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In memoriam prof. dr. Ioan A. Silberg

MASS SPECTRA OF THE NEW HYDRAZIDO- HYDRAZONES OBTAINED BY THE CONDENSATION OF THE IZONICOTINIC ACID HYDRAZIDE (HIN) WITH CITRAL, (+)–CARVONE AND β-IONONE

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ABSTRACT. Mass spectra of some new hydrazido-hydrazones of the izonicotinic acid hydrazide (HIN) with citral, (+)-carvone and β-Ionone were recorded and discussed by comparison with the mass spectra of the starting compounds.

INTRODUCTION

In a previous contributions to the chemistry of the terpenoids we described the synthesis of new hydrazido-hydrazones and hydrazones based on the condensation of some hydrazides and pyrimidyl hydrazines with terpenoid carbonyl compounds (aldehydes and ketones) from the terpenoid class and related compounds [1]. Our new hydrazido-hydrazones and hydrazones were assigned based on IR and UV-VIS spectra [1] and TLC [2]. In addition, we already reported the effect of gamma irradiation using electron spin resonance (ESR) and UV radiation of some terpenoid hydrazones and hydrazido-hydrazones [3,4]. In the field of terpenoids, new 1,3-dioxanic derivatives thereof we previously described [5]. The biological activity of the new compounds was tested [6].

The aim of the present work is the investigation of the mass spectra of new hydrazido-hydrazones **1, 2** and **3 (Scheme 1)** available by the condensation of the izonicotinic acid hydrazide with citral, (+)-carvone and β-ionone, respectively.

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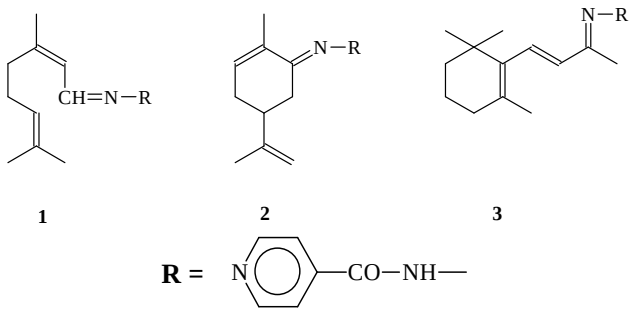


Scheme 1

RESULTS AND DISCUSSIONS

Mass spectra of the hydrazido-hydrazones **1**, **2** and **3** are presented in the Figures **1**, **2** and **3**.

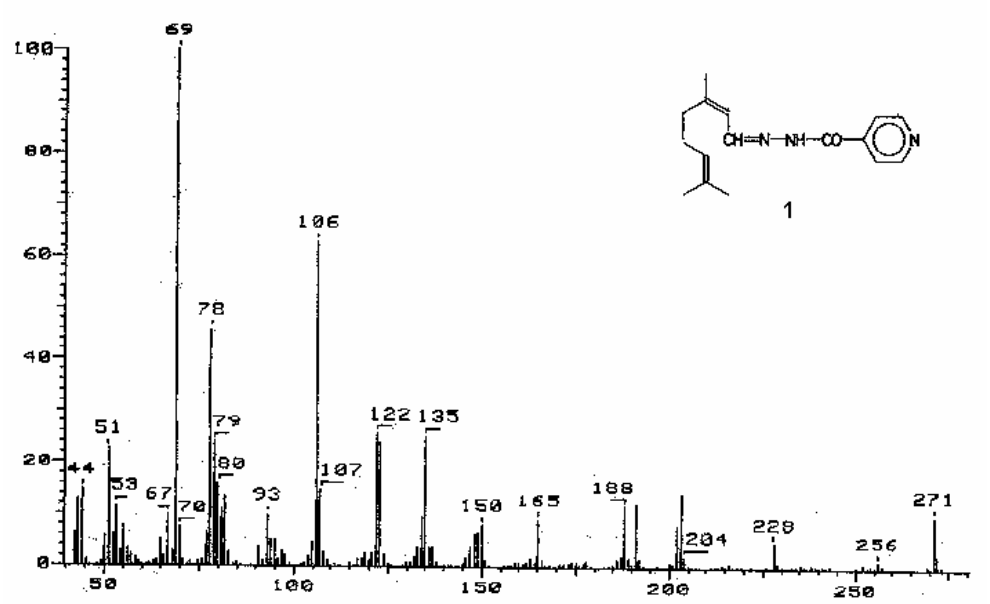


Figure 1. Mass spectrum of the hydrazido-hydrazone **1**

Table **1** lists the m/z values of the first eight main fragments, their abundances, base peaks and molecular ions of the starting materials: HIN, citral, (+) carvone and β-ionone available from the literature [7].

Table **2** lists the m/z values of the first eight main fragments, their abundances, base peaks and molecular ions of the hydrazido-hydrazones **1**, **2** and **3.**

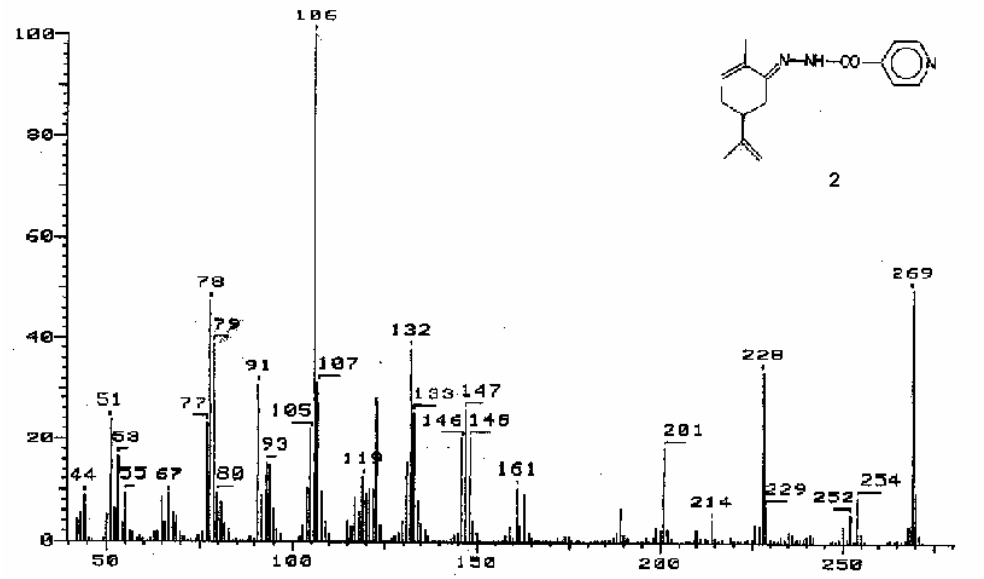


Figure 2. Mass spectrum of the hydrazido-hydrazone **2**

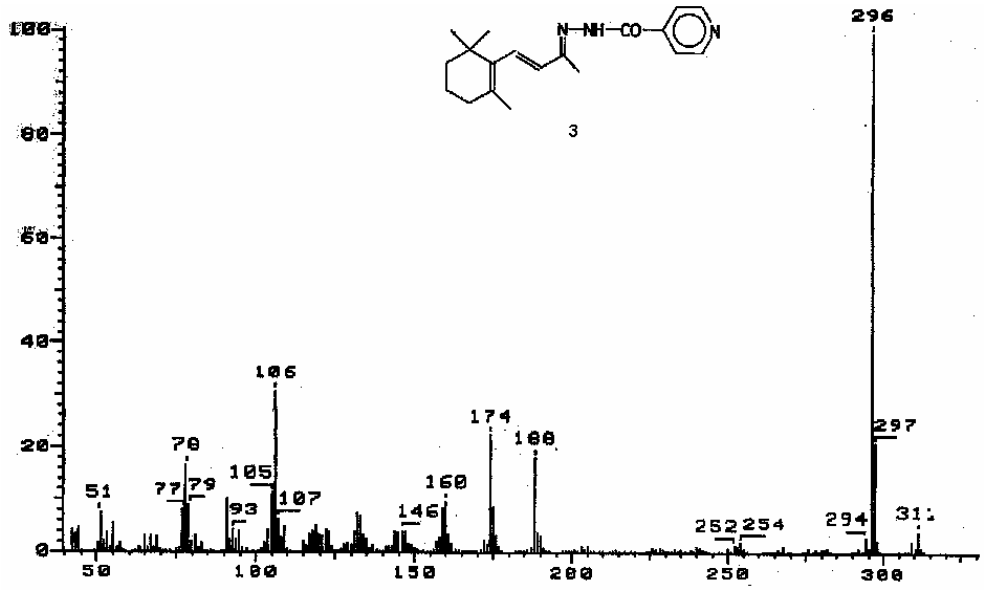


Figure 3. Mass spectrum of the hydrazido-hydrazone 3

Table 1.
The m/z values of the first eight main fragments, their abundances (%), base peaks and molecular ions of HIN, citral, (+) carvone and β-ionone [7].

Com-pouds	Mol. ions	Base peaks	m/z fragments (%)						
HIN	137 (54)	78 (100)	106 (99)	137 (54)	51 (53)	50 (16)	79 (15)	31 (13)	107 (11)
Citral	152 (8,3)	69 (100)	41 (69)	84 (30)	39 (19)	94 (16)	27 (13)	53 (10)	83 (10)
Carvo-ne	150 (7,2)	82 (100)	54 (65)	39 (50)	41 (35)	108 (35)	93 (30)	27 (28)	53 (22)
β-Iono-ne	192 (6,8)	177 (100)	43 (74)	41 (22)	123 (18)	91 (16)	39 (15)	135 (14)	178 (14)

Table 2.
The values, m/z of the first eight main fragments, their abundances (%), base peaks and molecular ions of the hydrazido-hydrazones **1**, **2** and **3**.

Comp ounds	Mol. ions	Base peaks	m/z fragments (%)						
1	271 (10)	69 (100)	106 (63)	78 (45,7)	122 (25,7)	135 (25,4)	79 (24,6)	123 (24,3)	51 (23)
2	269 (49,3)	106 (100)	269 (49,3)	78 (47)	79 39,3)	132 (38,6)	228 (33,6)	107 (31,8)	91 (30,7)
3	311 (4,3)	296 (100)	106 (31)	174 (22,7)	297 (21,2)	188 (18)	78 (16,5)	105 (11,5)	91 (10)

Considering the mass spectra of the hydrazido-hydrazones **1, 2** and **3** the followings can be observe and discuss.

*Hydrazido-hydrazone **1***

The molecular ion, m/z 271 (10 %) presents a relative low stability close to that of the molecular ion of the citral, m/z 152 (8.3%) and lower than that of the molecular ion of the HIN, m/z 137 (54%).

The base peak, m/z 69 is the same as in citral, while for the HIN is the fragment, m/z 78. The base peak, m/z 69 results from the molecular ion by an allylic cleavage able to afford two fragments stabilized by an allylic type resonance. Such fragmentation is supported by the presence in the mass spectrum of the corresponding ion, m/z 202 (Figure **1**) This type of fragmentation is confirmed by the metastable transition, m/z 271 → m/z 202 (Scheme **2**). The high resolution measurements confirm the presence of the $C_{11}H_{12}N_3O^+$ fragments, m/z 202 (Table **3**).

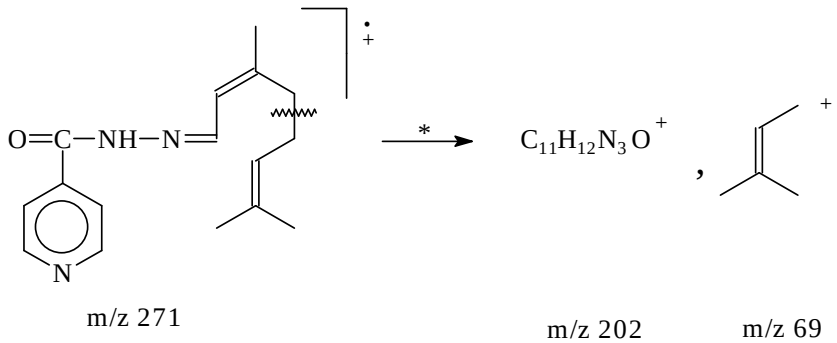
In fact, the same fragmentation takes place in the mass spectrum of the citral, supported by the presence in the mass spectrum of the fragment m/z 83 (10%) (Table **1**).

In the mass spectrum of the HIN the base peak (pyridilium ion), m/z 78 results from the acylium ion, m/z 106 (99%) by a decarbonylation process (Scheme **3**). The abundances of the two fragments are very close.

Table 3.

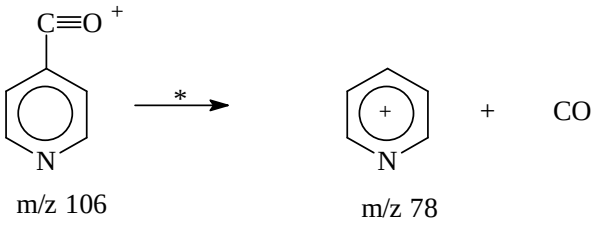
High resolution measurements of some fragments, m/z of the hydrazido-hydrazone **1, 2** and **3**.

Fragments, m/z	High resolution	
	measurements	calculated
m/z 78 - $C_5H_4N^+$ - $C_5H_2O^+$	 78.035 78.035	 78.035172 78.0105633
m/z 108 - $C_8H_{12}^{+\bullet}$	108.097	108.098952
m/z 161 - $C_8H_7N_3O^{+\bullet}$	161.059	161.0589077
m/z 163 - $C_{10}H_{15}N_2^+$	163.124	163.1235166
m/z 202 - $C_{11}H_{12}N_3O^+$	202.097	202.0980307
m/z 296 - $C_{18}H_{22}N_3O^+$	296.175	296.1762767



m/z 271 m/z 202 m/z 69

Scheme 2



Scheme 3

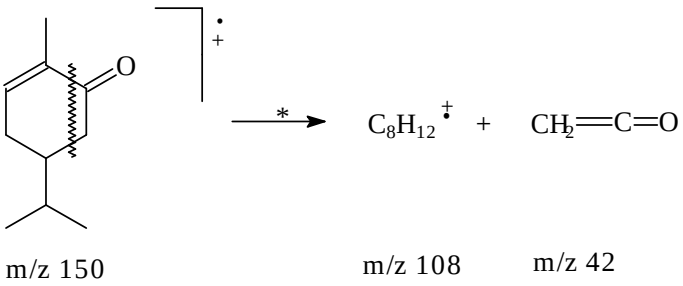
The presence of fragment, m/z 78 can also be obtained by elimination of hydrogen cyanide and hydrogen from m/z 106, generating the $C_5H_2O^+$ ion. The high resolution measurements confirm the presence of the $C_5H_4N^+$ fragments, m/z 78 (Table **3**).

We note that in the mass spectrum of the hydrazido-hydrazone **1** there are present the same m/z 106 and m/z 78 fragments, respectively like as in the mass spectrum of HIN. Their decreased abundance is m/z 106 > m/z 78.

*Hydrazido-hydrazone **2***

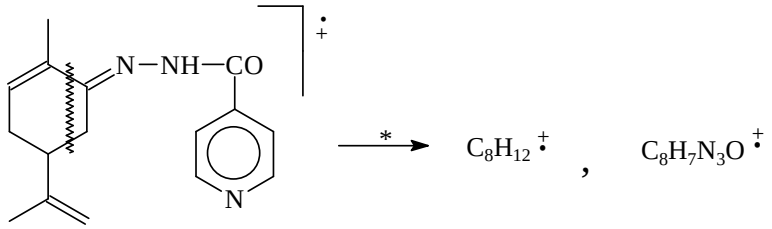
The molecular ion, m/z 269 (49,3%) presents higher stability in comparison with the molecular ion of the (+)- carvone, m/z 150 (7,2%), closed to the molecular ion of the HIN, m/z 137 (54%).

This stability allow us to suppose that blocking of the carbonyl group by the condensation with the izonicotinic acid hydrazide (HIN) disadvantages the braking up of the linkage in which it is directly involved. Taking into account the characteristic fragmentation of the α, β-unsaturated ketones [8], in the mass spectrum of the (+) carvone, the $C_8H_{12}^{+\bullet}$ m/z 108 fragment (35%) is present (Table **1**) (Scheme **4**).



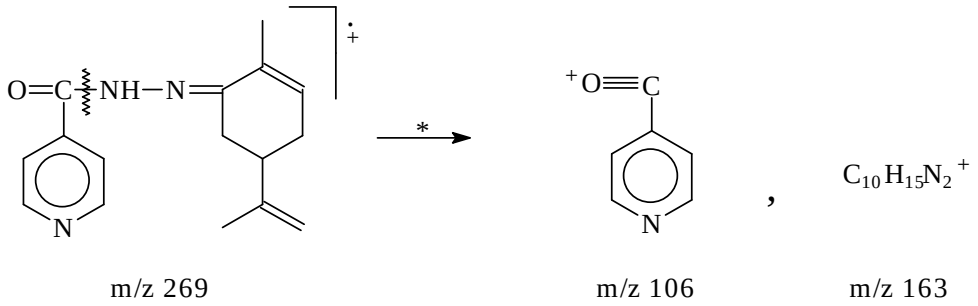
Scheme 4

If a similar cleavage takes place in the mass spectrum of the hydrazido-hydrazone **2** it is expected to find the $C_8H_{12}^{+\bullet}$ m/z 108 fragment, and the $C_8H_7N_3O^{+\bullet}$ m/z 161 fragment, respectively (Scheme **5**). The high resolution measurements confirm the presence in the mass spectrum of the hydrazido-hydrazone **2** of the $C_8H_{12}^{+\bullet}$ m/z 108 fragment and of the $C_8H_7N_3O^{+\bullet}$ m/z 161 fragment, respectively (Table **3**), but their abundance is small (Figure **2**). The differences between the abundance of the m/z 108 fragment, in (+)-carvone (35%) and in the hydrazido-hydrazone **2** (10%) confirm such a supposition.



Scheme 5

The base peak, m/z 106 (acylium ion) results from the molecular ion, m/z 269 by the fragmentation presented in Scheme **6**.



Scheme 6

Such fragmentation is supported by the presence in the mass spectrum of the corresponding ion, m/z 163 (Figure **2**). The high resolution measurements confirm the presence of the $C_{10}H_{15}N_2^+$ m/z 163 fragment, (Table **3**).

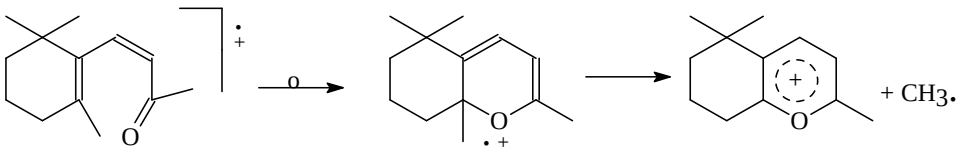
We note that in the mass spectrum of the hydrazido-hydrazone **2** there are present the same fragments, m/z 106 and m/z 78, respectively as observed in the mass spectrum of the hydrazido-hydrazone **1** and in the mass spectrum of the HIN. Their abundance decreased as m/z 106 > m/z 78.

*Hydrazido-hydrazone **3***

The molecular ion, m/z 311 presents a low abundance (4,3%) even lower than that of the corresponding ion of the β-ionone, m/z 192 (6,8%) and much lower than that of the molecular ion of the HIN, m/z 137 (54%).

The base peak, m/z 296 results from molecular ion, m/z 311 by a demethylation process (M-CH_3).

A systematic previous reported study focus on the mass spectra of the doubly unsaturated carbonyl compounds A. F. Thomas et al. [9] shows the main characteristic feature of the mass spectrum of the β-ionone, namely the presence of the fragment M-15. It results from the molecular ion by loss of a methyl group linked to the double bond of the cycle, as proved by the behaviour of the properly deuterated compound. By this kind of fragmentation the base peak, m/z 177 stabilized by resonance (aromatization) (Scheme **7**) results.



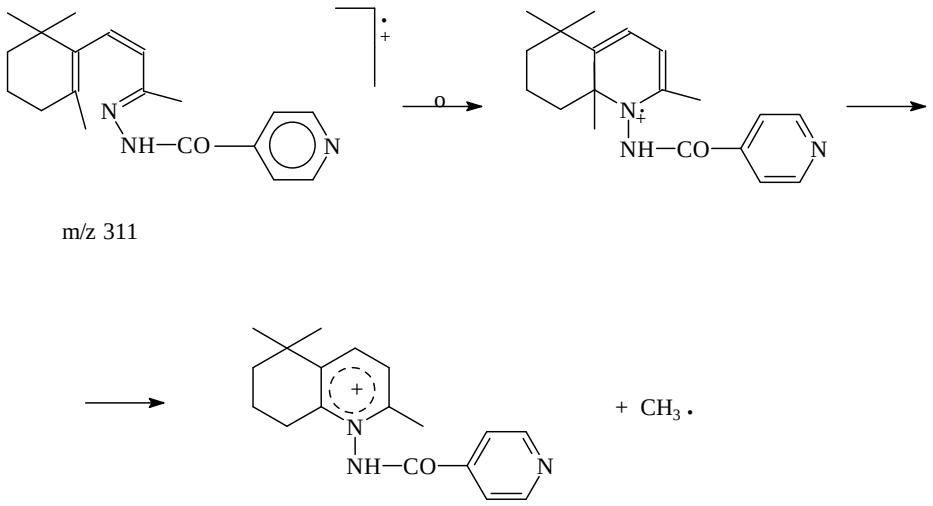
m/z 192 m/z 177

Scheme 7

Taking into account the literature data [9] we consider that in the mass spectrum of the hydrazido-hydrazone **3** a similar demethylation process takes place, yelding the cyclic aromatic system which has, in this case, the nitrogen as heteroatom (Scheme **8**). The high resolution measurements confirm the presence of the $C_{18}H_{22}N_3O^+$ fragment, m/z 296 (Table **3**).

We note the relative high abundance of the acylium ion, m/z 106 (31%) like as in the mass spectra of the hydrazido-hydrazones **1** and **2**.

We also note that in the mass spectrum of the hydrazido-hydrazone **3** there are present the same fragments, m/z 106 and m/z 78, respectively as observed in the mass spectra of the hydrazido-hydrazones **1** and **2** and in the mass spectrum of the HIN. Their abundance decreased in the same order, m/z 106 > m/z 78, in reversed than that order observed in the mass spectrum of HIN.



Scheme 8

CONCLUSIONS

We have presented and discussed the mass spectra of three new hydrazido-hydrazones issued from the condensation of the izonicotinic acid hydrazide (HIN) with citral, (+)-carvone and β-ionone, respectively. The molecular ions of the hydrazido-hydrazones exhibit low stability close to that of the starting terpenoids and much lower than that of the HIN's molecular ion, except the hydrazido-hydrazone **2**. The base peaks contain pyridine nucleus except hydrazido-hydrazone **1**. In the mass spectrum of the hydrazido-hydrazone **3** a very stable ion is observed as a result of a demethylation (M-15) and cyclization processes involving the nitrogen atom.

EXPERIMENTAL PART

The synthesis of the hydrazido-hydrazones **1**, **2** and **3** we described in a previous paper [1]. Theirs purity was checked by TLC.

The mass spectra were recorded by using a high resolution Varian-MAT 312 mass spectrometer with double focalization equipped with an ionization source of 70 eV.

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