HN}=\text{NH}$, CO	$[\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3\text{S}]^+ 336 (21.30)$ $[\text{C}_{17}\text{H}_{10}\text{O}_2\text{S}]^+ 278 (100)$	337(35.07), 304(42.01), 303(21.30), 279(95.50), 258(47.17), 239(30.47), 232(10.01), 217(19.46), 216(30.31), 149(31.20), 145(10.41), 133(10.07), 132(13.37), 107(22.90), 71(14.50).
9	$[\text{C}_{25}\text{H}_{16}\text{N}_2\text{O}_3\text{S}]^+ 424 (2.50)$	PhCN , NH_2 CO C ₂ S COOH	$[\text{C}_{18}\text{H}_9\text{O}_3\text{S}]^+ 305 (100)$ $[\text{C}_{17}\text{H}_9\text{O}_2\text{S}]^+ 277 (4.22)$ $[\text{C}_{15}\text{H}_9\text{O}_2\text{S}]^+ 221 (6.08)$ $[\text{C}_{14}\text{H}_8\text{S}]^+ 176 (9.71)$	423($\text{M}^+ - 1$, 1.02), 307(52.00), 304(13.15), 303(10.19), 301(52.70), 294(37.01), 291(10.05), 278(14.34), 222(5.95), 177(2.82), 170(2.84), 163(2.24), 152(1.41), 151(1.07), 139(1.13).
10	$[\text{C}_{20}\text{H}_{11}\text{N}_2\text{ClO}_3\text{S}]^+ 394 (14.59)$	Cl , N_2 , $\text{CH}=\text{CH}$ CO C ₂ S COOH C ₃ H	$[\text{C}_{18}\text{H}_9\text{O}_3\text{S}]^+ 305 (100)$ $[\text{C}_{17}\text{H}_9\text{O}_2\text{S}]^+ 277 (13.38)$ $[\text{C}_{15}\text{H}_9\text{O}_2\text{S}]^+ 221 (17.03)$ $[\text{C}_{14}\text{H}_8\text{S}]^+ 176 (18.55)$ $[\text{C}_{11}\text{H}_7\text{S}]^+ 139 (31.57)$	396($\text{M}^+ + 2$, 5.07), 351(13.08), 350(51.40), 306(45.37), 304(11.45), 285(16.74), 284(50.82), 279(14.10), 278(23.84), 251(8.51), 250(18.30), 195(19.24), 194(20.12), 174(20.12), 173(10.20), 171(20.12), 168(5.14), 151(12.04), 150(11.01), 141(14.024), 140(10.57).

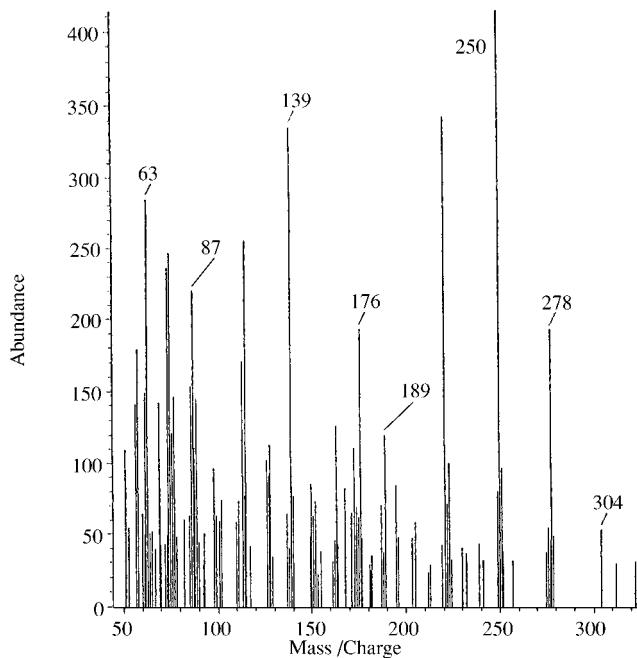


FIGURE 1 70 eV mass spectrum of compound **3**.

The electron impact ionization mass spectra of compounds **4b**, **5**, and **8a, b** show a base peak of m/z 278, while the base peak of compound **3** and **7** is m/z 250 and m/z 139. In contrast, compounds **4a** had a m/z 74 fragmented resulting cleavage or a rearrangement fragmentation.

Compounds 9 and 10

The mass spectra of compounds **9** and **10** gave a characteristic fragmentation pattern with a very stable fragment of m/z 305 which has further broken via a similar way of the compounds **3–8**.

EXPERIMENTAL

Melting points were determined in capillaries with a Thomas-Hover Uni-Melt apparatus and are uncorrected. Infrared spectra were taken on a Perkin-Elmer 337 spectrophotometer using KBr wafers. Proton NMR spectra were obtained on a Varian EM 360 spectrometer using solutions in hexadeuteriodimethyl sulfoxide with tetramethylsilane as the internal standard. Mass spectra were recorded on a VG Autospec GEI FAB⁺ and a Hewlett Packard MS-Engine thermospray and ionization

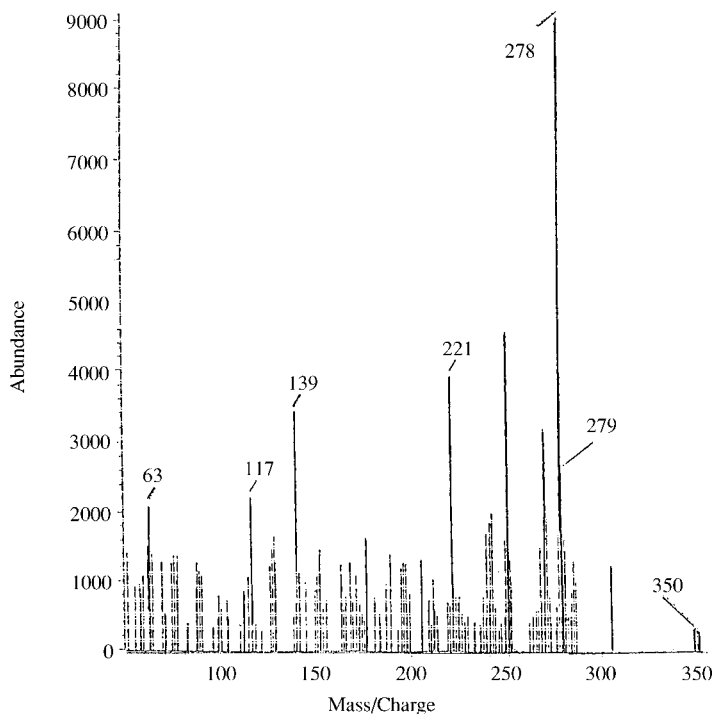


FIGURE 2 70 eV mass spectrum of compound **4b**.

by electron impact at 70 eV. The accelerating voltage was 6 kv, the temperature of the source was $\sim 200^\circ$, and the emission current ~ 100 mA. Microanalyses were conducted using on a Perkin-Elmer 2408 CHN analyzer.

3-(2'-Formyl-1'-chlorovinyl)benzo[5,6]coumarin(**2**)

3-(2'-Formyl-1'-chlorovinyl)benzo[5,6]coumarin (**2**) was prepared according to literature procedure.¹³ The crude product was recrystallized (ethanol) to give **2** as yellow crystals, yield 2.41gm (85%), m.p.: 95°C . ν_{max} (KBr): 3082, 1721, 1668, 1614, 790 cm^{-1} . δ_{H} (CDCl_3): 7.15–8.20 (m, 8 H, Ar-H and olefinic proton), 10.23 (d, 1H, CHO). Anal. $\text{C}_{16}\text{H}_9\text{ClO}_3$ for Calcd: C, 67.49; H, 3.16; Cl, 12.48. Found: C, 67.03; H, 2.97; Cl, 12.01.

3-(5'-(2'-Hydroxycarbonyl)thienyl]benzo[5,6]coumarin(**3**)

A mixture of **2** (0.01 mmol), thioglycolic acid (0.01 mmol), fused sodium acetate (0.03 mmol), and acetic anhydride (0.01 mmol), was fused on a

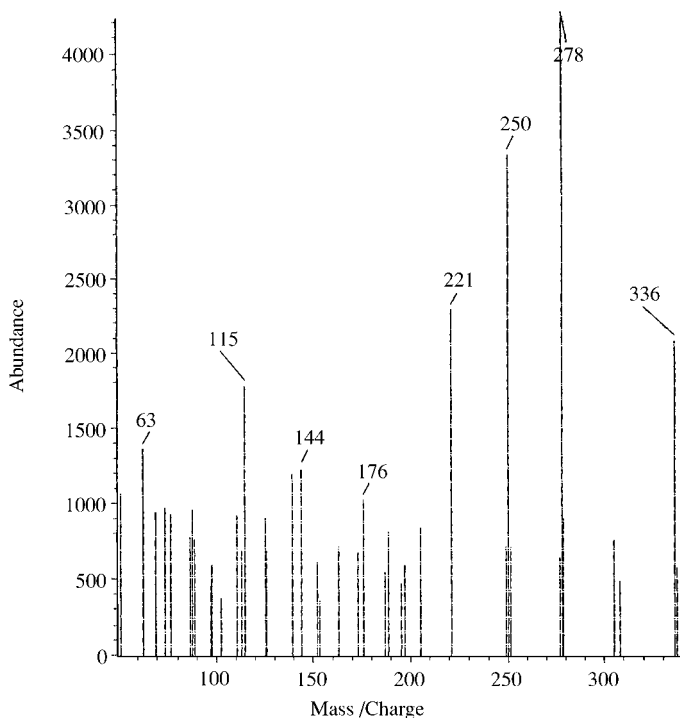


FIGURE 3 70 eV mass spectrum of compound **8a**.

hot plate for 5–10 min. The reaction mixture was added to acetic acid (50 mL), and the new solution was heated under reflux for 8 h, then cooled, and poured into the water. The resulting product was filtered off, washed with water, dried, and recrystallized (ethanol) to give **3** as yellow crystals, yield 2.42 gm (75%), m.p.: 150°C. ν_{\max} (KBr): 3390–2825 (br. OH), 1723, 1705, 1625, 1610, 1096 cm^{-1} . δ_{H} (DMSO- d_6): 7.01–8.35 (m, 9 H, Ar–H, pyran and thiophene ring), 11.35 (br.s, 1H, OH) ppm. Anal. $\text{C}_{18}\text{H}_{10}\text{O}_4\text{S}$ for Calcd: C, 67.08; H, 3.10; S, 9.94. Found: C, 66.98; H, 3.01; S, 9.57.

3-[5'-(2'-Alkoxy carbonyl)thienyl]benzo[5,6]coumarins (**4a**, **b**)

A mixture of **3** (0.01 mmol), alcohols (namely methanol and ethanol) (20 mL), and conc. sulphuric acid (10 mL) in benzene (50 mL) was heated under reflux for 6 h. The reaction mixture was cooled, and poured into the water. The benzene layer was separated, and evaporated. The deposited solid was recrystallized (ethanol) to give **4**.

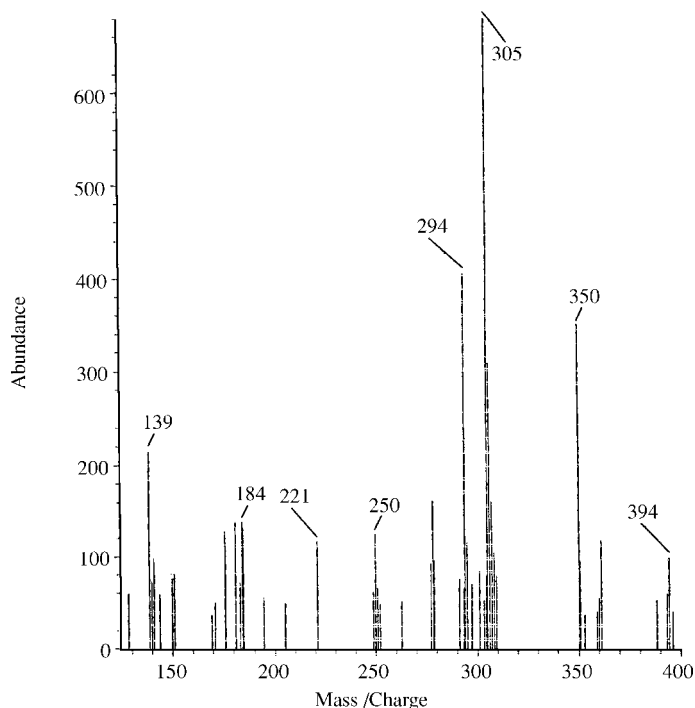


FIGURE 4 70 eV mass spectrum of compound **10**.

3-[5'-(2'-Methoxycarbonyl)thienyl]benzo[5,6]coumarin (**4a**), yield 2.46 g (73%), m.p.: 70°C. ν_{\max} (KBr): 1765, 1719, 1628, 1605, 1120, 1035 cm^{-1} . δ_{H} (CDCl₃): 3.89 (s, 3 H, OCH₃), 7.03-8.33 (m, 9 H, Ar-H, pyran and thiophene ring) ppm. Anal. C₁₉H₁₂O₄S for Calcd: C, 67.86; H, 3.57; S, 9.52. Found: C, 67.52; H, 3.35; S, 9.29.

3-[5'-(2'-Ethoxycarbonyl)thienyl]benzo[5,6]coumarin (**4b**), yield 2.63 g (75%), m.p.: 73°C. ν_{\max} (KBr): 1762, 1720, 1626, 1607, 1125, 1030 cm^{-1} . δ_{H} (CDCl₃): 1.30 (t, 3H, CH₃), 4.30 (q, 2 H, OCH₂), 7.01-8.34 (m, 9 H, Ar-H, pyran and thiophene ring) ppm. Anal. C₂₀H₁₄O₄S for Calcd: C, 68.57; H, 4.00; S, 9.14. Found: C, 68.32; H, 3.88; S, 9.02.

3-[5'-(2'-Aminocarbonyl)thienyl]benzo[5,6]coumarin (**5**)

A mixture of **4a**, **b** (0.01 mmol) and ammonium acetate (0.04 mmol) was fused in oil-bath at 100°C for 2 h. The reaction mixture was cooled and poured into water. The deposited solid was filtered, washed with water, dried, and recrystallized (ethanol) to give **5** as yellow crystals, yield 2.18 g (68%), m.p.: 270°C. ν_{\max} (KBr): 3389, 3168 (NH₂), 1720, 1685,

1627, 1608, 1130 cm^{-1} . δ_{H} (DMSO- d_6): 5.89 (s, 2 H, NH_2), 7.01–8.35 (m, 9 H, Ar–H, pyran and thiophene ring) ppm. Anal. $\text{C}_{18}\text{H}_{11}\text{NO}_3\text{S}$ for Calcd: C, 67.29; H, 3.42; N, 4.36; S, 9.97. Found: C, 67.01; H, 3.26; N, 4.16; S, 9.59.

3-[5'-(2'-Acetylaminoacarbonyl)thienyl]benzo-[5,6] coumarin (6)

A solution of **5** (0.01 mmol) in acetic anhydride (30 mL) was heated under reflux for 10 h, then cooled and poured into water. The resulting product was filtered off, washed with water, dried, and recrystallized (ethanol) to give **6** as pale yellow crystals, yield 2.79 g (77%), m.p.: 210°C. ν_{max} (KBr): 3219 (NH), 1721, 1695–1686, 1627, 1605, 1038 cm^{-1} . δ_{H} (DMSO- d_6): 2.23 (s, 3 H, CH_3), 7.02–8.34 (m, 9 H, Ar–H, pyran and thiophene ring) 10.32 (s, 1 H, CONH) ppm. Anal. $\text{C}_{20}\text{H}_{13}\text{NO}_4\text{S}$ for Calcd: C, 66.11; H, 3.58; N, 3.85; S, 8.81. Found: C, 66.00; H, 3.37; N, 3.51; S, 8.62.

3-[5'-(2'-Hydroxyaminocarbonyl)thienyl]benzo-[5,6] coumarin (7)

A mixture of **4** (0.01 mmol), hydroxylamine hydrochloride (0.01 mmol), and fused sodium acetate (0.02 mmol) in ethanol (50 mL) was heated under reflux for 8 h. The reaction mixture was cooled and poured into water. The resulting product was filtered off, washed with water, dried, and recrystallized (ethanol) to give **7** as pale yellow crystals, yield 2.63 g (78%), m.p.; 130–131°C. ν_{max} (KBr): 3395–3051 (br. OH), 3252 (NH), 1719, 1689, 1623, 1607, 135, 1039 cm^{-1} . δ_{H} (CDCl_3): 7.02–8.35 (m, 9 H, Ar–H, pyran and thiophene ring) ppm. Anal. $\text{C}_{18}\text{H}_{11}\text{NO}_4\text{S}$ for Calcd: C, 64.09; H, 3.26; N, 4.15; S, 9.49. Found: C, 63.92; H, 3.03; N, 4.00; S, 9.21.

3-[5'-(2'-Alkylhydrazinylcarbonyl)thienyl]benzo-[5,6] coumarins (8a,b)

A mixture of **4a,b** (0.01 mmol), hydrazine derivatives (such as hydrazine sulphate, and phenylhydrazine sulphate) (0.01 mmol), and fused sodium acetate (0.02 mmol) in ethanol (50 mL) was heated under reflux for 8 h. The reaction mixture was cooled, poured into water, and acidified with dilute hydrochloric acid (2 mmol/L). The solid formed was filtered off, washed with water, dried, and recrystallized (ethanol) to give **8a,b**.

3-[5'-(2'-Hydrazinylcarbonyl)thienyl]benzo[5,6]coumarin (**8a**), yield 2.69 g (80%), m.p.: 164°C. ν_{max} (KBr): 3335, 3227, 3171, 1720, 1684,

1626, 1610, 1096 cm^{-1} . δ_{H} (DMSO- d_6): 5.15 (br. s, 2 H, NH_2), 7.02–8.34 (m, 9 H, Ar-H, pyran and thiophene ring), 10.21 (br. s, 1 H, CONH) ppm. Anal. $\text{C}_{18}\text{H}_{12}\text{N}_2\text{O}_3\text{S}$ for Calcd: C, 64.28; H, 3.57; N, 8.33; S, 9.52. Found: C, 64.01; H, 3.38; N, 8.03; S, 9.29.

3-[5'-(2'-Phenylhydrazinylcarbonyl)thienyl]benzo[5,6]coumarin (**8b**), yield 3.13 g (76%), m.p.: 120–121°C. ν_{max} (KBr): 3281, 3145, 1721, 1684, 1623, 1607, 1085 cm^{-1} . δ_{H} (DMSO- d_6): 5.63 (s, 1 H, NH-Ar), 6.98–8.35 (m, 14 H, Ar-H, pyran and thiophene ring), 10.31 (br. s, 1 H, CONH) ppm. Anal. $\text{C}_{24}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$ for Calcd: C, 69.90; H, 3.88; N, 6.79; S, 7.76. Found: C, 69.63; H, 3.53; N, 6.49; S, 7.43.

3-[5'-(2'-Benzylidenehydrazinylcarbonyl)thienyl]benzo[5,6]coumarin (**9**)

A mixture of **8a** (0.01 mmol), benzaldehyde (0.01 mmol), and triethylamine (1 mL) in ethanol (50 mL) was heated under reflux for 10 h. The reaction mixture was cooled, poured into water, and acidified with diluted hydrochloric acid (2 mmol/L). The resulting solid was filtered off, washed with water, dried, and recrystallized (ethanol) to give **9**, yield 3.35 g (79%), m.p.: 175–176°C. ν_{max} (KBr): 3227, 1722, 1689, 1630, 1612, 1607, 1035 cm^{-1} . δ_{H} (DMSO- d_6): 6.59–8.36 (m, 15 H, Ar-H, olefinic proton, thiophene and pyran ring), 10.31 (br. s, 1 H, CONH) ppm. Anal. $\text{C}_{25}\text{H}_{16}\text{N}_2\text{O}_3\text{S}$ for Calcd: C, 70.75; H, 3.77; N, 6.60; S, 7.54. Found: C, 70.47; H, 3.48; N, 6.39; S, 7.41.

3-[2'-(2''-Chloromethyl-1'',3'',4''-oxadiazol-5''-yl)-thien-5'-yl]benzo[5,6]coumarin (**10**)

A mixture of **8a** (0.01 mmol), ethylchloroacetate (0.01 mmol), and triethylamine (1 mL) in ethanol (50 mL) was heated reflux for 10 h. The reaction mixture was cooled, poured into water, and acidified with dilute hydrochloric acid (2 mmol/L). The resulting product was filtered off, washed with water, dried, and recrystallized (ethanol) to give **10** as yellow crystals, yield 3.11 g (79%), m.p.: 200°C. ν_{max} (KBr): 1723, 1630, 1609, 1310, 1035 cm^{-1} . δ_{H} (DMSO- d_6): 3.70 (s, 2 H, CH_2Cl), 7.03–8.33 (m, 9 H, Ar-H, pyran and thiophene ring) ppm. Anal. $\text{C}_{20}\text{H}_{11}\text{N}_2\text{ClO}_3\text{S}$ for Calcd: C, 60.83; H, 2.78; N, 7.09; Cl, 8.99; S, 9.11. Found: C, 60.57; H, 2.61; N, 6.83; Cl, 8.58; S, 8.00.

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