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SPECTRAL ANALYSIS OF AMIDE DERIVATIVES LUPININE ALKALOID

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ABSTRACT

Research on the modification of natural biologically active substances is an integral part of the more general problem of elucidating the relationship between the structure and biological activity of compounds of this kind. Of course, these studies are of practical interest, leading in some cases to the creation of new valuable medical products.

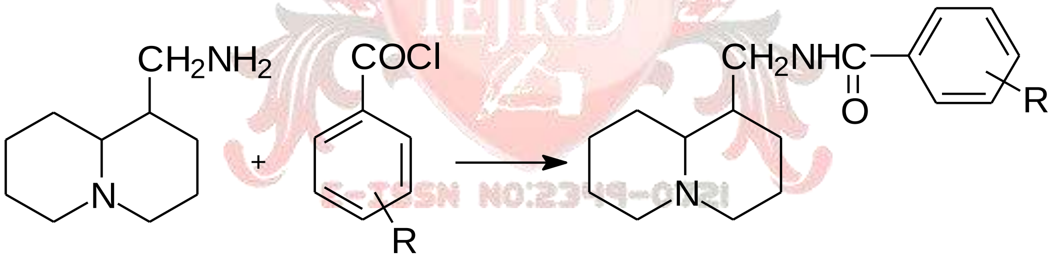
Among such compounds, an important place is occupied by alkaloids, because many well-known highly effective drugs are their analogues [1-4].

***Key words: alkaloid, lupinine, aminolupinine, shintesis, PMR- spektroskopy, IR- spektroskopy, mass-spektroskopy, structure, derivative*.**

INTRODUCTION

The purpose of the work. In order to find new highly effective physiologically active drugs among the derivatives of the alkaloid lupinine isolated from the plant Anabasis aphylla, we synthesized new derivatives of lupinine and showed that these substances are more specific and effective [5].

Materials and methods. lupinine derivatives with substituted benzoic acids with an amide bond were synthesized according to the scheme [5,6]:



R=p-CH_3(I); p-Br(II); o-CH_3(III); o-OCH_3(IV); o-Cl(V); o-Br(VI); o-COC_6H_5(VII);
m-CH_3(VIII); m-OCH_3(IX); m-Cl(X); m-Br(XI); m-I(XII); m-NO_2 (XIII); 2,4-Cl(XIV);
2,4-NO_2(XV);

The structure of the synthesized compounds was confirmed by the data of PMR, IR and mass spectra.

Discussion of the results. In the PMR spectrum of ortho-methoxybenzoylamidolupinine in the weak field region, two doublets are observed at 8.10 and 6.84 m. d., two pseudo-triplets at 7.27 and 7.00 m. d. based on the nature of signal splitting and the inclusion of substituent increments in the chemical shifts of aromatic protons, these signals are related to protons H2, H4, H5 and H3. In the weak field region at 7.85 m. d., the wide single-proton singlet belongs to the amide proton. Metoxylene group protons resonate at of 3.97 m. d. in the form of intensive triplet. Two multiplets at 2.71 and 2.45 m. d. they belong to individual protons of the methylene group of the exocyclic substituent. Their nonequivalence is due to the presence of a neighboring asymmetric center at C7 and the anisotropic properties of the substituent. Signal splitting is associated with spin-spin interactions with H7 and NH protons. The two-proton doublet at 2.67 m. d. with 1~10 Hz belongs to the equatorial protons H2e and H10e located in the α-position to nitrogen. The signals of the remaining protons resonate in the region of the "methylene elevation” of 1.1-2.2 m. d.

The PMR spectra of lupinine amides (I-III, V-XIII) contain a complex signal in the region of 3.52-3.98 m.d, related to the protons of the CH_2 - N fragment. Signals of aromatic protons are observed at 7.0-7.8 m. d. , in the region of 7.35-8.84 m. d. the signal belonging to the NH-proton is noted. The signals in the region of 1.2-2.2 m. d. belong to protons of the quinolizidine fragment. The position of other signals depends on the specific type of substituent and the obtained spectra confirm the structure of the synthesized derivatives of lupinine amides.in the ir spectrum iii, there is an absorption band at a frequency of 3300 cm-1 due to valence vibrations of nh groups, and an absorption band at 1530 cm-1 due to deformation vibrations of nh. the composite absorption band with frequencies of 1630 cm-1, 1640 cm-1 and with an inflection at 1670 cm-1 is caused by valence vibrations of c=o groups. all these absorption bands indicate the presence of amide groups in the molecule iii.

The benzene part of the molecule III match the following absorption bands: the absorption bands at frequencies 3020 cm-1, 3060 cm-1, caused by valent oscillations of relations of C-H of benzene ring; the absorption band at a frequency of 1600 cm-1, caused by valent oscillations of the carbon skeleton of benzene ring and in-plane deformation vibrations of the CH bonds of benzene ring; absorption bands at frequencies 701 cm-1, 650 cm-1, 640 cm-1 are due to out of plane vibrations of CH bonds of benzene ring; most of the absorption bands between 1200 cm-1 and 800 cm-1 are also caused by vibrations of the benzene part of molecule III.

There are no significant differences between the IR spectrum III and IV, i.e. different positions of CH_3 groups in the benzene part of these molecules do not have a certain effect on the electronic structure of the benzene part.In the IR spectrum I, all absorption bands due to vibrations of the benzene part of the molecule differ significantly compared to the spectra III and VIII. Consequently, in molecules I, the CH_3 group seems to strongly influence the electronic structure of the benzene part of molecules I through conjugation.

In the IR spectrum IV, the absorption bands related to the benzene part of the molecule also differ in comparison with the spectrum III. Hence, the formation of a simple ether bond with the benzene part strongly affects the electronic structure of the benzene part of the IV molecules.

The absorption bands of the benzene part in the IR spectrum VII are strongly changed in comparison with the spectrum III, i.e., the electronic structure of the benzene part of molecules VIII is changed in comparison with III.

The absorption bands due to vibrations of the benzene part of the molecule VI differ little from the corresponding absorption bands in the spectrum XI, but in the IR spectrum II, these absorption bands differ significantly. Therefore, in molecule II, the bromine atom most strongly affects the electronic structure of the benzene part.

If we compare the IR spectra of V and XIV, then significant differences between their absorption bands related to the benzene part of these molecules also seem to be related to the position of the chlorine atom bound to the benzene ring.

In the IR spectrum XV, in comparison with the spectrum III, strong absorption bands appeared at frequencies of 1540 cm-1 and 1550 cm-1, the first of which is due to valence vibrations of N-O bonds, and the second to valence vibrations of C-N bonds. These absorption bands indicate the presence of NO_2 groups in XV molecules.

The absorption bands resulting from vibrations of the benzene part of the XV molecule have significantly changed in comparison with the spectrum III. Consequently, the addition of NO_2 groups to the benzene part XV strongly affected the electronic structure of this benzene part.

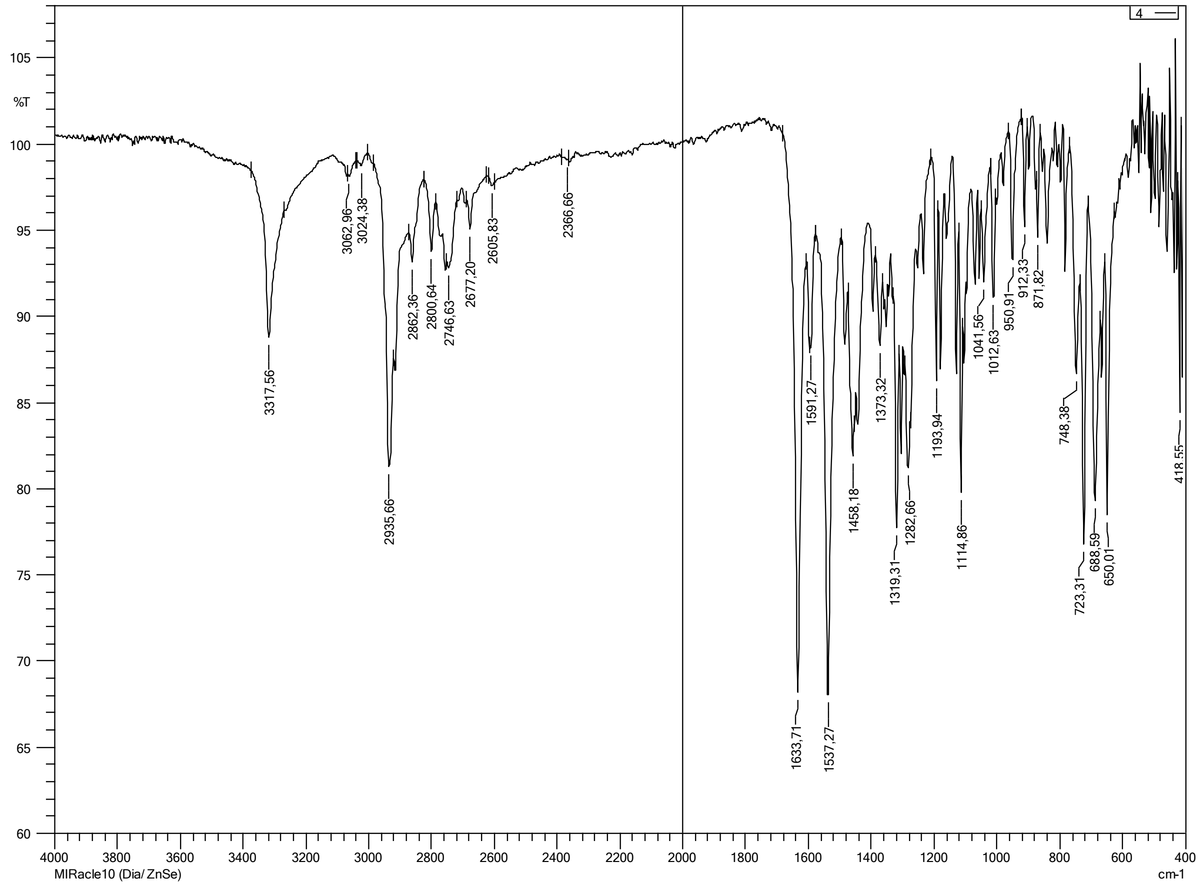


Figure 1. The IR spectrum of 2-methilbenzoinamidolupinine (III).

The absorption bands resulting from vibrations of the benzene part of the XV molecule have significantly changed in comparison with the spectrum III. Consequently, the addition of NO_2 groups to the benzene part XV strongly affected the electronic structure of this benzene part.

The mass-spectrometric decomposition of lupinine and epilupinine derivatives, in particular organophosphorus, simple and complex esters and a number of other derivatives, has been studied in some detail [7,8].

It is shown that the alkaloids lupinine and epilupinine are characterized by β or β’ decay, as a result of which ions with m/e 111, 110, 97, 83 can be formed directly or subsequently. From the molecular ion, as a result of decarboxylation, ions with m/e 138. 137, 136 can be formed.

Indeed, in the mass spectra studied by us, there is an intense peak of the ion with m / e 362 and intense peaks of the reduced ions are observed. Therefore, we present the proposed scheme of mass-spectroscopic decay of compound XV as an example:

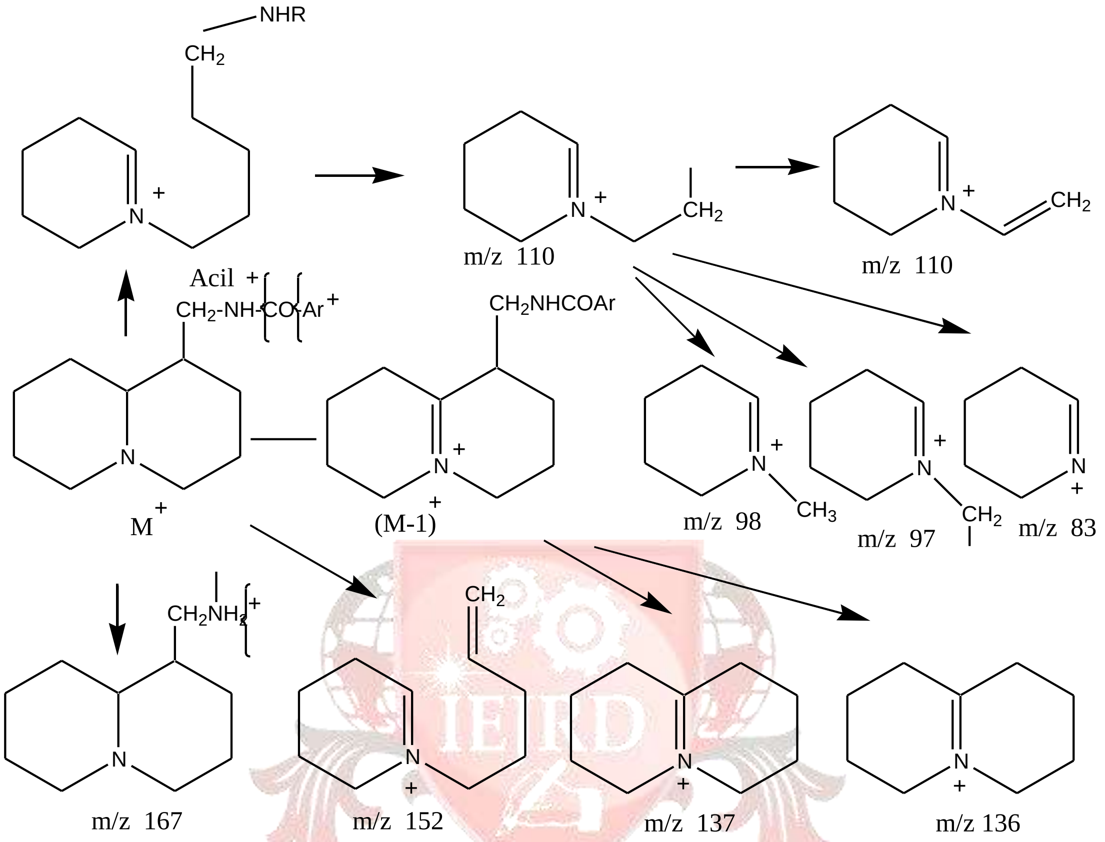


Figure 2. Scheme of mass spectrometric decay amino derivatives of lupinine.

Similar ion peaks are observed in the spectra of synthesized compounds (I-XIV).

CONCLUSION

It is proved that the results of studies of PMR, IR and mass spectra fully correspond to the correctness of the structures of the synthesized compounds.

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