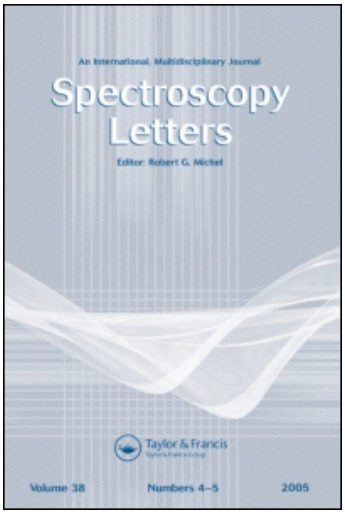

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Mass Spectrometric Investigation of Some Pyronylpyrazole Derivatives

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MASS SPECTROMETRIC INVESTIGATION OF SOME PYRONYLPYRAZOLE DERIVATIVES

Key Words: Mass Spectra, pyronylpyrazoles, 2-pyrones, 3,5-disubstituted N-phenylpyrazoles

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ABSTRACT

The electron impact ionization mass spectra of some pyronylpyrazoles were investigated. The 6-substituted 4-hydroxy-2-pyrone ring in all compounds fragments according to the common mechanisms. The fragmentations of the 3,5-disubstituted N-phenylpyrazole moiety are strongly dependent on the nature and positions of the substituents.

INTRODUCTION

The condensation of unsymmetrical β-difunctional compounds with alkyl- or arylhydrazine usually yields two isomeric pyrazole derivatives, structure assignment of which often demands serious analysis.[1] The ^{1}H and ^{13}C NMR spectroscopy has been preferably employed for the distinction between such isomers.[2-7]

The problems of identification of isomers are more pronounced in the case of condensation products of β-polyfunctional compound with alkyl- or arylhydrazines, since more than two isomers may be obtained.

In our work we were dealing with such β-polyfunctional compound, ethyl 2-hydroxy-4-(4-hydroxy-6-methyl-2-pyron-3-yl)-4-oxo-2-butenoate and 3,5-disubstituted N-phenylpyrazoles produced by its condensation with phenylhydrazine.[8,9] The structure determination of resulting two pairs of pyrazole isomers (**1,4** and **2,5**) was achieved by ^{1}H and ^{13}C NMR spectroscopic and mass spectrometric data. Mass spectrometry has proven to be a specialy valuable method in this case.

In this paper the electron impact mass spectra of recently described compounds (**1-6**)[9] are compared and discussed with the aid of high resolution mass measurements and metastable peak analysis.

EXPERIMENTAL

Mass spectra were recorded on a Varian MAT CH-7 mass spectrometer at 70 eV ionization energy, 3 kV accelerating voltage and 100 μA ionization current. High-resolution measurements data were obtained with EXTREL-FTMF-2001-DD mass spectrometer at 70 eV. All samples were introduced into the ion source through the direct insertion probe.

RESULTS AND DISCUSSION

The mass spectra of compounds **1-6** (Fig. 1 and 2) show an intense peak at m/z 340 (100-50%) corresponding to the molecular ion for **1** and **4**, to $(M-H2O)^+$ ion for **2** and **5**, and to $(M-CH_2CO)^+$ ion for **3** and **6**. All the fragmentation patterns originate from this ion.

Although the open ring structure of compounds **2** and **5** was determined by IR and ^1H NMR spectroscopy data, M^+ ions were not observed in their mass spectra and the fragmentation patterns are almost identical with those for corresponding cyclized products **3** and **6**. Loss of water from molecular ions of **2** and **5** was not substantiated by metastable ion, and it seems probablly that this is thermal rather than electron impact-induced process. Thus, both **2** and **5** begin to fragment as pyronylpyrazole derivatives.

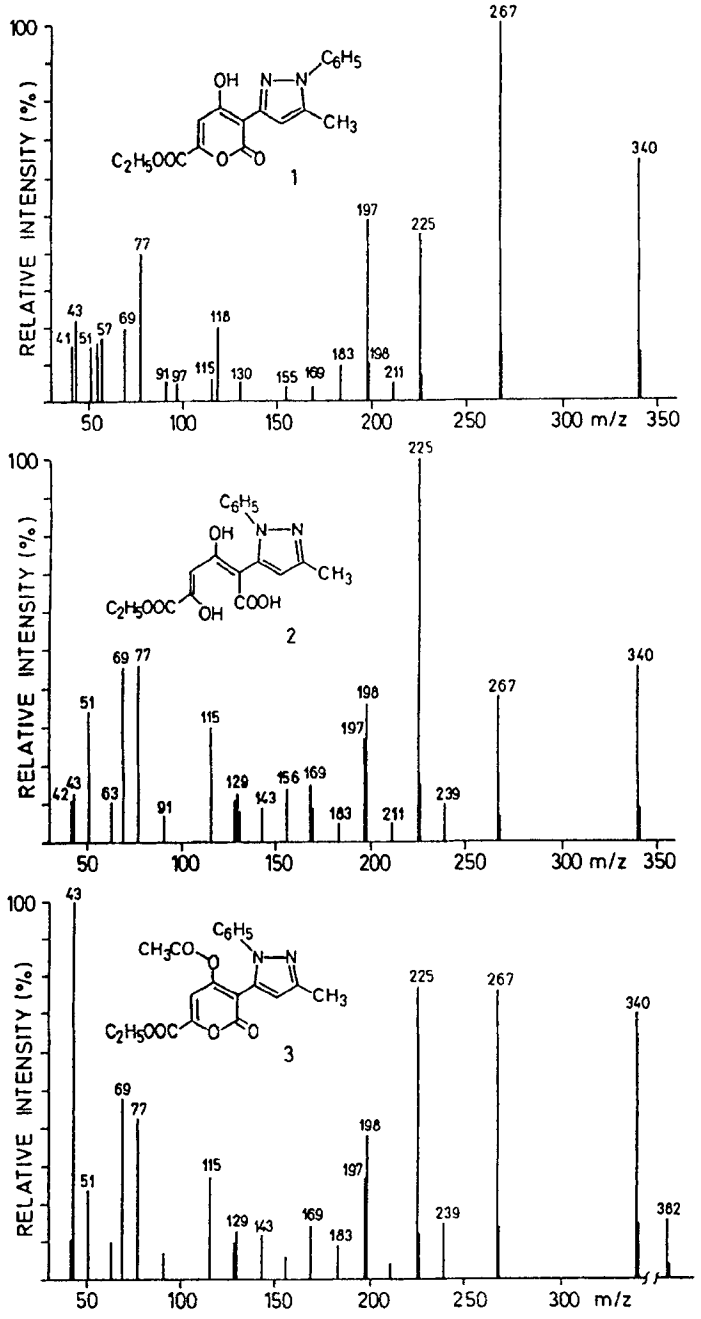

Fig. 1. The 70 eV mass spectra of compounds 1 – 3

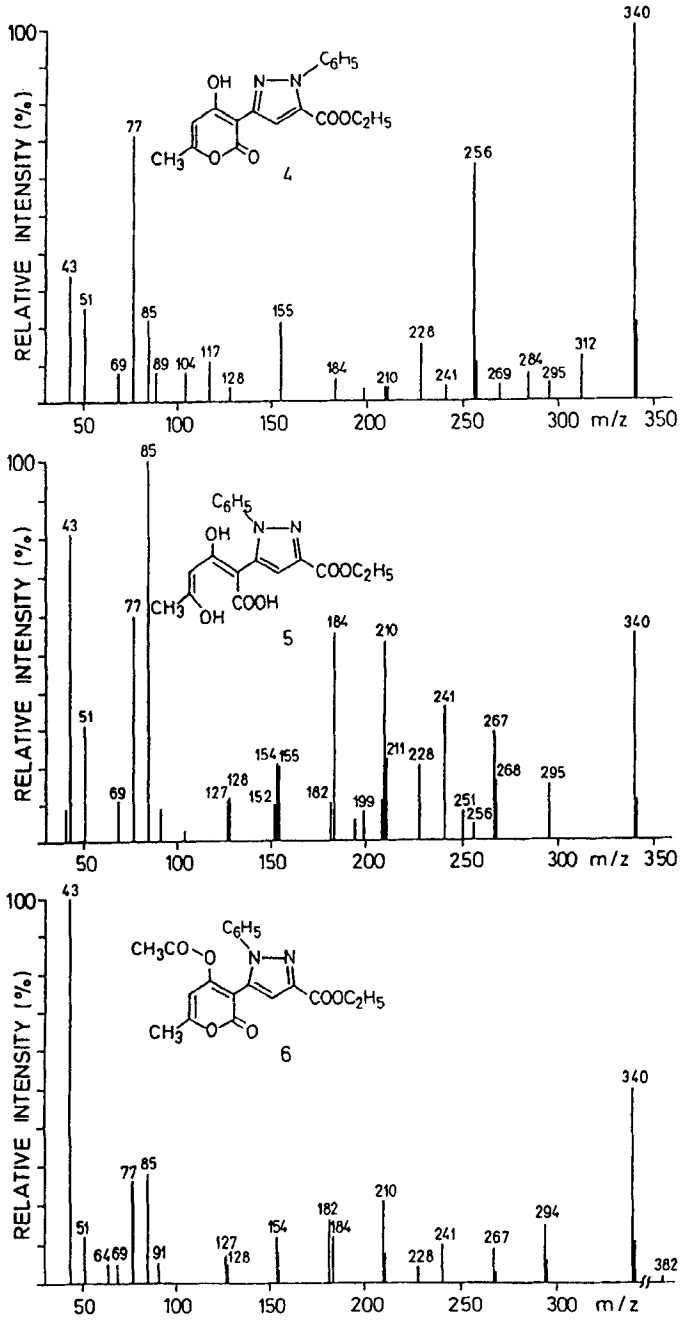

Fig. 2. The 70 eV mass spectra of compounds 4 - 6

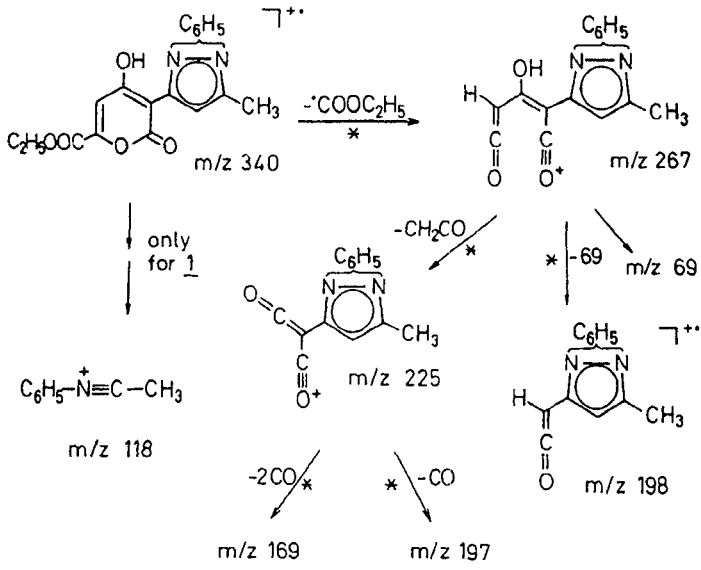

Fig. 3. Characteristic fragmentation modes of 1 - 3

The most characteristic fragmentation modes are proposed and summarized in Fig. 3 and 4. In general, α-cleavage reaction of 2-pyrone ring with loss of C-6 substituent (ethoxycarbonyl) yielding ion at m/z 267, is the initial fragmentation process for compounds 1-3 (Fig. 3). The ion m/z 267 fragments further by loss of ketene to give m/z 225 (base peak in spectrum of 2). Expulsions of carbon monoxide molecules from this ion afford m/z 197 and m/z 169. The alternative pathway originating from m/z 267 ion is the charge distribution on the two fragments at m/z 198 and m/z 69. The formation of the m/z 198 ion may be rationalized also

by a retro-Diels-Alder reaction (RDA) from m/z 340, but this process is not supported by the appropriate metastable ion.

A notable feature in the spectrum of compound **1** is an abundant peak at m/z 118, which may be assumed to have the $C_6H_5 - N^+ \equiv C-CH_3$ structure. The inspection of the mass spectra of some N-phenylpyrazoles bearing a methyl group at C-5 reveals that m/z 118 has a significant abundance and reduces to a much smaller share in the case of 3-methyl-1-phenyl substituted pyrazoles.[10] Thus the m/z 118 ion provides a supporting evidence for the presence of 5-methyl-1-phenylpyrazole moiety in the molecule of compound **1**.

The characteristic fragmentation pathway of series **4–6** is the retro-Diels-Alder reaction giving ion at m/z 256 (Fig. 4). Retention of charge on the opposite fragment, formed by RDA mechanism with hydrogen transfer, results in an intense m/z 85 ion (base peak in spectrum of **5**). Formation of m/z 85 ion provided an excellent support for the proposed structures of this series, since this is the common ion seen in the mass spectra of 4-hydroxy-6-methyl-2-pyrones.[11]

A reason for a very lowly abundant RDA ion m/z 256 in the spectrum of **5** (contrast to **4**) may be a concomitant expulsion of $COOC_2H_4$ resulting in the formation of an abundant pyrazolyl-ketene radical ion

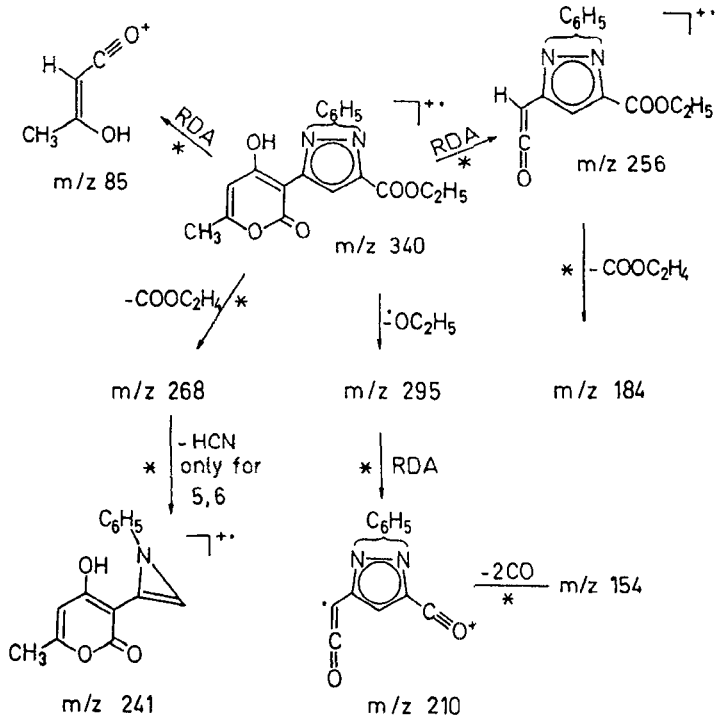

Fig. 4. Characteristic fragmentation modes of **4** - **6**

at m/z 184 (55%). The corresponding daughter ion amounts to 6% only in the spectrum of compound **4**.

It is obvious that expulsion of ethoxycarbonyl group is not a favored process for compound **4**. This is also in line with the fact that no peak (m/z 268, m/z 267) occurs in the spectrum of **4** due to the loss of $COOC_2H_4$ or $COOC_2H_5$ from the molecular ion. Besides that, some other fragmentation patterns also clearly illustrate the different substituent position in the case of **4** and **5**.

The characterizing difference between fragmentation pathways of compounds **4** and **5** is the formation of ion at m/z 241. Accurate mass measurement proved that these ions are isobaric. While in the case of **5** abundant ion at m/z 241 ($C_{14}H_{11}NO_3$) is formed by sequential loss of $COOC_2H_4$ and then HCN from m/z 340 ion, low intensity isobaric ion (m/z 241; $C_{13}H_9N_2O_3$) in spectrum of **4** may be formed by two possible routes: 340→312→269→241 and 340→312→284→241.

That mass spectral fragmentation of pyrazole derivatives are strongly dependent on the nature and positions of the substituents has been already demonstrated.[12-15]

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REFERENCES

1. Elguero J. in *Comprehensive Heterocyclic Chemistry*, eds. A.R. Katritzky and C.W. Rees, Pergamon Press, Oxford 1984; **5**: 273.

2. Moore J.A. and Habraken C.L., J. Am. Chem. Soc. 1964; **86**: 1456.

3. Elguero J., Jacquier R. and Tien Duc H.C.N., Bull. Soc. Chim. Fr. 1966; **5**: 3727.

4. Claramunt R., Elguero J. and Jacquier R., Org. Magn. Reson. 1971; **3**: 595.

5. Timmermans P.B.M.W.M., Uyttewaal A.P. and Habraken C.L., J. Heterocycl. Chem. 1972; **9**: 1373.

6. Axenrod T., Watnick C.M. and Wieder M.J., Org. Magn. Reson. 1979; **12**: 476.

7. Sohar P., Feher O. and Tihanyi E., Org. Mag. Reson. 1979; **12**: 205.

8. Brbot-šaranović A., Katušin-Ražem B. and Sušnik I., Heterocycles 1989; **29**: 1559.

9. Brbot-šaranović A., Katušin-Ražem B. and Vicković I., Heterocycles, in press.

10. Brbot-šaranović A. and Katušin-Ražem B., Unpublished results.

11. Porter Q.N. and Baldas J., *Mass Spectrometry of Heterocyclic Compounds*, Wiley-Interscience, New York 1971: 139.

12. Hmelnickii R.A., Krasnoshek A.P., Polakova A.A. and Grandberg I.I., Zh. Org. Khim. 1967; **3**: 1540.

13. Krasnoshek A.P., Hmelnickii R.A., Polakova A.A. and Grandberg I.I., Zh. Org. Khim. 1968; **4**: 689.

14. Luijten W.C.M.M. and van Thuijl J., Org. Mass Spectrom. 1979; **14**: 577.

15. Singh S.P. and Vaid R.K., Org. Mass Spectrom. 1986; **21**: 77.

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