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Mass Spectral Studies of Some 6-(5-Aryl-4,5-dihydropyrazol-3-yl)flavones and Chromones

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Mass spectral fragmentation patterns of some 6-(5-aryl-4,5-dihydropyrazol-3-yl)flavones as well as chromones are being reported in present publication. Distinct pattern of fragmentation have been observed. These studies were carried out to provide additional support to the structures assigned to compounds.

Key Words: Mass spectral fragmentation, 6-(5-Aryl-4,5-dihydropyrazol-3-yl)chromones and flavones, Retro-Diels Alder fragmentation.

INTRODUCTION

Chromones and flavones constitute a distinct class of organic compounds of medicinal importance. This system bearing heterocycles at different positions are among the compounds associated with a number of biological activities like anti-inflammatory[1], antibacterial and antifungal[2], anticomplementary[3], central nervous system (CNS) disorders[4] and diuretic[5] activities. Besides, pyrazoles are with a number of medicinal activities, for instance, phenylbutazone is antirheumatic factor[6], oxyphenylbutazone (tandearil) is antiinflammatory[7] but is less toxic than phenylbutazone. They are hyperglycemic[8] and antifungal[9] as well as diuretic[3a,10]. Compounds containing both these moieties are medicinally important.

Mass spectrometery is a wonderful tool in the hands of organic chemists to support structures of newly synthesised compounds as well as to determine their molecular formula and molecular weight[11]. A lot of work has been done on mass spectral fragmentation of chromone derivatives to support their structures[12-14] through fragmentation modes. Mass spectral fragmentation patterns of 6-(5-aryl-4,5-dihydropyrazol-3-yl)chromones (**I-VII**) are being reported in this publication.

EXPERIMENTAL

6-(5-Aryl-4, 5-dihydropyrazol-3-yl)chromones/flavones were synthesised from chalcones[3]. Purity of the compounds was checked on silica get-G coated TLC-plates. Mass spectra were scanned on VG 70-S mass spectrometer using 11-250

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Jt-system and Hawett-Packard GC/MS 5985 operating at 70 eV. The figures given in parentheses represent relative intensities corresponding to the base peak.

RESULTS AND DISCUSSION

Mass spectral studies of 6-(5-aryl-4,5-dihydropyrazol-3-yl)chromones and flavones: Mass spectra of **I-VII** were analyzed in order to provide further support to the structures assigned to them.

An inspection of the mass spectra of these compounds revealed that the molecular ions were in complete agreement with their molecular weights. A characteristic feature of the mass spectra of these compounds was that, (though the molecular ion was quite intense), it did not constitute the base peak. In addition to looking for the molecular ions, these spectra were also examined with a view to delineate the characteristic modes of fragmentations expected from their molecular framework. It was found that scission of molecular ion of all the seven compounds followed similar pattern, except for some very minor variations in the case of a couple of daughter ions. Thus, the molecular ions as well as some daughter ions appearing as intense peaks underwent fragmentation mainly through five distinct pathways: (i) elision of N_1-acyl moiety from the 2-pyrazoline component involving three competitive modes of fission of the N_1-C bond; (ii) fission of pyrazoline ring across 1, 2, 3 and 4 bonds; (iii) cleavage of C-C bond between pyrazoline and aryl moiety; (iv) fission of the C-C bond between pyrazoline and chromone moiety and (v) fission of the chromone ring in the daughter ions, involving the typical RDA cleavage.

The molecular ion of **I** ($M^{+\cdot}$, m/z 408), for instance, was in conformity with its molecular weight. Electron impact-induced fragmentation of this ion proceeded *via* the following pathways:

(1) The presence of 1-acetyl moiety in the molecular ion triggered the expulsion of ketene (arrows) generating an intense ion A (m/z 366) which constituted the base peak [the daughter ion A appeared as a base peak in the spectra of **I, II, III** and **IV** whereas it appeared as peak of moderate to weak intensity in the case of **V, VI** and **VII**]. Further, fragmentation of A took place as under:

Fission of pyrazoline ring along path a generated ion B (m/z 247). In a competitive process, the ion A underwent similar cleavage involving hydrogen transfer to generate K (m/z 248).

Elision of $^{\bullet}$CN from B (path e) gave F (m/z 221) which could have also arisen by the expulsion of HCN from K (path f). The RDA cleavage of chromone ring in F gave H (m/z 119).

Sequential losses of two molecules of CO from H resulted in the formation of I (m/z 91) and J (m/z 63), respectively.

Formation of, F could also be rationalized by a competitive mode of fission of C-C bond linking pyrazoline and chromone rings (path c) as evident by the generation of V (m/z 145).

The presence of chromone ring in B and K also triggered RDA cleavage followed by sequential losses of two molecules of CO in each case and generated C (m/z 145), D (m/z 117) and E (m/z 89) in case B; whereas L (m/z 146), M (m/z 118) and N (m/z 90), in case of K.

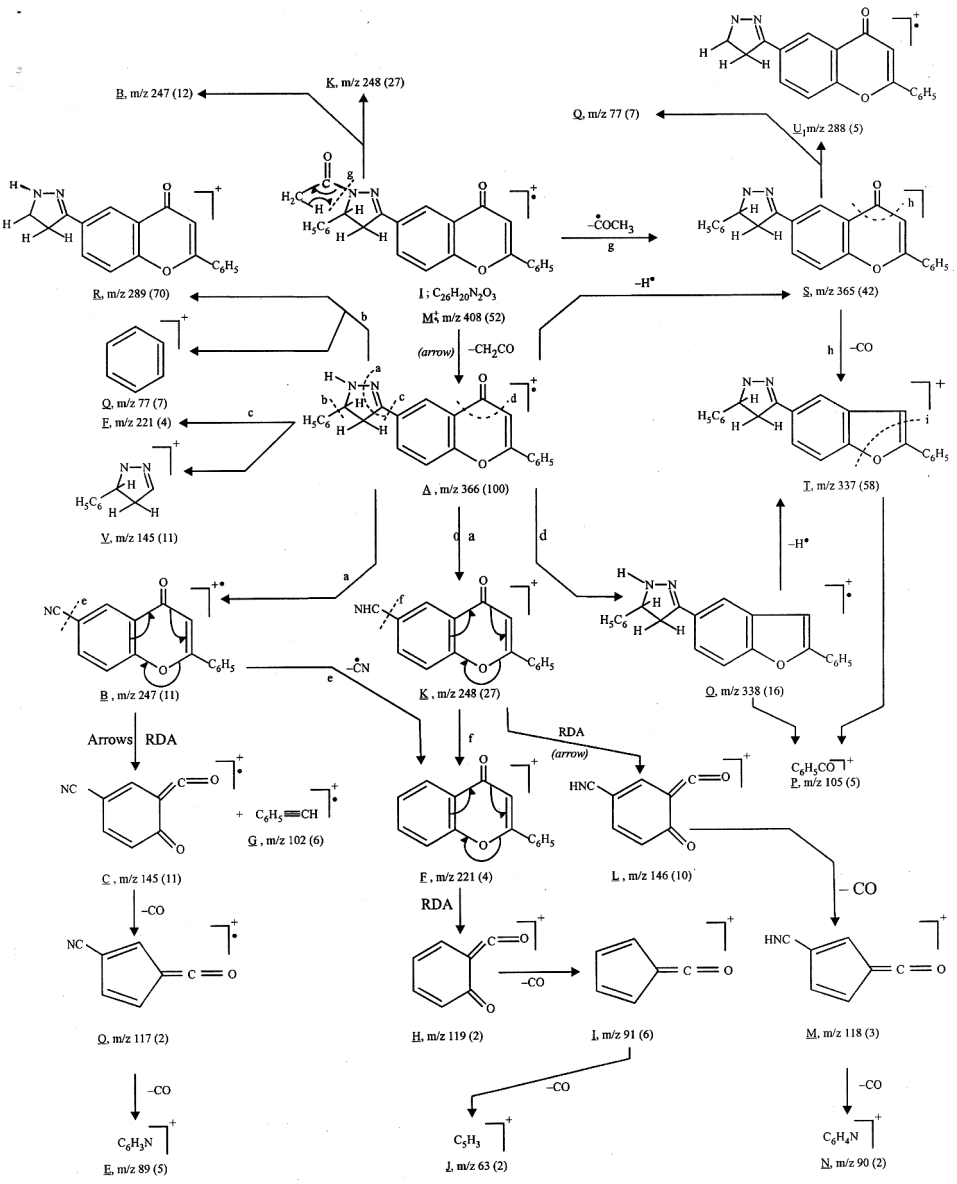
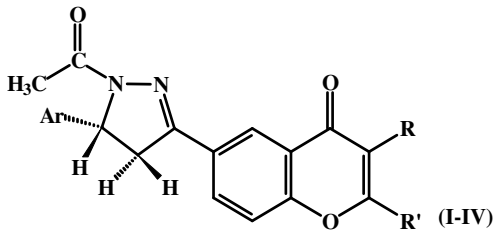


Chart-I

Cleavage of C-C bond between phenyl moiety and pyrazoline along path b gave phenyl radical ion Q (m/z 77) and another abundant ion R (m/z 289). Presence of chromone ring in A triggered the expulsion of CO (path d) generating O (m/z 338) which having a benzofuran nucleus, further cleaved to give benzoyl cation P (m/z 105).

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



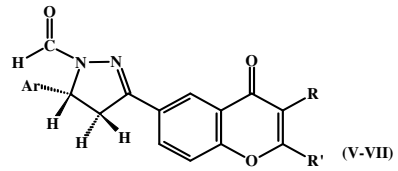
(I-IV)

	I R = H Ar = R' = Ph	II R = H Ar = R' = 2-Thienyl	III R = R' = CH_3, Ar = Phenyl	IV R = R' = CH_3, Ar = 4-ClC_6H_4
$M^{\bullet+}$	408 (52)	420 (50)	360 (59)	394/396 (62)
Fragment ions				
A	366 (100)	378 (100)	318 (100)	352/354 (100)
B	247 (12)	253 (34)	199 (12)	199 (16)
C	145 (11)	145 (19)	145 (9)	145 (7)
D	117 (2)	117 (3)	117 (4)	117 (4)
E	89 (5)	89 (6)	89 (7)	89 (9)
F	221 (4)	227 (7)	173 (1)	173 (5)
G	102 (6)	108 (17)	–	–
H	119 (2)	119 (2)	119 (3)	–
I	91 (6)	91 (3)	91 (8)	91 (4)
J	63 (2)	63 (5)	63 (2)	–
K	248 (27)	254 (42)	200 (24)	200 (18)
L	146 (10)	146 (7)	146 (6)	146 (6)
M	118 (3)	–	118 (4)	–
N	90 (2)	90 (3)	90 (2)	90 (6)
O	338 (16)	350 (20)	290 (2)	324/326 (9)
P	105 (5)	111 (10)	–	–
Q	77 (7)	83 (3)	77 (8)	–
R	289 (70)	295 (71)	241 (75)	241 (46)
S	365 (42)	377 (64)	317 (52)	–*
T	337 (58)	349 (38)	289 (47)	323/325 (26)
U	288 (5)	294 (2)	240 (6)	–*
V	145 (11)	1	145 (9)	–*

*In the case of IV, the fragments S, U and V are not seen. It seems that in this case, the molecular ion does not eliminate $CH_3^{\bullet}CO$ nor does the ion A expel $H^{\bullet}$. The appearance of ion T, however, could be rationalized by the elision of $H^{\bullet}$ from O.

(2) In a competitive process (path g), extrusion of $CH_3^{\bullet}CO$ from the molecular ion gave another abundant ion S* (m/z 365) [*In the mass spectrum of IV, it was observed that the molecular ion did not eliminate $CH_3CO^{\bullet}$. Therefore, it was devoid of peaks due to ions S, Q and U. The appearance of ion T, however, could be rationalized by elision of $H^{\bullet}$ from Q. In addition, ion V was also not seen] which could also arise by the elision of $H^{\bullet}$ from A. Other modes of fragmentation of S involved: (i) Elision of CO from chromone ring (path h) to form T (m/z 337). Alternatively, T could also be formed by the loss of $H^{\bullet}$ from the ion O; cleavage of benzofuran ring in O and T formed P; (ii) Cleavage of C-C bond linking phenyl and pyrazoline moieties (path i) in S generated U (m/z 288) along with Q.

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



(V-VII)

	V Ar = R' = C_6H_5 R = H	VI R' = R = CH_3 Ar = C_6H_5	VII R = R' = CH_3 Ar = 4Cl C_6H_4
M^+	394 (50)	346 (48)	380/382 (60)
Fragment ions			
A	366 (19)	318 (13)	352/354 (10)
B	247 (6)	199 (7)	199 (14)
C	145 (17)	145 (8)	145 (15)
D	117 (6)	117 (3)	117 (11)
E	89 (15)	89 (5)	89 (26)
F	221 (6)	173 (1)	173 (2)
G	102 (19)	54 (1)	54 (5)
H	119 (8)	119 (4)	119 (2)
I	91 (19)	91 (5)	91 (10)
J	63 (8)	63 (1)	63 (10)
K	248 (67)	200 (61)	200 (100)
L	146 (10)	146 (7)	146 (13)
M	118 (8)	118 (4)	118 (5)
N	90 (6)	90 (2)	90 (6)
O	338 (2)	280 (2)	324/326 (2)
P	105 (11)	–	–
Q	77 (39)	77 (6)	111/113 (6)
R	289 (100)	241 (100)	241 (66)
S	365 (41)	317 (36)	351/353 (23)
T	337 (5)	289 (4)	323/325 (2)
U	288 (5)	240 (6)	240 (3)
V	145 (17)	145 (8)	–

The fragmentation modes of I depicted in Chart-I were further established by the appearance of corresponding ions in the mass spectra of III and IV. The significant ions in the mass spectra of these compounds arranged in Table-1 display peak-to-peak correspondence of various fragment ions.

A comparison of mass spectral fragmentation of I, II, III, IV with V, VI, VII revealed that though in the latter cases, the molecular ions eliminated CO and $^{\bullet}$CHO giving low intensity ion A and S, the ion R constituted the base peak in case of V and VI, whereas the ion K appeared as base peak in the case of VII. Other modes of fragmentation of A and S followed the same pattern as in the case of I, II, III and IV. Significant ions observed in the mass spectra of V, VI and VII are listed in Table-2.

Interestingly the mass spectral studies of I, II, III, IV, V, VI and VII have clearly proved that commonly observed RDA cleavage of the chromone nucleus does not take place directly from the molecular ion. Rather, it occurs only after the fission of pyrazoline ring. Thus, it may be concluded that the mass spectral fragmentation of pyrazolines is energetically more feasible than that of the chromones.

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