Electron Ionization Mass Spectrometric Studies of 3-Propyl-3-Methylisocoumarin and 3-Methyl-3,4-dihydroisocoumarin and Related Compounds

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Summary: Electron ionization mass spectra of 3-propyl-3-methylisocoumarin (**1** and **2**), 3-methyl-3, 4-dihydroisocoumarin (**5**) and related compounds (**3** and **4**) are discussed. The mass fragmentation patterns are assigned with the help of LREIMS and HREIMS peak matching of molecular ion peaks obtained by EIMS are also given.

Introduction

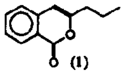
Naturally occurring 3-propylisocoumarin (1) was isolated from the roots of *Felicia wriglii* [1]. Extraction of 3-methylisocoumarin (2) and its 3,4-dihydro- derivative (3) from natural sources is not yet known. We have already reported [2] the syntheses of the compounds (1-5). In this article we report EIMS studies of compounds (**1-5**). The molecular formulae of these compounds have been further confirmed by the high resolution electron ionization mass spectral (HREIMS) peak matching of molecular ion peaks exhibited by low resolution electron ionization mass spectra (LREIMS) and are listed in Table-1

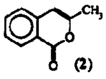
Table-1: HREIMS of Molecular Ion Peaks of the compounds (1-3)

Compounds	Mol. Formulae	M⁺(*m/z*) Calcd.	Found
1	$C_{12}H_{12}O_2$	188.0837	188.0834
2	$C_{10}H_8O_2$	160.0524	160.0529
3	$C_{10}H_{10}O_3$	177.9926	177.9925
4	$C_{11}H_{12}O_3$	192.0786	192.0789
5	$C_{10}H_{10}O_2$	161.9976	161.9978

Results and Discussion

The mass fragmentation patterns of the compounds (**1-5**) are assigned with the help of LREIMS and are depicted in scheme **1-3**.


(1)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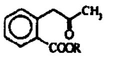
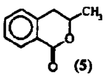


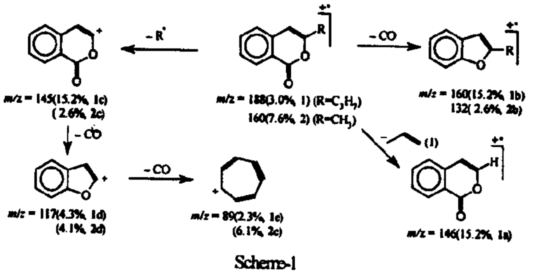
(3, R=H)
(4, R=CH₃)



(5)

3-Propyl- and 3-methylisocoumarin (1,2)

The EIMS of (1 and 2) exhibited molecular radical cations at *m/z* 188 ($C_{12}H_{12}O_2$, 1) and 160 ($C_{10}H_8O_2$, **2**). Removal of propyl radical from (1) and methyl radical from (2) yielded isocoumarin cation at *m/z* 145 ($C_9H_5O_2$, **1c-2c**) followed by the removal of a CO molecule to yield a cation at *m/z* 117 (C_8H_5O, **1d-2d**). Further removal of another CO molecule from these cations (**1d-2d**) produced a tropyllium cation at *m/z* 89 (C_7H_5, **1e-2e**). Loss of a CO molecule from molecular ions furnished radical cations at *m/z* 160 ($C_{11}H_{12}O$, **1b**) and 132 (C_9H_8O, **2b**). Loss of propene molecule from the molecular ion (1) afforded isocoumarin radical cation at *m/z* 146 ($C_9H_6O_2$, **1a**) (Seheme-1).



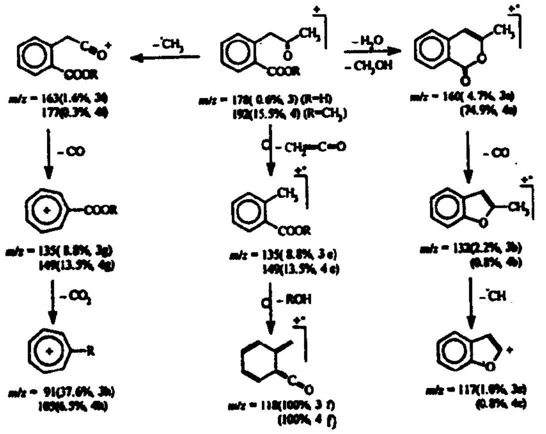
Scheme-1

2-(2'-Oxopropyl)benzoic acid (3) and methyl 2-(2'-oxopropyl)benzoate (4)

The EIMS of compounds (**3** and **4**) afforded radical cations at *m/z* 178 ($C_{10}H_{10}O_3$) and 192 ($C_{11}H_{12}O_3$) respectively. The fragmentation pattern of these cations is recorded in scheme-2.

3-Methyl-3,4-dihydroisocoumarin (5)

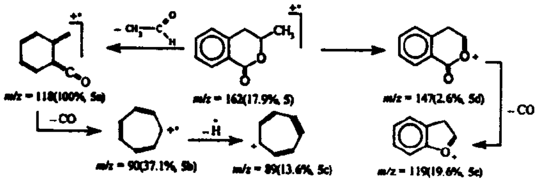
The EIMS of **5** afforded radical cation at *m/z* 162 ($C_{10}H_{10}O_2$). The fragmentation pattern of this cation is recorded in scheme-3.



Scheme-2

Experimental

Compounds (1-5) were prepared according to the literature procedure [2]. All of these compounds were characterized by IR, MS and ^{1}H-NMR spectral data. The EIMS were recorded on MAT-311 instrument with an accelerating voltage of 3 kV and ionization energy of 70 eV. The temperature of the ion source was maintained at 250 °C.



Scheme-3

References

1. F. Bohlmann and C. Zdero, *Phytochemistry,* **15** (8), 1318 (1976).
2. M. T. Hussain, N. H. Rama and A. Malik, *Indian J. Heterocyclic Chem.,* **8** (4), 273 (1999).