

Mass Spectrometric Studies of The Principal Dihydroisocoumarins of *Ononis natrix* and Some Related Compounds

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Summary: Mass spectra of the principal dihydroisocoumarins of *Ononis natrix* (3d-e) and some related compounds (1a/1b, 2a-c & 3a-c) are discussed. The mass fragmentation patterns are assigned with the help of EIMS. The molecular formulae of the compounds are also confirmed by elemental analysis.

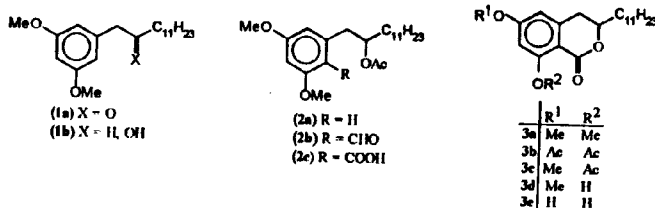
Introduction

Diuretic, antirheumatic and antibacterial properties [1] have been ascribed to extracts of the plant *Ononis natrix*. A.S. Feliciano *et. al.* [2,3] have isolated dihydroisocoumarins (3d-3e) and confirmed their structures by spectroscopy. We have already reported [4] the synthesis of these dihydroisocoumarins. As a continuation of our previous EIMS studies [5,6] on isocoumarins and 3,4-dihydroisocoumarins, we report EIMS studies of undecyl-6,8-bisubstituted-3,4-dihydroisocoumarins (3a-e) along with some related compounds, 1-(3,5-dimethoxyphenyl)tridecan-2-one/ol (1a/b) and 1-(2'-carboxy-, 1-(2'-formyl- and 1-(3,5-dimethoxybenzyl)dodecan-2-yl acetate (2c, 2b, & 2a).

The molecular formulae of the compounds (1a/b, 2a-c & 3a-e) are confirmed by elemental analysis as listed in Table 1.

Table 1: Elemental analyses of the compounds (1a/b, 2a-c & 3a-e).

Compd	Mol. Formulae	Mol. Wt	Calc.(%)		Found (%)	
			C	H	C	H
1a	C ₂₁ H ₃₄ O ₃	334.5	75.44	10.25	75.40	10.20
1b	C ₂₁ H ₃₆ O ₃	336.5	74.95	10.78	74.72	10.59
2a	C ₂₃ H ₃₈ O ₄	378.6	72.98	10.12	72.91	10.12
2b	C ₂₄ H ₃₈ O ₅	406.6	70.90	9.42	70.87	9.39
2c	C ₂₄ H ₃₈ O ₆	422.6	68.22	9.06	68.46	9.16
3a	C ₂₃ H ₃₄ O ₄	362.5	72.89	9.45	72.63	9.43
3b	C ₃₄ H ₃₄ O ₆	418.5	68.82	8.12	68.71	8.10
3c	C ₂₃ H ₃₄ O ₅	390.5	70.68	8.71	70.55	8.68
3d	C ₂₁ H ₃₂ O ₄	348.5	72.38	9.26	72.39	9.35
3e	C ₂₈ H ₃₀ O ₄	334.5	71.82	9.04	71.62	8.91



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Results and Discussions

The general fragmentation patterns of these compounds are assigned with the help of LREIMS as depicted in Schemes 1-3.

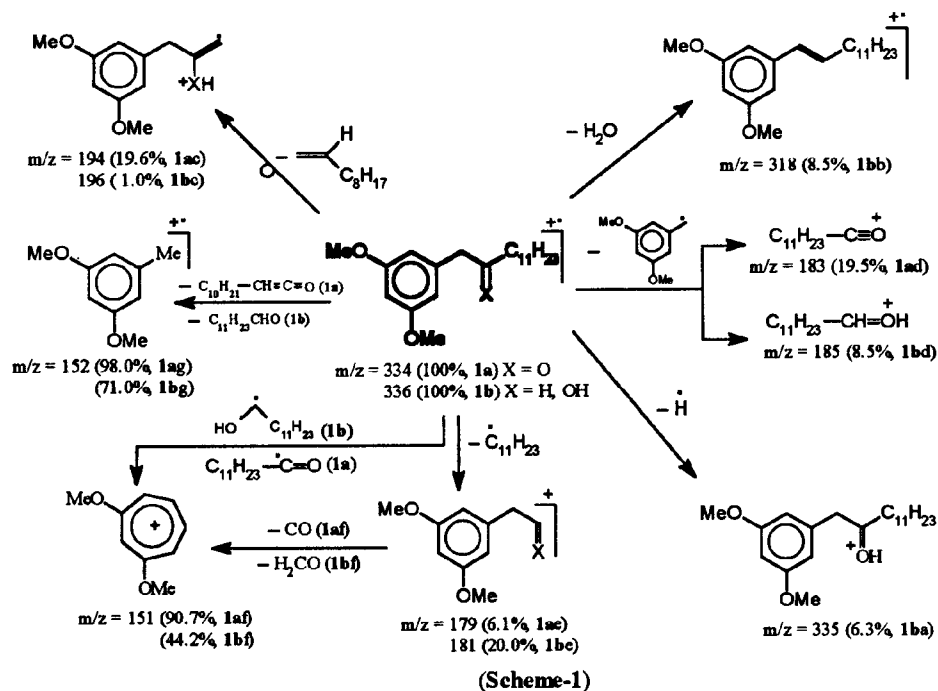
1-(3,5-Dimethoxyphenyl)tridecan-2-one/ol (1a/1b)

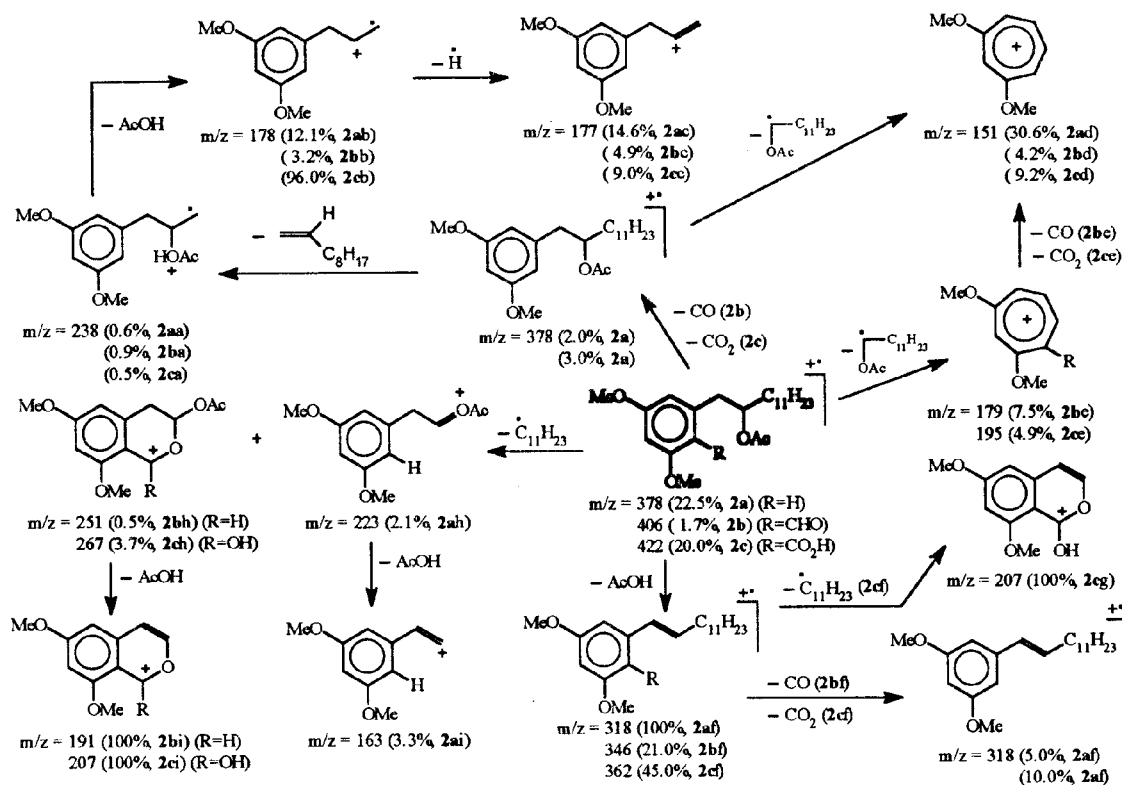
The EIMS of (1a/1b) afforded a radical cation at m/z 334 ($C_{21}H_{34}O_3$, 1a) and 336 ($C_{21}H_{36}O_3$, 1b) respectively. The loss of H radical and H_2O from (1b) yielded a cation and radical cation at m/z 335 ($C_{21}H_{35}O_3$, 1ba) and 318 ($C_{21}H_{34}O_2$, 1bb) respectively. The γ -hydrogen (McLafferty) rearrangement of (1a/1b) afforded radical cations at m/z 194 ($C_{11}H_{14}O_3$, 1ac) and 196 ($C_{11}H_{16}O_3$, 1bc) respectively. This rearrangement is obviously much more likely with (1a) than (1b) and probably explains the much greater abundance of (1ac). The loss of 3,5-dimethoxybenzyl radical from (1a) and (1b) yielded cations at m/z 183 ($C_{12}H_{23}O$, 1ad) and 185 ($C_{12}H_{25}O$, 1bd) respectively. The loss of undecyl radical from (1a/b) afforded cations at m/z 179 ($C_{10}H_{11}O_3$, 1ae) and 181 ($C_{10}H_{13}O_3$, 1be) followed by the loss of CO and H_2CO to yield cations at m/z 151 ($C_9H_{11}O_2$, 1af & 1bf). The loss of $C_{11}H_{23}C=O$ from

(1a) and dodecanoyl radical from (1b) afforded (1af & 1bf) respectively. The loss of $C_{10}H_{21}CH=C=O$ from (1a) and dodecanal from (1b) afforded radical cations at 152 ($C_9H_{12}O_2$, 1ag & 1bg) respectively (Scheme-1).

1-(2-Carboxy-, 1-(2-formyl- and 1-(3,5-dimethoxybenzyl)tridecan-2-yl acetate (2c, 2b & 2a).

The EIMS of (2a-c) afforded radical cations at m/z 378 ($C_{23}H_{38}O_4$, 2a), 406 ($C_{24}H_{38}O_5$, 2b) and 422 ($C_{24}H_{38}O_6$, 2c) respectively. The loss of CO from (2b) and CO_2 from (2c) afforded the radical cation (2a) at m/z 378 ($C_{23}H_{38}O_4$) followed by the γ -hydrogen rearrangement to yield radical cations at m/z 238 ($C_{13}H_{18}O_4$, 2aa-ca). The loss of AcOH from radical cations (2aa-ca) afforded radical cations at m/z 178 ($C_{11}H_{14}O_2$, 2ab-cb) followed by the loss of H radical to yield cations at m/z 177 ($C_{11}H_{13}O_2$, 2ac-cc). The loss of dodecyl ethanoate radical from (2a) afforded cations at m/z 151 ($C_9H_{11}O_2$, 2ad-cd). The loss of dodecyl ethanoate radical from (2b-c) yielded cations at m/z 179 ($C_{10}H_{11}O_3$, 2be) and 195 ($C_{10}H_{11}O_4$, 2ce) followed by the loss of CO molecule





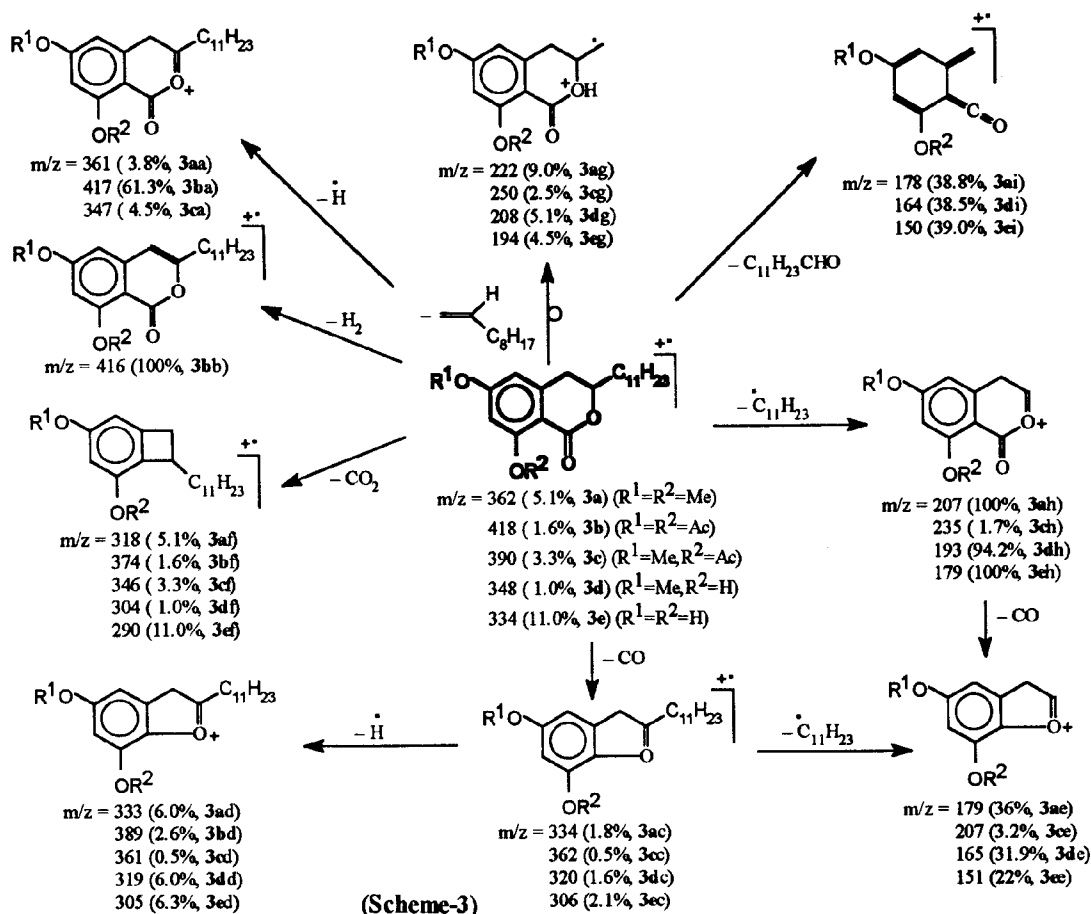
(Scheme-2)

from (**2be**) and CO₂ from (**2ce**) to afford cations at m/z 151 (C₉H₁₁O₂, **2bd-cd**). The loss of AcOH from (**2a-c**) afforded radical cations at 318 (C₂₁H₃₄O₂, **2af**), 346 (C₂₂H₃₄O₃, **2bf**) and 362 (C₂₂H₃₄O₄, **2cf**). The loss of CO and CO₂ from (**2bf**) and (**2cf**) yielded radical cations at m/z 318 (C₂₁H₃₄O₂, **2af**). The loss of undecyl radical from (**2cf**) afforded a cation at m/z 207 (C₉H₁₁O₄, **2cg**). The loss of undecyl radical from (**2a-c**) yielded cations at m/z 223 (C₁₂H₁₅O₄, **2ah**), 251 (C₁₃H₁₅O₅, **2bh**) and 267 (C₁₃H₁₅O₆, **2ch**) followed by the loss of AcOH molecule to give cations at m/z 163 (C₁₀H₁₁O₂, **2ai**), 191 (C₁₁H₁₁O₃, **2bi**) and 207 (C₁₁H₁₁O₄, **2ci**). (Scheme-2).

3-Undecyl-6,8-bisubstituted-3,4-dihydroisocoumarins (**3a-e**)

The EIMS of (**3a-e**) afforded radical cations at m/z 362 (C₂₂H₃₄O₄, **3a**), 418 (C₂₄H₃₄O₆, **3b**), 390

(C₂₃H₃₄O₅, **3c**), 348 (C₂₁H₃₂O₄, **3d**) and 334 (C₂₀H₃₀O₄, **3e**) respectively. The loss of H radical from (**3a-b** and **3d**) yielded cations at m/z 361 (C₂₂H₃₃O₄, **3aa**), 417 (C₂₄H₃₃O₆, **3ba**) and 347 (C₂₁H₃₁O₄, **3da**) and the loss of H₂ molecule from (**3b**) afforded a radical cation at m/z 416 (C₂₄H₃₂O₆, **3bb**). The loss of CO from (**3a**, **3c-e**) yielded radical cations at m/z 334 (C₂₁H₃₄O₃, **3ac**), 362 (C₂₂H₃₄O₄, **3cc**), 320 (C₂₀H₃₂O₃, **3dc**) and 306 (C₁₉H₃₀O₃, **3ec**) followed by the loss of H radical to afford cations at m/z 333 (C₂₁H₃₃O₃, **3ad**), 389 (C₂₃H₃₃O₅, **3bd**), 361 (C₂₂H₃₃O₄, **3cd**), 319 (C₂₀H₃₁O₃, **3dd**) and 305 (C₁₉H₂₉O₃, **3ed**). The loss of undecyl radical from (**3ac-ec**) yielded cations at m/z 179 (C₁₀H₁₁O₃, **3ac**), 207 (C₁₁H₁₁O₄, **3ce**), 165 (C₉H₉O₃, **3de**) and 151 (C₈H₇O₃, **3ee**). The loss of CO₂ from (**3a-e**) afforded radical cations at m/z 318 (C₂₁H₃₄O₂, **3af**), 374 (C₂₃H₃₄O₄, **3bf**), 346 (C₂₂H₃₄O₃, **3cf**), 304 (C₂₀H₃₂O₂, **3df**) and 290 (C₁₉H₃₀O₂, **3ef**). The γ -hydrogen rearrangement of (**3a-e**) yielded radical cations at



m/z 222 ($C_{12}H_{14}O_4$, **3ag**), 250 ($C_{13}H_{14}O_5$, **3cg**), 208 ($C_{11}H_{12}O_4$, **3dg**) and 194 ($C_{10}H_{10}O_4$, **3eg**). The loss of undecyl radical from (**3a**, **3c-e**) afforded cations at m/z 207 ($C_{11}H_{11}O_4$, **3ah**), 235 ($C_{12}H_{11}O_5$, **3ch**), 193 ($C_{10}H_9O_4$, **3dh**) and 179 ($C_9H_7O_4$, **3eh**) followed by the loss of CO from (**3ah**, **3ch-e**) to yield cations (**3ae**, **3ce-ee**). The loss of dodecanal from (**3a**, **3d-e**) afforded radical cations at m/z 178 ($C_{10}H_{10}O_3$, **3ai**), 164 ($C_9H_8O_3$, **3di**) and 150 ($C_8H_6O_3$, **3ei**). The loss of $CH_2=C=O$ molecule from (**3c**) yielded a radical cation at m/z 348 ($C_{21}H_{32}O_4$, **3d**) (Scheme-3).

Experimental

Compounds (**1a/b**, **2a-c** & **3a-e**) were prepared according to the literature procedure [4]. All of them were characterized by IR and 1H NMR spectral data. Molecular formulae of all the compounds were confirmed by 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

1. P. Font quer, *Plantas Medicinales*, S. A. Labor, Barcelona. 1973, p.363.
2. A. S. Feliciano, A. F. Barrero, M. Medarde, J. M. Miguel del Corral, M. V. Calle, *Phytochemistry* **22**, 2031 (1983).
3. A. S. Feliciano, J. M. Miguel del Corral, L. M. Canedo, M. Medarde, *Phytochemistry* **29**, 945 (1990).
4. N. H. Rama, A. Saeed and C. W. Bird, *Liebigs Ann. Chem.*, 1331 (1993).
5. N. H. Rama, R. Iqbal and KH. Zamani, *J. Chem. Soc. Pak.* in press, (1997).
6. N. H. Rama, R. Iqbal, KH. Zamani, A. R. Raza and M. A. Malana, *J. Chem. Soc. Pak.* **19**(4), 324, (1997).