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Mass Spectral Studies of 6-Cinnamoyl Chromones

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Mass spectral fragmentation modes of 6-cinnamoyl chromones constitute subject matter of this publication which have exhibited a definite pattern of fragmentation. These studies were carried out to provide additional support to the structures assigned to compounds.

Key Words: 6-Cinnamoyl chromones, Retro-Diels Alder fragmentation.

INTRODUCTION

Chromones are immensely important compounds with multiferous uses. Chromones[1-4] as well as α,β-unsaturated carbonyl compounds[5-9] (*e.g.*, cinnamoyl compounds) have shown various biological activities. For instance, antibacterial and antifungal[1], antiinflammatory[2], anticomplementary[3], diuretic[4] activities of chromones and antiinflammatory[5], antibacterial[6], antitumor[7,8] and antiviral[9] activities of α,β-unsaturated carbonyl compounds (chalcones). Therefore, chalcones of chromones *i.e.*, cinnamoyl chromones were synthesised and their structures were identified on the basis of IR, PMR and mass spectral studies. Mass spectral fragmentation modes of cinnamoyl chromones (**I-VI**) are being reported in present communication.

EXPERIMENTAL

6-Cinnamoyl chromones were synthesized form *o*-hydroxy carbonyl compounds or *p*-hydroxy acetophenone[3]. Purity of the compounds was checked on silica gel-G coated TLC plates. Mass spectra were scanned on VG 70-S mass spectrometer using 11-250 Jt-system and Hawett Packard GC/MS 5985 operating at 70 eV. The figures given in parentheses represent relative intensities compared to the base peak.

RESULTS AND DISCUSSION

Mass spectral studies of 6-cinnamoyl chromones (I-VI): A number of 6-cinnamoylchromones synthesized during the course of investigations, have been characterized by their mass spectral studies. On the basis of these studies, it has been possible to make some generalizations regarding various fragmentation modes.

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The mass spectra of six 6-cinnamoylchromones (**I-VI**) were analyzed in order to provide further support to the structures assigned to them. The molecular ions, appearing as base peaks in all the cases, except **VI** were in conformity with their molecular weights. In addition to locate the molecular ions, the mass spectra were analyzed to get an insight into the significant modes of their cleavages. These ions underwent fragmentations involving α-cleavage of the enone moiety at both the sites. In addition, a prominent mode of cleavage involved loss of a radical of hydrogen generating an intense benzpyrillium ion. In a competitive process, loss of CO from the enone moiety was also observed.

The RDA cleavage of chromone ring took place only after the fission of molecular ion by one of the above modes of fragmentation.

The molecular ion of **I**, a typical compound, appearing as a base peak, at m/z 352 underwent cleavage along the following distinct pathways:

- The presence of enone moiety in **I** triggered α-cleavage (path a) of the molecular ion producing abundant ion A (m/z 103) and B (m/z 249). Two consecutive losses of C_2H_2 from A gave rise to C (m/z 77) followed by D (m/z 51). Extrusion of CO from ion B gave rise to flavone cation E (m/z 221).

The RDA fragmentation of E followed by sequential losses of two molecules of CO afforded the quinonoid ion F (m/z 119), ion G (m/z 91) and ion H (m/z 63), respectively. In a competitive process, B would undergo RDA cleavage to generate I (m/z 147). Loss of CO from I gave F.

- Another α-cleavage of the molecular ion (path b) formed ions E and J (m/z 131). The latter ion lost CO to give A.
- Elision of CO from molecular ion (path c) formed the radical ion K (m/z 324) which further cleaved along path d, involving hydrogen transfer to yield flavone radical ion L (m/z 222). The expected RDA cleavage of L was responsible for the appearance of phenylacetylene radical ion P (m/z 102) and the quinonoid ion M (m/z 120). Sequential losses of two molecules of CO from M afforded ion N (m/z 92) and O (m/z 64), respectively. In a competitive pathway, elimination of CO from L resulted in the formation of 2-phenylbenzofuran radical ion Q (m/z 194). Cleavage of Q along path f formed benzoyl cation R (m/z 105) which upon expulsion of CO gave rise to C.

Another mode of fission of the ion K involved extrusion of C_2H_2 (path e) accompanied by a rearrangement process to give the ions S (m/z 298). The RDA cleavage of S followed by sequential losses of two molecules of CO generated T (m/z 196), U (m/z 168) and V (m/z 140), respectively, along with P.

- Loss of hydrogen radical from the molecular ion was a very significant process as evident by the appearance of the most abundant benzpyrillium ion W (m/z 351),

*It may be pointed out here that the loss of H• from molecular ion in these compounds does not seem to involve the flavone moiety as evident by the appearance of an intense [M-1] ion in the case of **IV** and **VI**. Thus, it can be concluded that the loss of H• has occurred from the cinnamoyl side chain forming the benzpyrillium ion, W.

next to the base peak*. Elimination of acylium radical B from W produced an ion X (m/z 102) which, in turn, expelled C_2H_2 producing benzyne radical ion Y (m/z 76). In a competitive scission of [M-1], there was a loss of CO forming ion Z (m/z 323). The fragmentation modes of **I**, depicted in Fig. 1, were further corroborated by the appearance of the corresponding ions in the mass spectra of **II**, **III**, **IV**, **V** and **VI**. The significant ions observed in the mass spectra of these compounds, arranged in Tables 1 and 2, display peak-to-peak correspondence of various fragment ions.

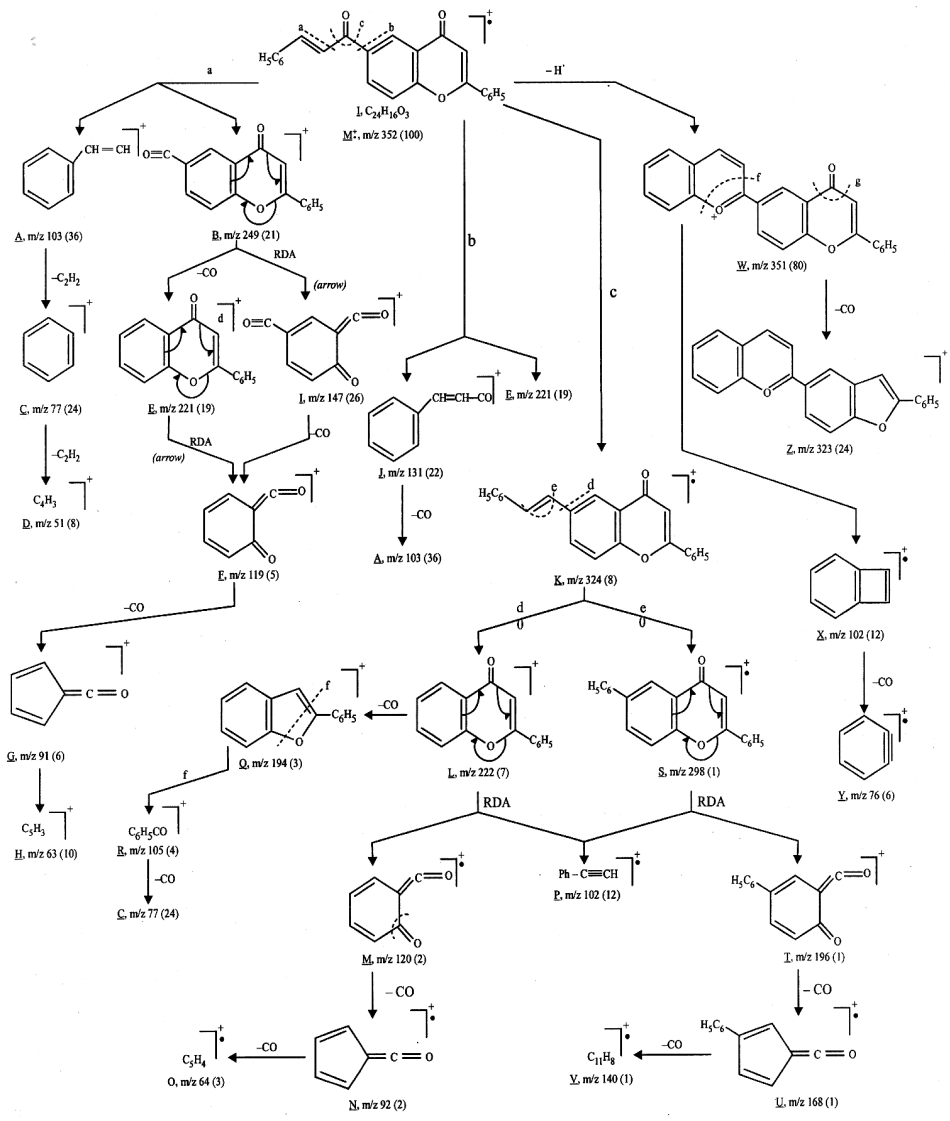
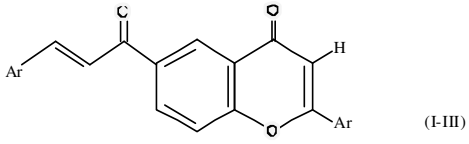


Fig. 1

TABLE-1
SIGNIFICANT MASS SPECTRAL DATA OF **I**, **II**, **III** (ARRANGED TO DISPLAY THE PEAK-TO-PEAK CORRESPONDENCE OF FRAGMENT IONS)

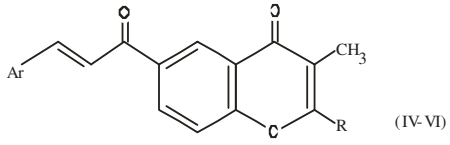


(I-III)

	(**I**) Ar = Phenyl	(**II**) Ar = 2-Thienyl	(**III**) Ar = 2-Furyl
$M^{+\bullet}$	352 (100)	364 (100)	332 (100)
Fragment ions			
A	103 (36)	109 (35)	93 (6)
B	249 (21)	255 (22)	239 (70)
C	77 (24)	83 (5)	67 (2)
D	51 (8)	57 (8)	–
E	221 (9)	227 (12)	211 (9)
F	119 (5)	119 (6)	119 (10)
G	91 (6)	91 (8)	91 (10)
H	63 (10)	63 (9)	63 (24)
I	147 (26)	147 (55)	147 (36)
J	131 (32)	137 (53)	121 (34)
K	324 (8)	336 (22)	304 (14)
L	222 (7)	228 (16)	212 (41)
M	120 (2)	120 (8)	120 (4)
N	92 (2)	92 (2)	92 (14)
O	64 (3)	64 (2)	64 (11)
P	102 (12)	108 (18)	92 (14)
Q	194 (3)	200 (8)	184 (6)
R	105 (4)	111 (9)	95 (4)
S	298 (1)	310 (1)	278 (23)
T	196 (1)	202 (1)	186 (7)
U	168 (1)	174 (1)	158 (5)
V	140 (1)	146 (3)	130 (2)
W	351 (80)	363 (18)	–
X	102 (12)	108 (18)	92 (14)*
Y	76 (6)	82 (4)	66 (3)*
Z	323 (24)	335 (91)	303 (27)*

*: Since [M-1] is not seen at all, these peaks could not be assigned. It may be possible that

TABLE-2
SIGNIFICANT MASS SPECTRAL DATA OF **IV**, **V** AND **VI** (ARRANGED TO DISPLAY THE PEAK-TO-PEAK CORRESPONDENCE OF FRAGMENT IONS)



(IV-VI)

	(**IV**) R = CH_3, Ar = C_6H_5	(**V**) R=CH_3, Ar = 4 - ClC_6H_4	(**VI**) R = H, Ar = C_6H_5

$M^{+\bullet}$	304 (100)	338/340 (100)	290 (56)
Fragment ions			
A	103 (35)	137/139 (23)	103 (21)
B	201 (32)	201 (54)	187 (12)
C	77 (43)	111/113 (3)	77 (15)
D	51 (14)	85/87 (1)	51 (2)
E	173 (5)	173 (8)	159 (8)
F	119 (3)	119 (3)	119 (1)
G	91 (16)	91 (10)	91 (2)
H	63 (9)	63 (2)	63 (2)
I	147 (11)	147 (22)	147 (1)
J	131 (39)	165/167 (49)	131 (18)
K	276 (13)	310/312 (9)	262 (6)
L	174 (4)	174 (6)	160 (2)
M	120 (3)	120 (3)	120 (1)
N	92 (7)	92 (4)	92 (1)
O	64 (4)	64 (1)	64 (1)
P	54 (1)	54 (1)	–
S	250 (1)	284/286	236 (1)
T	196 (1)	230/232	226 (4)
U	168 (1)	–	–
V	140 (1)	–	–
W	303 (99)	337/339 (50)	289 (100)
X	102 (9)	136/138 (3)	102 (5)
Y	76 (7)	110/112 (2)	76 (3)
Z	275 (47)	309/311	261(31)

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