

Electron Ionization Mass Spectrometric Studies of Some 3-Substituted Isocoumarins and Related Compounds

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Summary: Fragmentation pattern in mass spectra of some isocoumarins (1a-c), dihydroisocoumarins (2a-c) and related compounds (3-4a-c) are described with the help of EIMS. The molecular formulae are further confirmed by HREIMS peak matching of molecular ion peaks exhibited in EIMS.

Introduction:

We have recently reported [1] the synthesis of some 3-substituted isocoumarin (1a-c), 3-substituted-3,4-dihydroisocoumarins (2a-c) and their intervening intermediates (3-4a-c). These compounds were prepared to synthesize models for hydrangenol [2] (5), hydrangenol-8- β -D-glucoside [2] (6), phyllostulcin [2] (7) and macrophyllsoid A [3,4] (8). Here in we wish to report electron ionization mass spectrometric (EIMS) studies of these compounds which will serve as a reference library for these class of compounds.

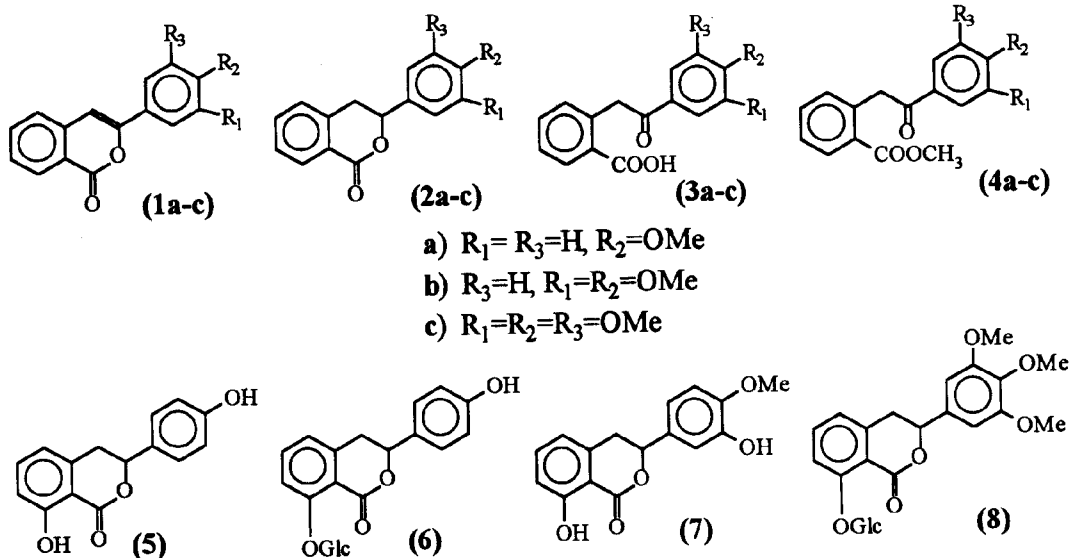
Molecular formulae of various compounds have been confirmed by high resolution electron ionization mass spectrometry (HREIMS) as illustrated in Table-1.

Results and Discussion

The general fragmentation pattern of these compounds are derived with the help of low resolution electron ionization mass spectra (LREIMS) as depicted in Schemes 1-4.

3-(4'-Methoxyphenyl)isocoumarin (1a), 3-(3',4'-Dimethoxyphenyl)isocoumarin (1b) and 3-(3',4',5'-Trimethoxyphenyl)isocoumarin (1c)

The EIMS of (1a-c) afforded molecular ions at m/z 252 ($C_{16}H_{12}O_3$, 1a), 282 ($C_{17}H_{14}O_4$, 1b) and 312 ($C_{18}H_{16}O_5$, 1c). Loss of a conjugated ketene radical from the respective molecular ions yielded the ions at m/z 135 ($C_8H_7O_2$, 1ad), 165 ($C_9H_9O_3$, 1bd) and 195 ($C_{10}H_{11}O_4$, 1cd), followed by a further loss of a CO molecule to afford ion peaks at m/z 107 (C_7H_7O , 1af), 137 ($C_8H_9O_2$, 1bf) and 167 ($C_9H_{11}O_3$,



1cf). These ion peaks also originated directly by the loss of isocoumarin radical from the corresponding M⁺ peaks (link scans measurements). Loss of

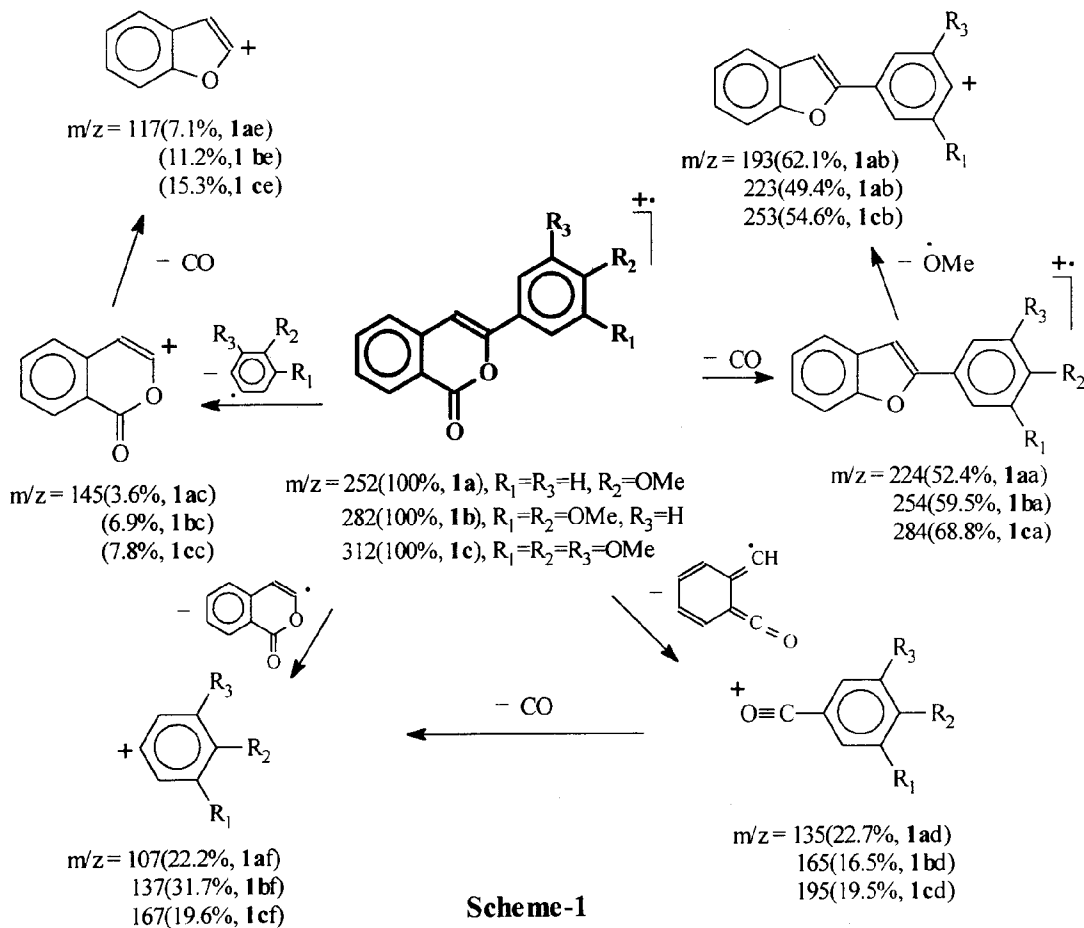
Table 1: HREIMS of Molecular Ion Peaks of Compounds (1-4a-c)

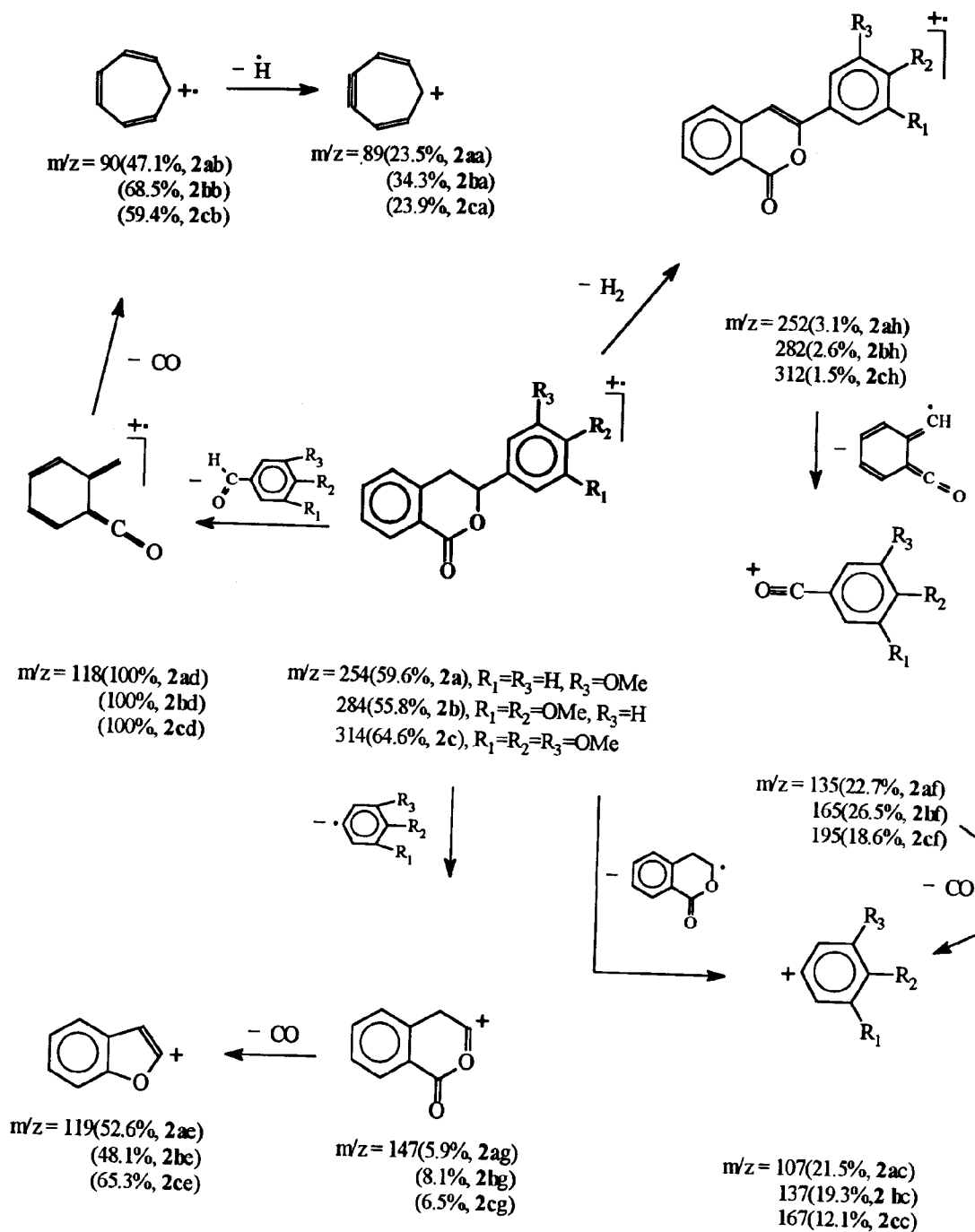
Compound	Mol. Formulae	M ⁺ (m/z)	
		Calculated	Found
1a	C ₁₆ H ₁₂ O ₃	252.0786	252.0795
1b	C ₁₇ H ₁₄ O ₄	282.0892	282.0902
1c	C ₁₈ H ₁₆ O ₅	312.0998	312.0990
2a	C ₁₆ H ₁₄ O ₃	254.0943	254.0955
2b	C ₁₇ H ₁₆ O ₄	284.1049	284.1031
2c	C ₁₈ H ₁₈ O ₅	314.1154	314.1165
3a	C ₁₆ H ₁₄ O ₄	270.0892	270.0885
3b	C ₁₇ H ₁₆ O ₅	300.0998	300.0502
3c	C ₁₈ H ₁₈ O ₆	330.1103	330.1095
4a	C ₁₇ H ₁₄ O ₄	284.1049	284.1071
4b	C ₁₈ H ₁₆ O ₅	314.1154	314.1165
4c	C ₁₉ H ₂₀ O ₆	344.1260	344.1275

substituted phenyl radicals from the molecular ions provided isocoumarin ion peaks at m/z 145 (C₉H₅O₂, 1ac-bc), followed by the loss of CO molecule to afford the peaks at m/z 117 (C₈H₅O, 1ae-ce). Removal of CO molecule from the molecular ion provided radical cations at m/z 224 (C₁₅H₁₂O₂, 1aa), 254 (C₁₆H₁₄O₃, 1ba) and 284 (C₁₇H₁₆O₄, 1ca) followed by the loss of methoxy radical to afford ion peaks at 193 (C₁₄H₉O, 1ab), 223 (C₁₆H₁₂O₃, 1bb) and 253 (C₁₆H₁₃O₃, 1cb) as shown in Scheme-1.

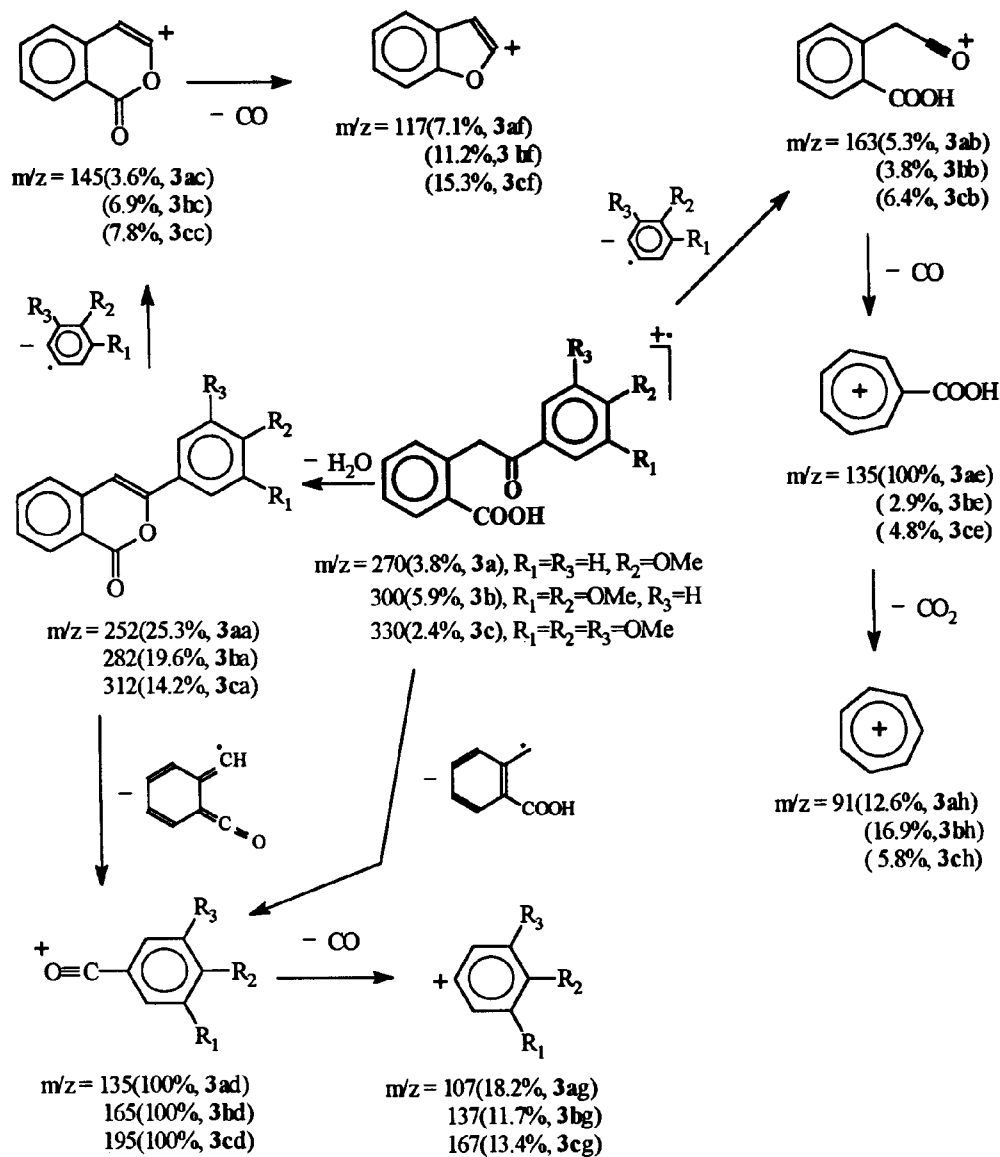
3-(4'-Methoxyphenyl)-3,4-dihydroisocoumarin (2a), 3-(3',4'-Dimethoxyphenyl)-3,4-dihydroisocoumarin (2b) and 3-(3',4',5'-Trimethoxyphenyl)-3,4-dihydroisocoumarin (2c)

EIMS of (2a-c) afforded the molecular ions at m/z 254 (C₁₆H₁₄O₃, 2a), 284 (C₁₇H₁₆O₄, 2b) and 314 (C₁₈H₁₈O₅, 2c). Further fragmentation pattern is shown in Scheme-2.





Scheme-2



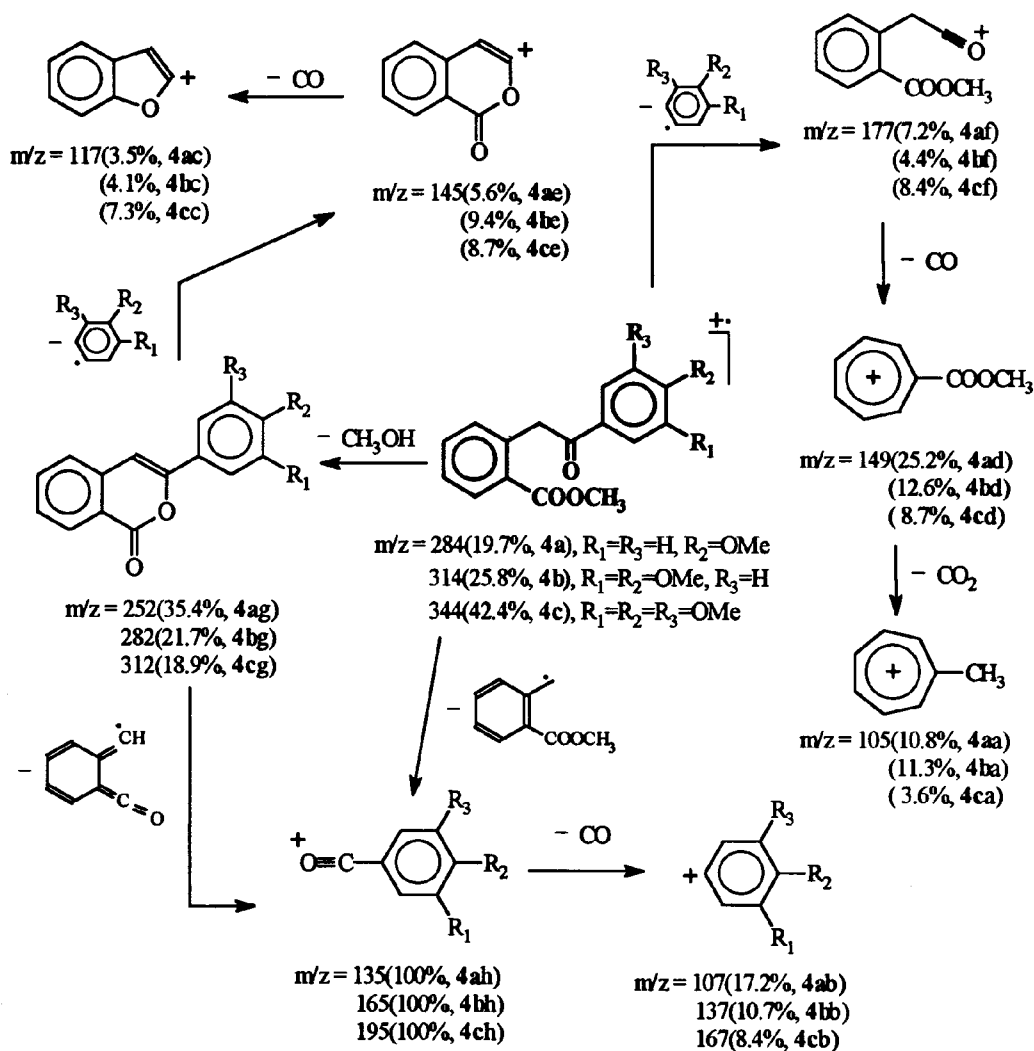
Scheme-3

3-(4'-Methoxybenzoylmethyl)benzoic acid (3a), 3-(3',4'-Dimethoxybenzoylmethyl)benzoic acid (3b) and 3-(3',4',5'-Trimethoxybenzoylmethyl)benzoic acid (3c)

Methyl 3-(4'-Methoxybenzoylmethyl)benzoate (4a), Methyl 3-(3',4'-dimethoxybenzoylmethyl)benzoate (4b) and Methyl 3-(3',4',5'-trimethoxybenzoylmethyl)benzoate (4c)

Molecular ions at m/z 270 ($C_{16}H_{14}O_4$, 3a), 300 ($C_{17}H_{16}O_5$, 3b) and 330 ($C_{18}H_{18}O_6$, 3c) were obtained in the EIMS of (3a-c). Further fragmentation pattern is shown in Scheme-3.

Molecular ions at m/z 270 ($C_{16}H_{14}O_4$, 4a), 300 ($C_{17}H_{16}O_5$, 4b) and 330 ($C_{18}H_{18}O_6$, 4c) were obtained in the EIMS of (4a-c). Further fragmentation pattern is shown in Scheme-4.



Scheme-4

Experimental

Compounds (1-4a-c) were prepared according to the literature [5] procedure. All of these were characterized by IR, mass, ^{13}C - and ^1H -NMR spectral data and elemental analysis. 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.

References

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