Asian Journal of Chemistry Vol. 22, No. 7 (2010), 5751-5758

Mass Spectral Fragmentation Modes of Chromon-6-yl Alkanoic Acids and Esters

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Mass spectral fragmentation modes of chromon-6-yl alkanoic acids and their esters are being reported in this paper which have shown a definite pattern of fragmentation.

Key Words: Chromon-6-alkanoic acids, Chromon-6-alkanoic esters, Mass spectral fragmentation, Retro-Diels Alder fragmentation.

INTRODUCTION

Mass spectroscopy is an important and prevalent tool to support structures assigned to newly synthesized organic compounds. Now-a-days mass spectrometry has been used as an additional technique to assign structure to a number of chromones[1-8]. Mass spectral fragmentation patterns of chromon-6-yl alkanoic acids and esters are being reported in this research work.

EXPERIMENTAL

Chromon-6-yl alkanoic acids and esters were synthesised by reported method[9]. Purity of the compounds was checked on silica gel-G coated TLC-plates. Mass spectra were scanned on VG70-S mass spectrometer using 11-250 Jt system and Hawett Packard GC/MS 5985 operating at 70 eV. Figures given is parentheses represent relative intensities corresponding to the base peak.

RESULTS AND DISCUSSION

Mass spectral studies of chromon-6-yl alkanoic acids and esters (**1-11**) reveal a set pattern of fragmentation of these compounds. Following characteristic features were visible in the mass spectrum of these compounds:

The mass spectra of (**1-4**) were analyzed in order to provide further support to the structures assigned to them. The molecular ions, generally, appearing as abundant ions, were in complete agreement with their molecular weights. In addition to locating the molecular ions, the mass spectra were also examined with a view to delineate the significant modes of fragmentations of these ions.

The most characteristic mode of fragmentation involved loss of hydrogen radical from molecular ion generating [M-1] ions as the base peaks. In addition, the other

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processes worth mentioning are (i) loss of •COOH from molecular ion, (ii) cleavage of molecular ion generating benzoyl cations and (iii) the well-known retro-Diels Alder fragmentation (RDA) of the chromone ring took place only after the losses of •COOH and CH_2O from the molecular ions.

The high intensity molecular ion of (**1**), a typical compound, appearing at m/z 324, was in conformity with its molecular weight. Various modes of cleavage of this ion as depicted in Fig. 1. were:

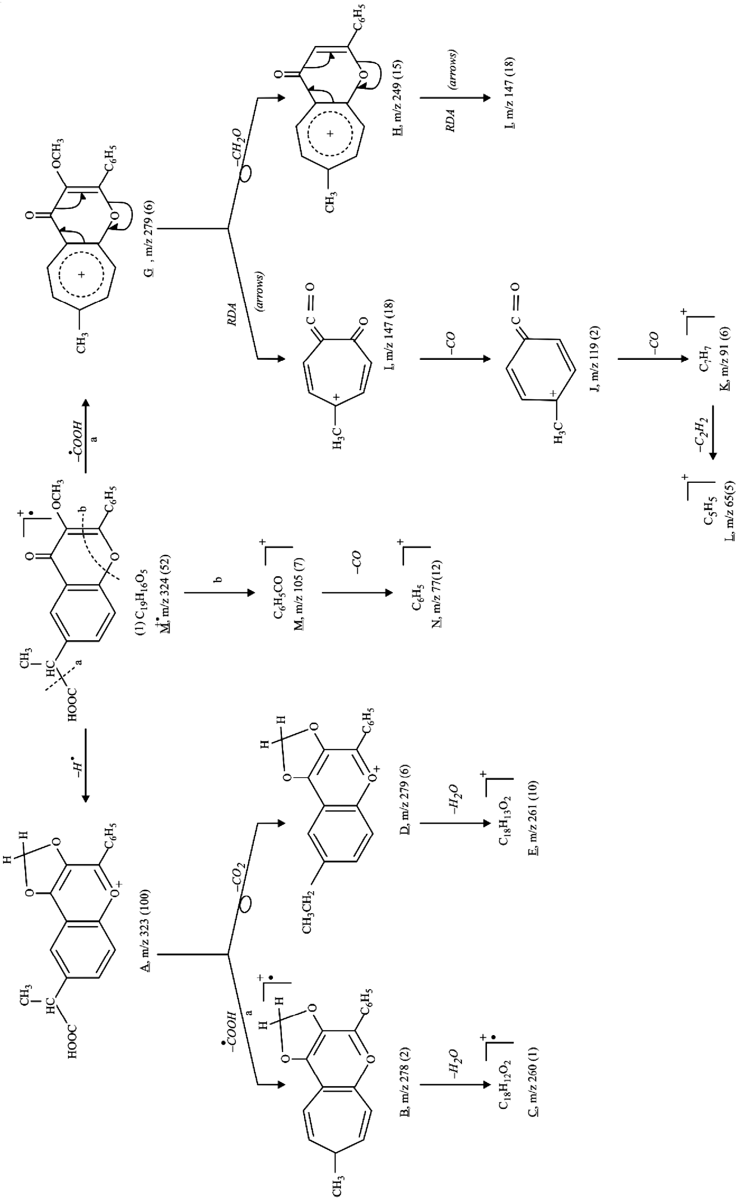


Fig. 1

- As observed in the case of 3-methoxyflavones[8], the loss of hydrogen radical from molecular ion generated the benzpyrillium ion <u>A</u> (m/z 323) which constituted the base peak. Elision of $^{\bullet}$COOH from <u>A</u> followed by a molecule of H_2O gave rise to ion <u>B</u> (m/z 278) and <u>C</u> (m/z 260), respectively. In an alternate mode, elimination of CO_2, with rearrangement, from <u>A</u> gave ion <u>D</u> (m/z 279) which after extrusion of a molecule of H_2O gave ion <u>E</u> (m/z 261). Loss of a molecule of H_2O from <u>A</u> generated <u>F</u> (m/z 305).
- The second significant fragmentation involved expulsion of $^{\bullet}$COOH (path a) from the molecular ion generating <u>G</u> (m/z 279) which is isomeric with <u>D</u> and is analogous to the well-known tropylium ion. The presence of 3-methoxy group was confirmed by the obtention of <u>H</u> (m/z 249) from <u>G</u> by the elision of a molecule of CH_2O. The presence of chromone ring in <u>H</u> triggered the well known RDA cleavage generating quinonoid ion <u>I</u> (m/z 147). Sequential losses of two molecules of CO from <u>I</u> followed by C_2H_2 yielded ions <u>J</u> (m/z 119), <u>K</u> (m/z 91) and <u>L</u> (m/z 65), respectively. In a competitive pathway, ion <u>G</u> may itself undergo RDA cleavage (arrows) generating ion <u>I</u>.
- Cleavage of chromone ring along path b followed by the loss of a molecule of CO has generated ion <u>M</u> (m/z 105) and <u>N</u> (m/z 77), respectively. These ions could also have been formed by a similar cleavage of <u>A</u> and <u>D</u>.

The fragmentation modes of (**1**), depicted in Fig. 1, were further established by the appearance of the corresponding ions in the mass spectra of compounds (**2**), (**3**) and (**4**). The significant ions observed in the mass spectra of these compounds are so arranged in Table-1 as to display the peak-to-peak correspondence of various fragment ions.

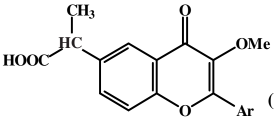
A look at the mass spectra of (**5-8**) revealed that the electron impact-induced fragmentation of these compounds followed the same pattern as in the case of the corresponding acids (Table-2). Some noteworthy features of the mass spectra of (**5-8**) are: (i) loss of hydrogen radical from molecular ions giving [M-1] as base peaks, (ii) elision of $^{\bullet}COOH_3$ from the molecular ion generating ion <u>G</u> which were quite intense in contrast to the same ions obtained from the corresponding acids and (iii) losses of $^{\bullet}COOCH_3$ and CO_2 from [M-1] ions gave ions <u>B</u> and <u>D</u> (isomeric with <u>G</u>), respectively.

Further, fragmentations of <u>A</u>, <u>B</u>, <u>D</u> and <u>G</u> followed the same path as depicted in Fig. 1 for acids.

The mass spectrum of acid (**9**) was also examined with a view to further establish the structure assigned to it. The high intensity molecular ion, appearing at m/z 308, was in conformity with its molecular weight. The significant fragmentations of the molecular ion are depicted in Fig. 2. Loss of hydrogen radical from the molecular ion gave rise to the characteristic [M-1] ion <u>A</u> (m/z 307) as the base peak.

Elision of $^{\bullet}$COOH from molecular ion resulted in the formation of the tropylium ion <u>B</u> (m/z 263).

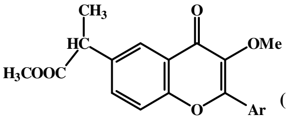
TABLE-1
SIGNIFICANT MASS SPECTRAL DATA OF (**1-4**) (ARRANGED TO DISPLAY THE PEAK-TO-PEAK CORRESPONDENCE OF FRAGMENT IONS)



(1-4)

	(**1**) Ar=C_6H_5	(**2**) Ar=4-$CH_3C_6H_4$	(**3**) Ar=4- $CH_3OC_6H_4$	(**4**) Ar=4-ClC_6H_4
$M^{+\bullet}$	324 (52)	338 (54)	354 (50)	358/360 (50)
Fragment ions				
A	323 (100)	337 (100)	353 (100)	357/359 (100)
B	278 (2)	292 (3)	308 (2)	312/314 (2)
C	260 (1)	274 (1)	290 (1)	294/296 (2)
D	279 (6)	293 (8)	309 (4)	313/315 (6)
E	261 (10)	275 (9)	291 (6)	295/297 (10)
F	305 (7)	219 (8)	335 (12)	339/341 (10)
G	279 (6)	293 (8)	309 (4)	313/315 (6)
H	249 (15)	263 (19)	279 (16)	283/285 (2)
I	147 (18)	147 (40)	147 (42)	147 (40)
J	119 (2)	119 (6)	119 (16)	119 (2)
K	91 (6)	91 (9)	91 (20)	91 (7)
L	65 (5)	65 (5)	65 (21)	65 (4)
M	105 (7)	119 (6)	135 (15)	139/141 (18)
N	77 (5)	89 (3)	107 (3)	111/113 (8)

TABLE-2
SIGNIFICANT MASS SPECTRAL DATA OF (**5-8**) (ARRANGED TO DISPLAY THE PEAK-TO-PEAK CORRESPONDENCE OF FRAGMENT IONS)



(5-8)

	(**5**) Ar=C_6H_5	(**6**) Ar=4- $CH_3C_6H_4$	(**7**) Ar=4-$CH_3OC_6H_4$	(**8**) Ar=4-ClC_6H_4
$M^{+\bullet}$	338 (53)	352 (55)	368 (56)	372/374 (48)
Fragment ions				
A	337 (100)	351 (100)	367 (100)	371/373 (100)
B	278 (3)	292 (4)	308 (4)	312/314 (4)
C	260 (1)	274 (2)	290 (1)	294/296 (3)
D	279 (21)	293 (25)	309 (24)	313/315 (23)
E	261 (10)	275 (17)	291 (17)	295/297 (12)
F	319 (5)	333 (2)	349 (2)	–
G	279 (21)	293 (25)	309 (24)	313/315 (23)
H	249 (13)	263 (24)	279 (26)	283/285 (24)
I	147 (21)	147 (56)	147 (59)	147 (59)
J	119 (2)	119 (14)	119 (12)	119 (5)
K	91 (8)	91 (22)	91 (14)	91 (25)
L	65 (5)	65 (7)	65 (6)	65 (14)
M	105 (7)	119 (14)	–	139 (18)
N	77 (10)	91 (22)	–	111 (14)

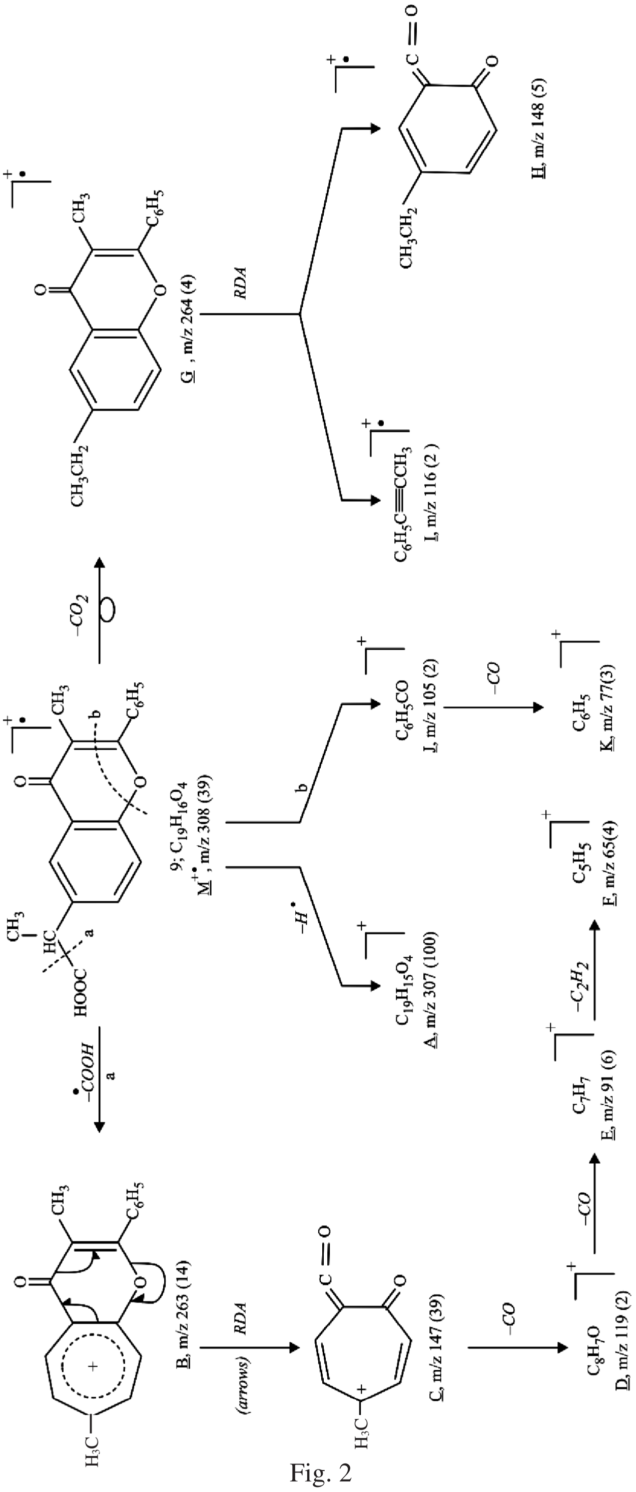

9; $C_{19}H_{16}O_4$
$M^{+\bullet}$, m/z 308 (39)
$-\overset{\bullet}{C}OOH$
a
b
$-CO_2$
G, m/z 264 (4)
RDA
I, m/z 116 (2)
$C_6H_5C{\equiv}CCH_3$
H, m/z 148 (5)
$-H^\bullet$
A, m/z 307 (100)
$C_{19}H_{15}O_4$
J, m/z 105 (2)
C_6H_5CO
$-CO$
K, m/z 77(3)
C_6H_5
B, m/z 263 (14)
(arrows)
RDA
C, m/z 147 (39)
$-CO$
D, m/z 119 (2)
C_8H_7O
$-CO$
E, m/z 91 (6)
C_7H_7
$-C_2H_2$
F, m/z 65(4)
C_5H_5

Fig. 2

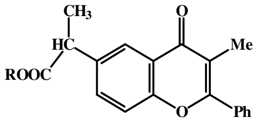
The presence of chromone ring in B triggered the well known RDA fragmentation generating an intense quinonoid ion C (m/z 147). Sequential losses of two molecules of CO from C followed by C_2H_2 yielded ions D (m/z 119), E (m/z 91) and F (m/z 65), respectively.

In a competitive mode, elision of CO_2, accompanied by rearrangement from the molecular ion generated ion G (m/z 264) which underwent the RDA cleavage to give ion H (m/z 148) along with I (m/z 116).

Cleavage of flavone ring in the molecular ion afforded the benzoyl cation J (m/z 105). Elision of CO from J gave the phenyl cation K (m/z 77).

As depicted in Table-3, the electron impact-induced fragmentation of ester (**10**) exhibited complete correspondence with various modes of fragmentations of (**9**) [cf. correspondence of fragmentation modes of (**5-8**) with those of (**1-4**)].

TABLE-3
SIGNIFICANT MASS SPECTRAL FRAGMENTATION DATA OF (**9**) AND (**10**) (ARRANGED TO DISPLAY THE PEAK-TO-PEAK CORRESPONDENCE OF FRAGMENT IONS)



(9-10)

	(**9**)	(**10**)
	R = H	R = CH_3
$M^{+\bullet}$	308 (39)	322 (10)
Fragment ions		
A	307 (100)	321 (100)
B	263 (14)	263 (44)
C	147 (39)	147 (56)
D	119 (2)	119 (3)
E	91 (6)	91 (25)
F	65 (4)	65 (14)
G	264 (4)	264 (12)
H	148 (5)	148 (8)
I	116 (2)	116 (2)
J	105 (2)	105 (3)
K	77 (3)	77 (7)

The structural assignments of the ester (**11**) were in complete agreement with its mass spectral fragmentation. The moderate intensity molecular ion, appearing at m/z 260, was in conformity with its molecular weight. Significant modes of fragmentations are depicted in Fig. 3. Unlike the flavone acids (**9**), (**1-4**) and esters (**10**) and (**5-8**), the loss of hydrogen radical did not constitute the major mode of fragmentation of the molecular ion. However, the elision of $^{\bullet}COOCH_3$ from the molecular ion generated the tropylium ion A (m/z 201) which constituted the base peak.

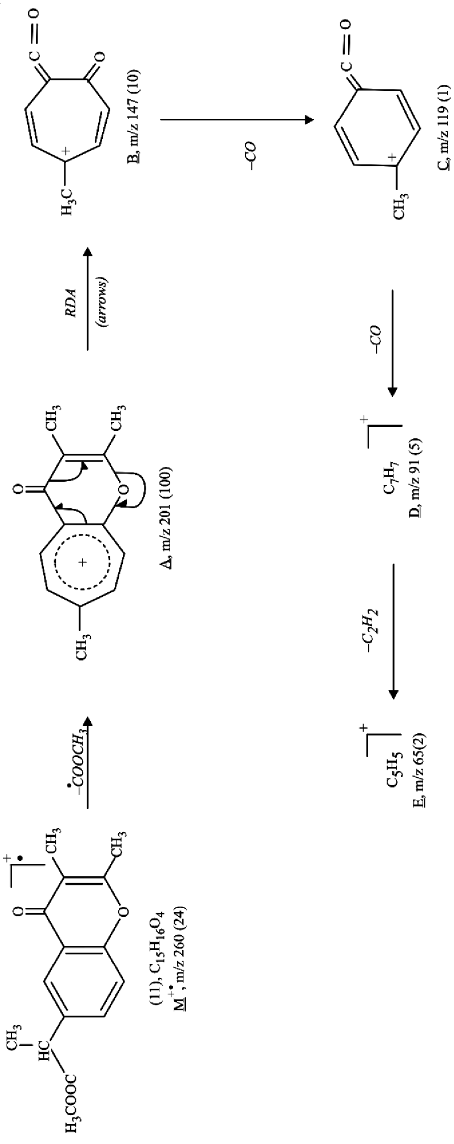


Fig. 3

The presence of chromone ring in A triggered the characteristic RDA fragmentation generating the quinonoid ion B (m/z 147). Sequential losses of two molecules of CO from B followed by elision of C_2H_2 yielded ions C (m/z 119), D (m/z 91) and E (m/z 65), respectively.

ACKNOWLEDGEMENTS

Facilities provided by Kurukshetra University and Financial assistance by CSIR are thankfully acknowledged.

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(*Received*: 4 January 2010; *Accepted*: 5 April 2010) AJC-8617