Research Paper Chemistry

Electron Impact Ionization Mass Spectra of 3 - Substituted-6, 8 – Dibromo Coumarins

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ABSTRACT

3- (Aroyl)amino-6,8-dibromo coumarins (2a,b) were prepared from 3,5-dibromo–2-hydroxybenzaldehyde with N-aroylglycine in presence of fused sodium acetate and acetic anhydride under fusion while, 3-(Arylamino)carbonyl-6,8-dibromo coumarins (5a-c) were synthesized via the condensation of 3-ethoxycarbonyl-6,8-dibromo coumarin (4) with aromatic amines under reflux. 3-(2-hydroxy phenylamino)carbonyl-6,8-dibromo coumarin (5c) was cyclized with $POCl^3$ to give 3-(benzoxazol-2-yl)-6,8-dibromo coumarin (6), while the 3-(benzaimidazol-2-yl)-6,8-dibromo coumarin (8) was prepared from condensation of 4 with o-phenylenediamine under fusion in acidic medium. The electron impact ionization mass spectra show strong and weak molecular ion peaks. The base peaks of compounds 2a,b were at m/z 105,139 and m/z 330 for compounds 5a-c resulting from a cleavage fragmentations. Compounds 4 and 8 give a characteristic fragmentation pattern with a very stable fragment at m/z 86 and m/z 80, respectively.

Keywords : 3-ethoxycarbonyl-6,8-dibromo coumarin, mass spectral analysis

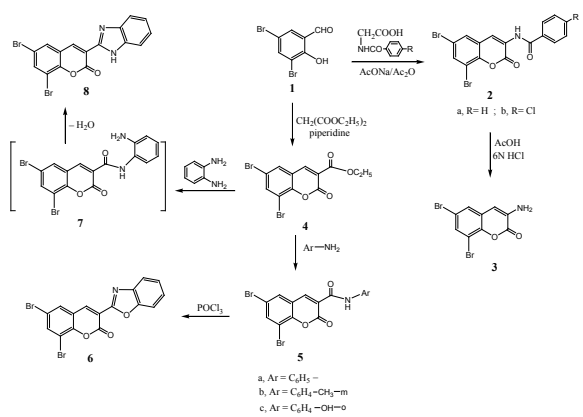
1. Introduction

Coumarin derivatives constitute an important class of heterocycles in medicinal chemistry because many derivatives have attracted intense interest in recent years for their diverse pharmacological properties [1-6]. This paper now reports the synthesis and electron impact of mass spectra of some 3-substituted-6,8-dibromo coumarins using 3,5-dibromo-2-hydroxy benzaldehyde (1) as a key starting material.

2. Results and discussion

2.1. Chemistry

Treatment of 3,5-dibromo-2-hydroxy benzaldehyde (1) with N-benzoylglycine and /or N-(p-chloro) benzoylglycine in presence of fused sodium acetate and acetic anhydride under fusion produced the 3-(Aroyl)amino-6,8-dibromo coumarins (2a and 2b; Scheme 1). Hydrolysis of compounds 2a and 2b with hydrochloric acid (6N) in acetic acid under reflux led to the formation of 3-amino-6,8-dibromo coumarin (3). The 6,8-dibromo-3-ethoxycarbonyl coumarin (4) was prepared from 3,5-dibromo-2- hydroxyl benzaldehyde (1) with diethyl malonate in the presence of piperidine according to a literature method. Condensation of 6,8-dibromo-3- ethoxycarbonyl coumarin (4) with aromatic amines (such as aniline, m-toluidine and 2-aminophenol) in presence of acid medium under fusion produced the 6,8- dibromo-3-(arylamino)carbonyl coumarins (5a-c). Cyclization of 3-(2-hydroxyphenylamino) carbonyl-6,8-dibromo coumarin (5c) with phosphorus oxychloride afforded the corresponding 6,8-dibromo-3- benzoxazol-2-yl)coumarine (6; Scheme 1). 6,8-dibromo-3-(benzaimidozol-2-yl)coumarin (8) was synthesized via condensation of compound 4 with o-phenylene diamine in presence of acid catalyst under fusion.



Scheme 1

2.2. Mass Spectrometry

As a part of structural investigation [8, 9], mass spectra of seven compounds belonging to this series were recorded and all the spectra showed suggested characteristic fragmentation pathways, as shown in table 1. The mass spectra of the seven compounds are fully consistent with the assigned structures. In most cases, intense molecular ion peaks were observed. The M+2 and M+4 peaks were observed along with the molecular ion peaks due to the presence of isotopes of two bromine atoms present in these compounds.

Table 1. EI mass spectra (70 eV) of compounds 2, 4, 5 and 8 m/z (relative intensity, %)

Compd.	M^+	Pathway A		Pathway B		Pathway C		Other Ions
		-M	m/z	-M	m/z	-M	m/z	
2a	$[C_{19}H_9NBr_2O_3]^+$ 421(73.20)	C_6H_5 NCO HBr HBr CO CO	$[C_{10}H_4Br_2O_3]^+$ 344(11.60) $[C_9H_4Br_2O_2]^{\cdot+}$ 302(8.35) $[C_9H_3BrO_2]^{\cdot+}$ 222(6.51) $[C_9H_2O_2]^{\cdot+}$ 142(2.35) $[C_8H_2O]^{\cdot+}$ 114(2.35) $[C_7H_3]^+$ 87(7.70)	C_7H_5O NH C_2H CO HBr HBr O	$C_9H_4N\ Br_2O_2]^{\cdot+}$ 316(7.84) $[C_9H_3Br_2O_2]^{\cdot+}$ 301(11.25) $[C_7H_2Br_2O_2]^{\cdot+}$ 276(5.30) $[C_6H_2Br_2O]^{\cdot+}$ 248(8.17) $[C_6HBrO]^{\cdot+}$ 168(1.45) $[C_6O\ ]^{\cdot+}$ 88(1.30) $[C_6]^+$ 72(0.96)	$C_9H_4NBr_2O_2$ CO C_2H_2	$[C_7H_5O]^+$ 105(100) $[C_6H_5]^+$ 77(49.60) $[C_4H_3]^+$ 51(15.40)	425 (M^++4, 1.20), 423(M^++2, 71.20), 422(M^++1, 38.20), 420(M^+-1, 3.10), 343(1.00), 333(0.40), 274(0.50), 181(1.70), 180(1.30) ,162(0.40), 161(0.80), 143(0.70),141(0.10), 107(0.60) , 106(10.90), 104(13.20) , 100(1.10)), 99(1.10), 89(1.30), 87(1.00), 81(1.30), 78(1.70), 76(18.50), 75(2.50), 65(0.40), 61(0.80), 53(0.1), 51(15.00), 50(8.50)
2b	$[C_{16}H_8NClBr_2O_3]^+$ 455(73.46)	C_6H_4Cl NCO HBr HBr CO CO	$[C_{10}H_4NBr_2O_3]^{\cdot+}$ 344(11.60) $[C_9H_4Br_2O_2]^{\cdot+}$ 302(8.35) $[C_9H_3BrO_2]^{\cdot+}$ 222(6.51) $[C_9H_2O_2]^{\cdot+}$ 142(12.30) $[C_8H_2O]^{\cdot+}$ 114(2.35) $[C_7H_2]^{\cdot+}$ 86(7.70)	C_7H_4ClONH NH C_2H CO HBr HBr	$[C_9H_4Br_2O_2]^{\cdot+}$ 316(7.82) $[C_9H_3Br_2O_2]^{\cdot+}$ 301(11.25) $[C_7H_2Br_2O_2]^{\cdot+}$ 276(5.30) $[C_6H_2Br_2O]^{\cdot+}$ 248(8.17) $[C_9HBrO]^{\cdot+}$ 168(1.45) $[C_6O]^{\cdot+}$ 88(1.30)	$C_9H_4Br_2O_2$ CO C_2H_2	$[C_7H_4ClO]^{\cdot+}$ 139(100) $[C_6H_4Cl]^{\cdot+}$ 111(46.80) $[C_4H_2Cl]^{\cdot+}$ 85(13.42)	457(M^++2, 71.60), 454(M^+-1, 5.50), 420(M^+-3.10), 292(1.90), 291(0.80), 290(1.70), 262(1.40), 183(1.30), 182(0.40), 181(2.10), 156(2.50), 155(0.80), 154(1.30), 153(0.80), 143(0.50), 142(1.8), 141(74.20), 140(2.30), 138(3.50), 130(1.00), 114(1.00), 113(0.40), 112(1.8), 111(0.70), 107(0.60), 106(11.50), 104(2.70), 103(0.50), 102(3.20), 101(3.10), 100(2.20), 99(1.2), 98(1.4), 89(1.30), 88(1.20), 87(1.20), 86(1.80), 81(1.40), 78(1.70), 76(18.60), 75(2.20), 65(0.70), 61(0.90), 53(0.60), 51(15.60), 50(8.90)
4	$[C_{12}H_8Br_2O_4]^+$ 374(31.40)	C_2H_4O CO HBr HBr CO CO	$[C_{10}H_4Br_2O_3]^{\cdot+}$ 330(54.90) $[C_9H_4Br_2O_2]^{\cdot+}$ 302(29.40) $[C_9H_3BrO_2]^{\cdot+}$ 222(7.80) $[C_9H_2O_2]^{\cdot+}$ 142(2.30) $[C_8H_2O]^{\cdot+}$ 114(7.80) $[C_8H_2]^{\cdot+}$ 86(100)	$C_3H_6O_2$ CO CO Br Br	$[C_9H_2Br_2O_2]^{\cdot+}$ 300(3.60) $[C_8H_2Br_2O]^+$ 272(21.60) $[C_7H_2Br_2]^+$ 244(13.70) $[C_7H_2Br]^+$ 165(37.30) $[C_6H_2]^+$ 86(100)	C_2H_5O CO C_2H CO HBr HBr	$[C_{10}H_3Br_2O_3]^+$ 329(25.50) $[C_9H_3Br_2O_2]^+$ 301(39.20) $[C_7H_2Br_2O_2]^{\cdot+}$ 276(21.60) $[C_6H_2Br_2O]^{\cdot+}$ 248(13.70) $[C_6HBro]^{\cdot+}$ 168(15.70) $[C_6O]^{\cdot+}$ 88(33.30) $[C_6]^{\cdot+}$ 72(13.70)	378(M^++4, 21.60),376(M^++2, 33.30), 375(M^+-1, 31.40), 373(M^+ -1), 21.60), 333(23.50),332(31.40), 331(45.10), 328(33.30), 306(33.30) , 305(45.10) , 304(56.40) , 303(41.20), 302(29.40), 301(39.20) , 276(21.60), 275(13.70), 245(13.70) , 244(13.70), 226(15.70), 225(15.70), 224(7-80), 200(7.80), 199(9.80), 196(13.70), 195(11.80) , 194(5.90), 183(11.80), 169(13.70), 168(15.70), 166(27.50), 164(7.80), 156(9.80), 149(9.80), (129(9.80), 128(11.80), 127(25.50), 126(11.80), 125(9.80), 118(19.60), 117(9.80), 106(13.70), 105(84.30), 104(52.9), 88(33.3), 87(59.9), 85(33.30), 83(23.50), 82(39.20), 78(23.50), 77(49.00), 76(62.70), 75(19.60), 74(35.30), 71(17.60), 65(13.60), 63(31.40), 62(33.20), 61(33.20), 57(23.50), 53(51.00), 51(13.70), 50(15.70)

5a	$[C_{16}H_9NBr_2O_3]^{\cdot+}$ 421(19.50)	C_6H_5N CO -HBr -HBr CO CO C_2	$[C_{10}H_4Br_2O_3]^{\cdot+}$ 330(3.10) $[C_9H_4Br_2O_2]^{\cdot+}$ 302(10.40) $[C_9H_3BrO_2]^{\cdot+}$ 222(0.30) $[C_9H_2BrO_2]^{\cdot+}$ 142(0.30) $[C_8H_2O_2]^{\cdot+}$ 114(11.70) $[C_7H_2]^{\cdot+}$ 86(32.60) $[C_5H_2]^{\cdot+}$ 62(32.50)	C_6H_6N CO C_2H CO HBr HBr O	$[C_{10}H_3Br_2O_3]^{\cdot+}$ 329(42.90) $[C_9H_3Br_2O_2]^{\cdot+}$ 301(6.50) $[C_7H_2Br_2O_2]^{\cdot+}$ 276(6.31) $[C_6H_2Br_2O]^{\cdot+}$ 248(16.90) $[C_6HBrO]^{\cdot+}$ 168(1.70) $[C_6O]^{\cdot+}$ 88(15.60) $[C_6]^{+}$ 72(1.30)	$[C_{10}H_3Br_2O_3]^{\cdot+}$ HCN	$[C_6H_6N]^{\cdot+}$ 92(22.10) $[C_5H_5]^{\cdot+}$ 65(51.90)	425(M^{+}_{+}4, 20.80), 423(M^{+}+2, 32.50), 422(M^{+}-1, 48.10), 420(M^{+}-2, 28.60), 345(13.0), 344(10.40), 343(9.10), 332(54.50), 331(100), 328(41.60), 303(10.40), 253(16.90), 252(10.40), 251(16.50), 249(23.40), 248(16.90), 247(32.50), 246(28.60), 245(13.00), 169(11.70), 167(19.50), 166(14.30), 111(10.40), 108(11.70), 106(7.80), 105(16.90), 100(13.0), 99(14.30), 94(13.00), 93(22.10), 91(11.70), 87(49.40), 82(22.10), 81(22.10), 80(29.90), 79(35.10), 78(18.20), 77(42.90), 76(22.10), 75(22.10) ,68(11.70), 66(20.8), 64(36.40), 63(28.60), 61(22.10), 52(28.60), 51(40.30), 50(26.00)
5b	$[C_{17}H_{11}NBr_2O_3]^{\cdot+}$ 435(2700)	C_7H_7N CO -HBr -HBr CO CO C_2	$[C_{10}H_4Br_2O_3]^{\cdot+}$ 330(100) $[C_9H_4Br_2O_2]^{\cdot+}$ 302(5.90) $[C_9H_3BrO_2]^{\cdot+}$ 222 (2.6) $[C_9H_2O_2]^{+}$ 142(3.00) $[C_8H_2O_2]^{\cdot+}$ 114(4.30) $[C_7H_2]^{\cdot+}$ 86(24.70) $[C_5H_2]^{\cdot+}$ 62(21.70)	C_7H_8N CO C_2H CO -HBr -HBr O	$[C_{10}H_3Br_2O_3]^{\cdot+}$ 329(53.30) $[C_9H_3Br_2O_2]^{\cdot+}$ 301(4.60) $[C_7H_2Br_2O_2]^{\cdot+}$ 276(5.60) $[C_6H_2Br_2O]^{\cdot+}$ 248(9.50) $[C_6HBrO]^{\cdot+}$ 168(11.50) $[C_6O]^{\cdot+}$ 88(19.40) $[C_6]^{+}$ 72(3.30)	$C_{10}H_3Br_2O_3$ HCN CH_4	$[C_7H_8N]^{+}$ 106(19.10) $[C_6H_7]$ 79(29.90) $[C_5H_4]^{+}$ 63(21.10)	439(M^{+}+4,2530), 437(M^{+}+2, 49.00), 436(M^{+}_{+}1, 48.00), 434(M^{+}-1, 30.30), 411(12.80), 410(13.50), 409(20.40), 408(22.00), 407(14.10), 333(50.30), 332(43.10), 331(97.00), 328(59.80), 303(8.20), 300(3.30), 278(3.00), 277(1.30), 275(3.90), 253(20.10), 252(10.50), 251(23.70), 249 (18.40), 247(28.30), 246(16.10), 245(16.80), 224(2.30), 223(3.30), 221(3.00), 169(8.60), 167(11.80), 166(13.50), 165(7.60), 144 (3.00), 143(4.90), 141(3.90), 116(5.30), 115(4.30), 113(3.30), 108(15.10), 107(15.80), 100(5.60), 99(7.90), 91(32.20), 90(11.80), 89(10.20), 87(56.60), 80(12.20), 78(23.0), 77(54.60), 65(31.10), 61(21.70), 53(25.70), 51(23.00)

5c	$[C_{16}H_9NBr_2O_4]^{\cdot+}$ 437(13.30)	C_6H_5NO CO HBr HBr CO CO C_2	$C_{10}H_4Br_2O_3]^{\cdot+}$ 330(100) $[C_9H_4Br_2O_2]^{\cdot+}$ 302(5.30) $[C_9H_3BrO_2]^{\cdot+}$ 222(1.90) $[C_9H_2O_2]^{\cdot+}$ 142(2.30) $[C_8H_2O]^{\cdot+}$ 114(3.40) $[C_7H_2]^{\cdot+}$ 86(21.10) $[C_5H_2]^{\cdot+}$ 62(16.0)	C_6H_6NO CO C_2H CO HBr HBr O	$[C_{10}H_3Br_2O_3]^{\cdot+}$ 329(42.20) $[C_9H_3Br_2O_2]^{\cdot+}$ 301(2.90) $[C_7H_2Br_2O_2]^{\cdot+}$ 276(2.70) $[C_6H_2Br_2O]^{\cdot+}$ 248(7.80) $[C_6HBrO]^{\cdot+}$ 168(6.80) $[C_6O]^{\cdot+}$ 88(13.60) $[C_6]^{+}$ 72(1.90)	$C_{10}H_3Br_2O_3$ HCN H_2O	$[C_6H_6No]^+$ 108(85.30) $[C_5H_5O]^+$ 81(7.9) $[C_5H_3]^+$ 63(19.80)	441(M^++4, 11.70), 439(25.70), 438(M^++2, 28.50), 436(M^+-1, 14.80), 333(41.30), 332(50.80), 331(91.60), 328(54.60), 303(5.50), 301(2.90), 300(3.00), 278(1.50), 277(1.20), 275(2.20), 274(2.50), 250(8.30), 249(8.90), 247(17.50), 246(14.60), 245(9.30), 224(100), 223(1.70), 220(1.00), 169(5.30), 167(7.00), 166(7.00), 165(5.60), 143(2.20), 141(2.40), 140(2.10), 119(2.70), 118(1.60), 117(3.60), 116(3.80), 113(1.80), 109(11.00), 107(20.90), 100(2.90), 99(5.60), 89(5.00), 87(50.00), 85(9.00), 80(68.30), 79(28.20), 78(9.20), 75(9.30), 74(11.20), 65(8.10), 64(10.40), 61(10.10), 53(39.80), 52(38.00), 51(23.70), 50(15.20)
8	$[C_{16}H_8N_2Br_2O_2]^+$ 418(27.30)	CO Br_2 CO $-C_2$ $-C_2$ $-C_2$ CH_5NH_2 CN	$[C_{15}H_8N_2Br_2O]^+$ 390(24.20) $[C_{15}H_8N_2Br_2O]^+$ 232(24.20) $[C_{14}H_8N_2]^+$ 204(54.50) $[C_{12}H_8N_2]^+$ 180(18.20) $[C_{10}H_8N_2]^+$ 156(21.20) $[C_8H_8N_2]^+$ 132(6.10) $[C_7H_4N]^+$ 102(63.20) $[C_6H_4]^+$ 76(3.00)	$C_6H_2Br_2$ C_6H_4N O CO	$[C_{10}H_8N_2O_2]^+$ 186(0.30) $[C_4H_2NO_2]^+$ 96(18.20) $[C_4H_2NO_2]^+$ 80(100) $[C_3H_2N]^+$ 52(39.0)	$C_{10}H_2NBr_2$ H_2 HCN	$[C_6H_6N]^+$ 92(36.40) $[C_6H_4N]^+$ 90(15.60) $[C_5H_3]^+$ 63(69.70)	422(M^++4, 45.50), 420(M^++2, 69.70), 419(M^++1, 63.60), 417(M^+-1, 30.30), 394(39.40), 393(21.20), 392(36.40), 391(54.30), 389(42.40), 340(12.10), 283(30.30), 234(15.20), 233(33.30), 205(39.40), 203(45.50), 195(12.10), 182(27.30), 177(12.10), 155(12.10), 151(15.20), 143(21.20), 136(21.20), 134(24.20), 127(39.40), 126(21.20), 114(27.30), 113(21.20), 104(3.00), 103(37.30), 101(45.50), 99(29.20), 98(24.20), 96(18.20), 95(15.20), 82(33.30), 81(48.50), 79(51.50), 78(12.10), 72(21.20), 64(18.20), 62(21.20), 50(6.10)

Compounds 2a,b

The mass spectra of the compounds 2a (Fig. 1) and 2b showed intense molecular ion peaks at m/z 421 and m/z 455, consistent with the molecular formula C16H9NBr2O3 and C16H8NClBr2O3 respectively.

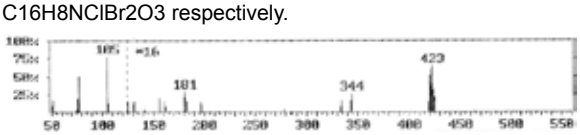
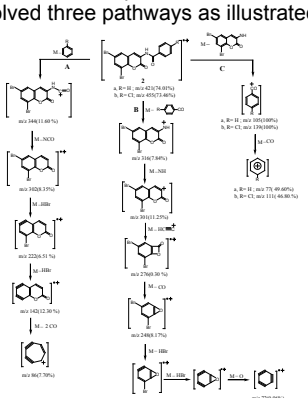


Figure 1: 70 eV mass spectrum of compound 2a

The molecular ion of compounds 2a and 2b fragmented further and involved three pathways as illustrated in scheme 2.



Scheme 2: main fragmentation pathway of compds 2a,b

The molecular ion of m/z 421 and m/z 455 fragmented via pathway A to give peak at m/z 334 by losing substituent phenyl radical cation. The ion at m/z 334 underwent fragmentation producing ion of m/z 302, corresponding to the molecular ion of 6,8-dibromocoumarin by losing isocyanate group (NCO). This fragmentation led to the formation of ions at m/z 222, 142, 114, 86 and m/z 62, respectively. Accordingly, the same molecular ion of m/z 421 and m/z 455 fragmented via the pathway B by cleavage of substituted benzoyl radical cation to give peak at m/z 316, which lost imino group (NH) to give peat at m/z 301. It further underwent loss of C2H, CO, and 2HBr to give peaks at m/z 276, 248, 168 and m/z 88, respectively.

Also, the same molecular ion of compound 2a and 2b underwent fragmentation via pathway C to give stable peaks at m/z 105 and m/z 139. The stable ion at m/z 105 and m/z 139 underwent loss of carbon monoxide to give peaks at m/z 77 and m/z 111, respectively.

Compound 4

From the study of mass spectra for compound 4 (Fig. 2), it was found that the molecular ion of the compound fragmented further into involved three pathways as illustrated in table 1 and scheme 3.

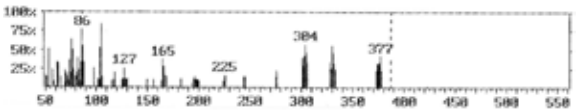
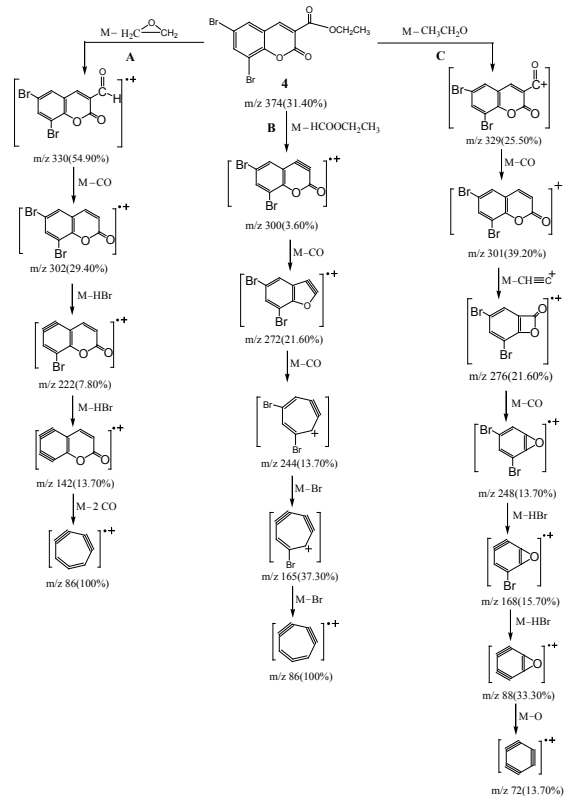


Figure 2: 70 eV mass spectrum of compd 4



Scheme 3: main fragmentation pathway of compd 4

Compound 5

Compounds 5a, 5b and 5c showed an intense molecular ion peaks at m/z 421, 435 and m/z 437, are corresponding to the molecular formula C16H9NBr2O3, C17H11NBr2O3 and C16H9NBr2O4, respectively.

The mass spectra of compounds 5a, 5b (Fig. 3) and 5c gave a characteristic fragmentation pattern which further broken via three various pathways as illustrated in scheme 4.

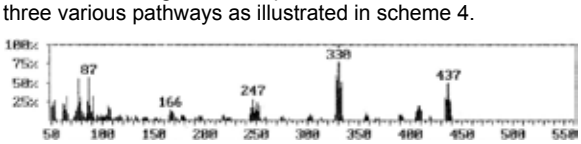
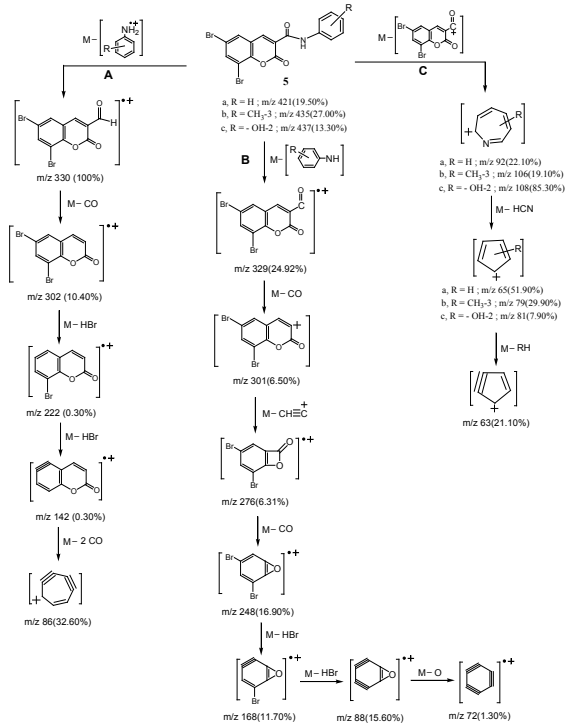


Figure 3: 70 eV mass spectrum of compd 5b

The molecular ion peaks at m/z 421, 435 and m/z 437 fragmented via the suggested pathway A to give a stable fragment ion of m/z 330, which further fragmented and gave a fragmentation of m/z 302 by losing carbon monoxide molecule. The fragment ion of m/z 302 underwent cleavage via the pathway A in the same fragmentation processes which was observed in pathway A for compound 2. Subsequently, the same molecular ion peaks of compounds 5a-c fragmented via the suggested pathway B to a fragmentation of m/z 329 by losing substituted phenyl amino radical cation.

$HC{\equiv}C^{+}$ Fragment ion of m/z 329 fragmented to give the fragment ion of m/z 301 which lost to give a fragment ion of m/z 276. The fragment of m/z 276 underwent fragmentation to produce peaks at m/z 248, 168, 88 and m/z 72, respectively.

Accordingly, the same molecular ion of compounds 5a-c fragmented via pathway C by losing 6,8-dibromo- coumarin-3-yl-carbonyl radical cation to give peaks at m/z 92, 106, and m/z 108, which lost hydrogen cyanide (HCN) to give a fragment ions at m/z 65, 79 and m/z 81, respectively.



Scheme 4: main fragmentation pathway of compds 5a,b,c

Compound 8

The mass spectra of compound 8 (Fig. 4) show relatively small molecular ion peak and a typical cleavage and rearrangement process type fragmentation.

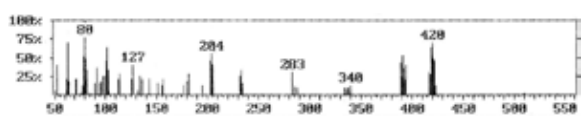
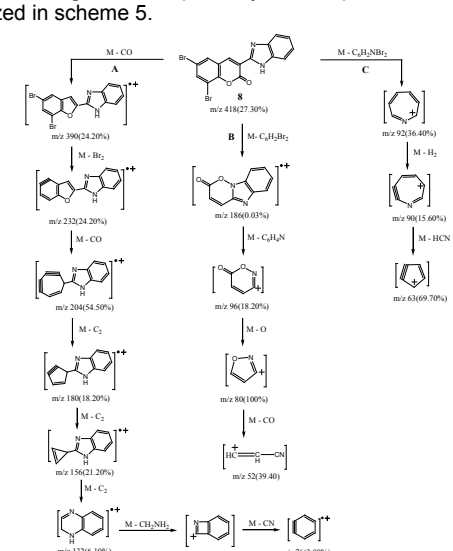


Figure 4: 70 eV mass spectrum of compd 8

The main fragmentation pathways of compound 8 were summarized in scheme 5.



Scheme 5: main fragmentation pathway of compd 8

The detection of both complementary fragments of the cleavage and rearrangement processes is attributed to their comparable ionization potentials. The molecular ion of m/z 418 fragmented via the suggested pathway A and gave fragment ion of m/z 390, which further fragment and gave a fragment ion of m/z 232 by losing bromine molecule (Br_2). Ion of m/z 232 fragmented to give ion of m/z 204, by losing carbon monoxide. This fragmentation led to ion of m/z 180, 156, 132, 102 and m/z 76, respectively. Accordingly, the same molecular ion of m/z 418 fragmented via the pathway B by a cleavage of 3,5-dibromo-1-benzyne to give the ion of m/z 186, which lost C_6H_4N to give the ion of m/z 96. The loss of oxygen atom from the ion with m/z 96 resulted in a stable ion at m/z 80, which lost carbon monoxide to give the ion of m/z 52. Also, the same molecular ion of compound 8 was broken via pathway C to give the ion of m/z 92, which lost hydrogen molecule to give the ion of m/z 90. The ion at m/z 90 underwent loss of hydrogen cyanide (HCN) to give peak at m/z 63.

3. Experimental

Melting points were determined on a Boetium Hostage apparatus and uncorrected. IR spectra were recorded on a perkin-Elmer FT/IR 1725 spectrometer. The ^{1}H-NMR spectra were recorded on a General Electric QE300, and chemical shifts were given with respect to TMS. Mass spectra were recorded on a VG Autspec CEI FAB$^+$ and a Hewlett Packard Ms-Engine thermospray and ionization by electron impact at 70 eV . The accelerating voltage was 6 kv, the temperature of the ion source was 200 ^{o}C and the emission current was ~100 mA . Microanalyses were conducted using an elemental analyzer 116.

3-(Aroyl)amino-6,8-dibromocoumarin (2a,b)

A mixture of 1 (0.01 mole), N-aroylglycine (such as N-benzoylglycine and N-(p-chloro)benzoylglycine) (0.01 mol), fused sodium acetate (0.03 mol) and acetic anhydride (0.03 mol) was fused an a hot plate for 2-3 min. The reaction mixture was heated on a water-bath for 2 hrs., then cooled and poured into water. The solid formed was filtered off, washed with water, dried and purified by recrystallization with ethanol to give 2.

3-(benzoyl)amino-6,8-dibromocoumerin (2a) as yellow crystals, yield 78%, m.p 220 oC. Ir (KBr): 3225 (NH), 1725, 1659 (C=O), 1081 (C-O) cm-1. 1H-NMR (DMSO-d6): 7.53- 8.10(m, 7H, Ar-H), 8.61(s, 1H, pyran-H), 9.75(s, 1H, NH) ppm. Found: C, 45.43; H, 2.01; N, 3.19; Br, 37.33. C16H9NBr2O3 requires: C, 45.61; H, 2.14; N, 3.32; Br, 37.53.

3-(P-chlorobenzoyl)amino-6,8-dibromocoumarin (2b) as yellow crystals, yield 73% , m.p. 183 oC. Ir (KBr): 3229(NH), 1730, 1693(C=O), 1607, 1588 (C=C), 1095 (C-O) cm-1. 1H-NMR (DMSO-d6): 7.51-8.11 (m, 6H, Ar-H), 8.58 (s, 1H, pyran-H), 9.81(s, H, NH) ppm. Found: C, 42.02; H, 1.67; N, 2.99; Cl, 7.58; Br, 34.54. C16H8NClBr2O3 requires: C, 42.20; H, 1.76; N, 3.08; Cl, 7.69; Br, 34.73.

6,8-Dibromo-3-amino coumarin (3)

A mixture of 2a and/or 2b (0.01mol) in acetic acid (15 ml) and 6N hydrochloric acid (15 ml) was heated under reflux for 2 hrs. The reaction mixture was cooled and neutralized with sodium carbonate. The solid formed was filtered off, washed with water, dried and purified by recrystalization with ethanol to give 3 as pale yellow, yield 53%, m.p. 163 oC. IR (KBr): 3325, 3145 (NH2), 1728 (C=O), 1605, 1589 (C=C), 1081 (C=O) cm-1. 1H-NMR (DMSO-): 5.20(s, 2H, NH2), 8.01(s,1H, Ar-H), 8.20 (s,1H,Ar-H), 8.63(s, 1H, pyran-H) ppm. 13C-NMR (DMSO-d6): 154.76(C=O), 150.49(C-O), 147.53, 147.19(C-Br), 138.47, 131.73, 120.62, 118.43, 116.25, 110.04(C- aromatic and pyrane) ppm. MS: m/z (%), 321(M+4, 17.50), 319(M+2, 34.50), 317(M+, 36.50), 305(12.01), 303(17.50), 301(19.30), 200(25.00),198(30.00), 197(25.00), 196(35.00), 167(35.00), 166(20.00), 135(30.00), 123(35.00), 122(35.00), 121(45.00), 118(30.00), 117(30.00), 107(20.00), 105(25.00), 104(55.00), 103(10.00), 98(35.00), 97(55.00), 91(45.00), 89(30.00), 88(30.00), 85(10.00), 84(50.00), 83(30.00), 82(35.00), 81(55.00), 80(65.00), 79(15.00), 78(10.00), 77(55.00), 76(10.00), 64(70.00), 63(35.00), 60(20.00), 59(100), 55(70.00), 54(65.00). Found: C, 33.89; H, 1.41; N, 4.24; Br, 49.63. C19H5NBr2O2 requires: C, 34.07; H, 1.58; N, 4.42; Br, 49.89.

6,8-Dibromo-3-ethoxycarbonyl coumarin (4)

A mixture of 1 (0.01 mol), diethyl malonate (0.01 mol) and piperidine (1 ml) was fused on a hot plate for 3-5 min., then cooled and acidified with diluted hydrochloric acid (2%). The product formed was collected by filtration, washed with water, dried; and recrystallization form ethanol to give 4 as colorless crystals, yield 78%, m.p. 165 oC. IR (KBr): 1755, 1713(C=O), 1608, 1518(C=O), 1180, 1065(C=O) cm-1. 1H-NMR (DMSO-d6): δ 1.2(t, 3H, CH3), 4.20(q, 2H, OCH2), 8.10(s, 1H, ArH), 8.21(s. 1H, ArH), 8.75(s, 1H, pyran- H) ppm. 13C-NHR (DMSO-d6): δ 161.94(CO of ester), 154.79(CO of pyrane), 150.40(C-O), 147.19, 138.38(C-Br), 131.70, 120.63, 119.21, 116.23, 110.03, (C-Ar and C-pyrane), 61.49(O-CH2), 13.49(CH3) ppm. Found: C, 38.35; H, 2.03; Br, 42.07. C12H8Br2O4 requires: C, 38.50; H, 2.14; Br, 42.24.

3-(Arylamino)carbonyl-6,8-dibromo coumarins (5 a-c)

A mixture of 4 (0.01 mol) and aromatic amines (namely, aniline, m-toludine and 2-aminophenol) (0.01 mol) in acetic acid (10 ml) was heated under reflux for 2 hrs, then cooled and poured into water. The solid formed was filtered off, washed with water, dried and purified by recrystalization with butanol to give 5.

6,8-dibromo-3-(phenylamino)carbonylcoumarin (5a) as a yellow crystals, yield 71%, m.p. 245 oC. Ir (KBr): 3225(NH), 1723, 1698(C=O), 1610, 1545(C=C), 1075(C-O) cm-1. 1H-NMR (DMSO-d6): δ 7.15-7.12(m, 5H, Ar-H), 8.20-8.28(s, 2H, Ar-H), 8.74(s, 1H, pyran-H), 10.50(s, 1H, NH) ppm. Found: C, 45.42; H, 2.02; N, 3.28; Br, 37.33. C16H9NBr2O3 requires: C, 45.61; H, 2.14; N, 3.32; Br, 37.53.

6,8-Dibromo-3-(m-toluidino)carbonyl coumarin (5b) as yellow, yield 73%, m.p. 325 oC. I R (Kbr): 3250(NH), 1721, 1697(C=O), 1609, 1587(C=C), 1083(C=O) cm-1. 1H-NMR (DMSO-d6): 2.31(s, 3H, CH3), 7.10-7.50(m, 4H, Ar-H), 8.25(s, 2H, Ar-H), 8.78(s, 1H, pyran-H), 10.44(s, 1H, NH) ppm. Found: C, 46.68; H, 2.42; N, 3.09; Br, 36.21. C17H11N-Br2O3 requires: C, 46.84; H, 2.53; N, 3.22; Br, 36.32.

6,8-Dibromo-3-(o-hydroxyphenylamino)carbonyl coumarin (5c) as yellow crystals, yield 74%, m.p. 325 oC. IR (KBr): 3350-3210(br-OH), 3270(NH), 1727, 1698(C=O), 1607, 1588 (C=C), 1210, 1085(C=O) cm-1. 1H-NMR (DMSO-d6): δ 6.83-6.97(m, 3H, Ar-H), 8.21-8.30(m, 3H, Ar-H), 8.71(s, 1H, pyran-H), 10.26(br. s, 1H, NH), 10.96(s, 1H, OH) ppm. Found: C, 43.76; H, 1.99; N, 3.03; Br, 36.05. C16H9NBr2O4 requires: C, 43.93; H, 2.06; N, 3.20; Br, 36.15.

3-(Benzoxazol-2-yl)-6,8-dibromo coumarin (6)

A solution of 5c (0.01 mol) in phosphorus oxychloride (20 ml) was heated on a water bath for 2 hrs. The reaction mixture was cooled and poured into ice-water. The solid obtained was filtered off, washed with water, dried and recrystallized from ethanol to give 6 as orange crystals, yield 63%; m.p. 246 oC. IR (KBr): 1728(C=O), 1625(C=N), 1605, 1595(C=C), 1135, 1085 (C=O) cm-1. 1H-NMR (DMSO-d6): 7.12-7.68(m, 4H, Ar-H), 8.21(s, 2H, Ar-H), 8.78 (s, 1H, pyran-H) ppm. Found: C, 45.65; H, 1.58; N, 3.22; Br, 37.61. C16H7NBr2O3 requires: C, 45.82; H, 1.67; N, 3.34; Br, 37.71.

3-(Benzaimidazol-2-yl)-6,8-dibromo coumarin (8)

A mixture of 4 (0.01 mol) and o-phenylenediamine (0.01 mol) in glacial acetic acid (3 ml) was heated under reflux for 6 hrs., then cooled and poured into water. The resulting solid was filtered off, washed with water, dried and purified by recrystallization from dimethyl formamide to give 8 as yellow crystals, yield 73%, m.p. 325 oC IR (KBr): 3270(NH), 1729(C=O), 1628 (C=N), 1608, 1588(C=C), 1095(C=O) cm-1. 1H-NMR (DMSO-d6): δ 7.23-7.26(m, 2H, Ar-H), 7.67-7.69(m, 2H, Ar-

H), 8.20(s, 2H, Ar-H), 9.07(s, 1H, pyran-H), 12.58(s, 1H, NH) ppm. Found: C, 45.81; H, 1.79; N, 6.63; Br, 73.63. C16H8N-2Br2O2 requires: C, 45.93; H, 1.91; N, 6.70; Br, 37.80.

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