SPECTROSCOPY OF CYTIZINE AND ITS DERIVATIVES

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Annotatsiya. Ushbu maqolada, sitizin va uning hosilalarining ultrabinafsha, mass spektroskopiya fizik tadqiqot usullari asosida moddalarning tarkibi va kimyoviy, fazoviy tuzilishlari haqida umumiy ma’lumotlar keltirilgan.

Kalit so’zlar: Sitizin, alkaloid, UB-spektroskopiya, mass spektrokopiya, PMR spektroskopiya.

Абстрактный. В статье представлены общие сведения о составе, химическом и пространственном строении цитизина и его производных, основанные на физических методах исследования ультрафиолетовой, масс-спектроскопии.

Ключевые слова: цитизин, алкалоид, УФ-спектроскопия, масс-спектроскопия, ПМР-спектроскопия.

Abstract. The article presents general information about the composition, chemical and spatial structure of cytisine and its derivatives, based on physical methods of ultraviolet and mass spectroscopy.

Key words: cytisine, alkaloid, UV spectroscopy, mass spectroscopy, PMR spectroscopy.

Japanese scientists Okida et al. [1] identified the 7R, 9S configuration of cytisine.

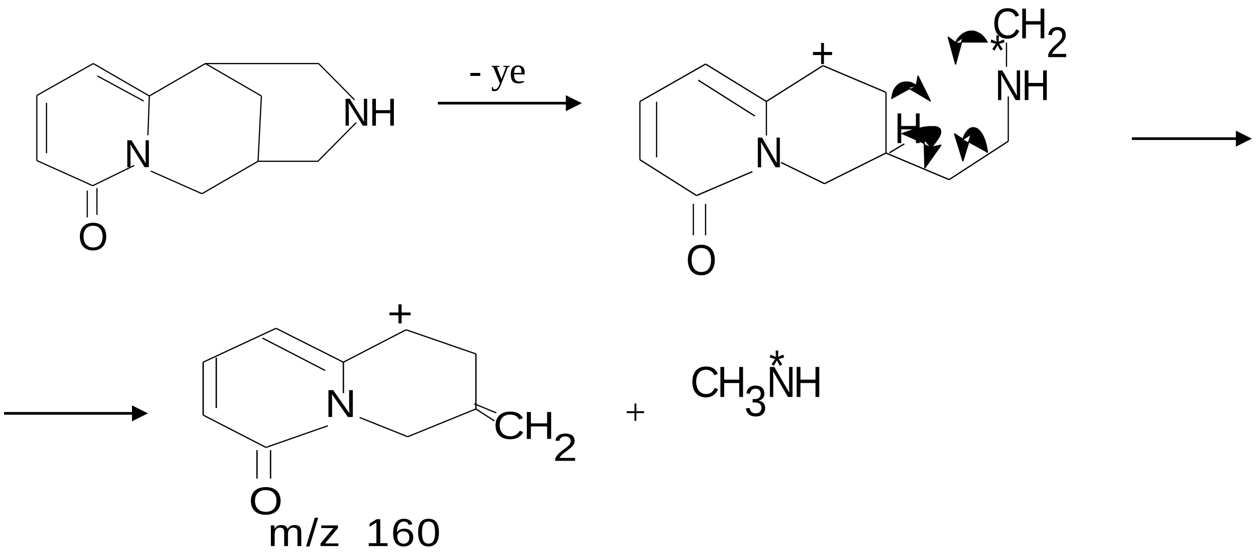
In the UV-spectrum of cytisine, there is an absorption maximum (l max 235, 308 nm) characteristic for the α-pyridone chromophore [2].

In the IR-spectrum of the alkaloid, the NH group (3350 cm-1), the six-membered lactam carbonyl (1640 cm-1), the connecting double bond (1600-1500 cm-1) and other vibrations are observed [3].

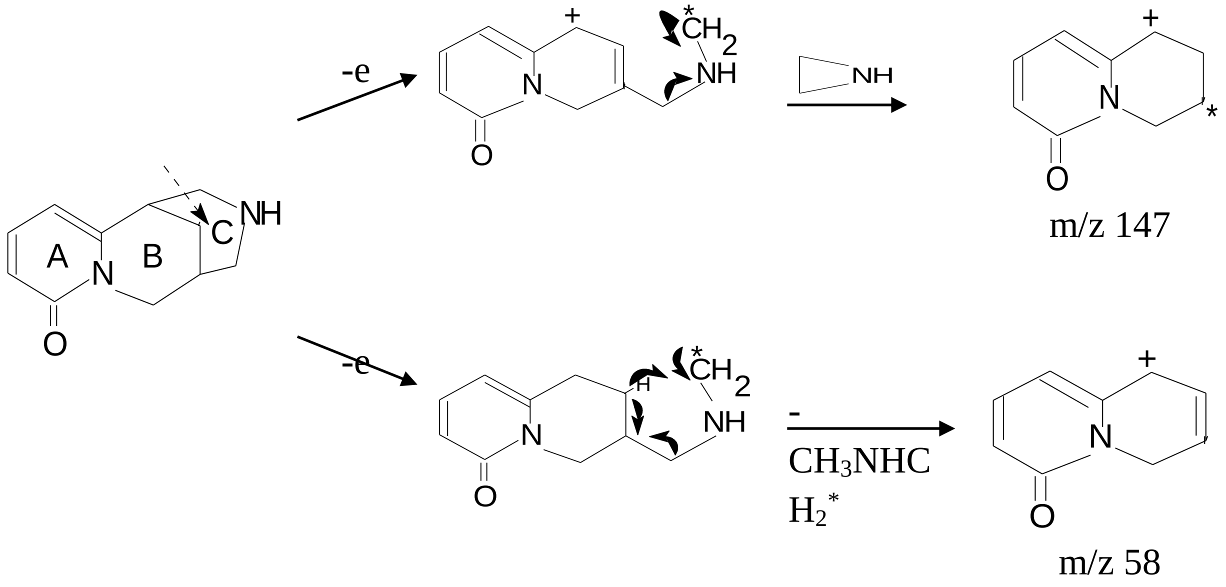
Neuner-Yeechli, Neswadba, Shpitellar [4] studied the mass spectra of cytisine and its various derivatives. The progress of fragmentation of these alkaloids depends on the basicity of the nitrogen atom. Therefore, the main fragments are sometimes formed from one part of the molecule, and sometimes from another part.

In the mass spectrum of cytisine, the peaks of ions with mass 160, 146, 147 are the main fragments.

An ion with a mass equal to 160 is formed as a result of the separation of the aminomethyl radical from the C ring:

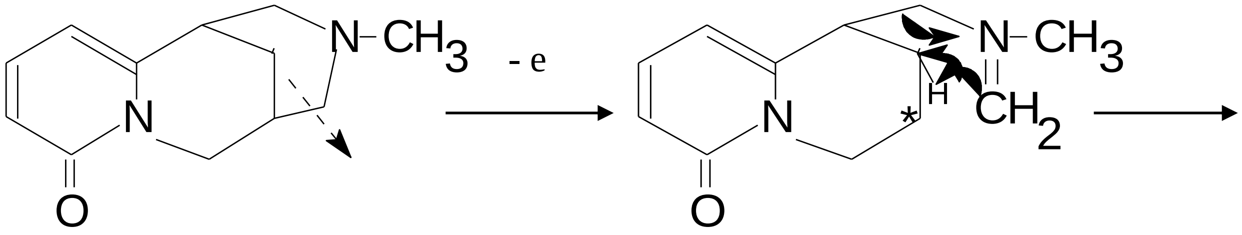


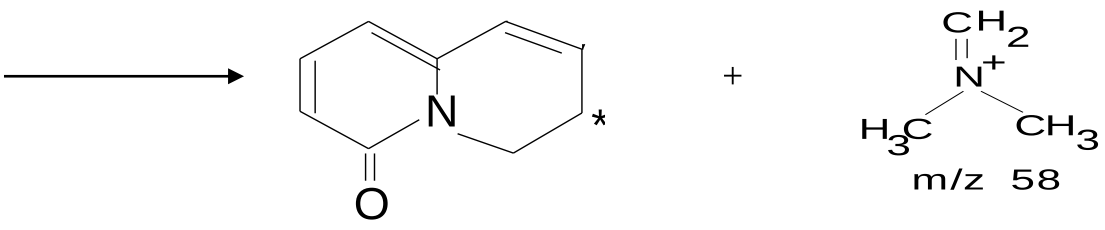
Fragments with mass 146, 147 can be formed as follows:



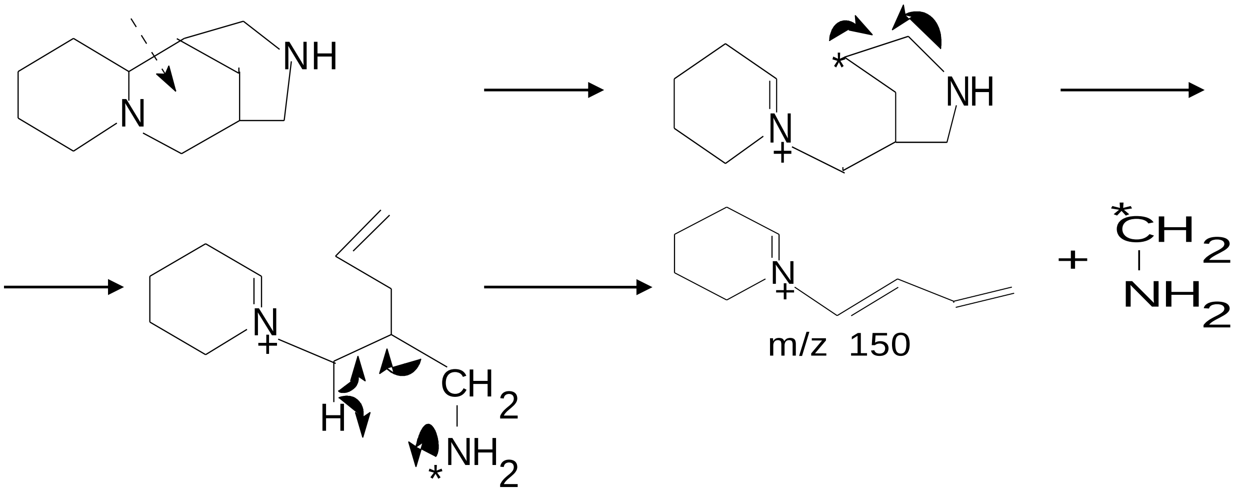
As can be seen from the mass spectrometric decomposition of (I), the main fragments are formed from rings A and V: [5]

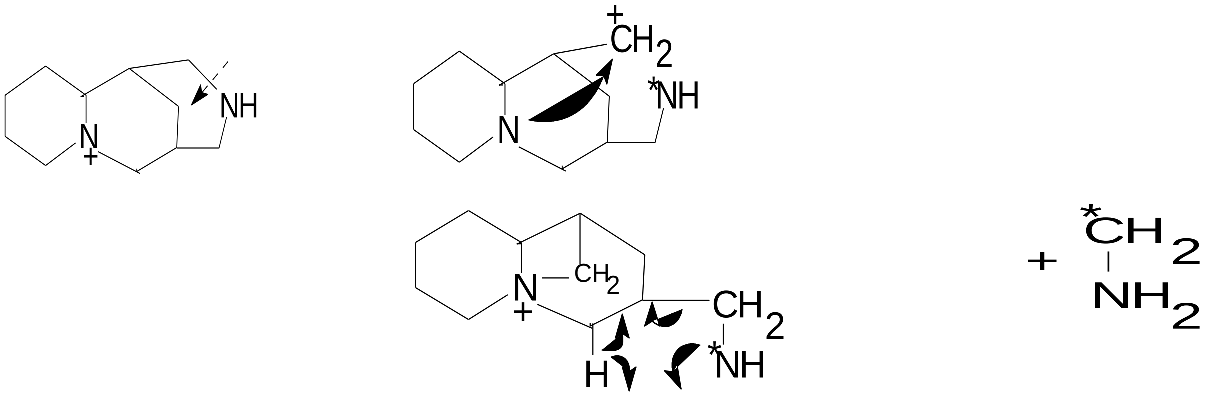
N-methylcytisine is the most intense ion with a mass of 58, in addition to characteristic ions with mass 160, 146, 147 in the mass spectrum:





In the mass spectrum of tetrahydrodeoxycytisine, the peak of m/z 150, 137, 136, 98, 97, 84 ions is the main one. The ion with mass 150 is formed as a result of the separation of the aminomethyl radical from the molecular ion. [6]

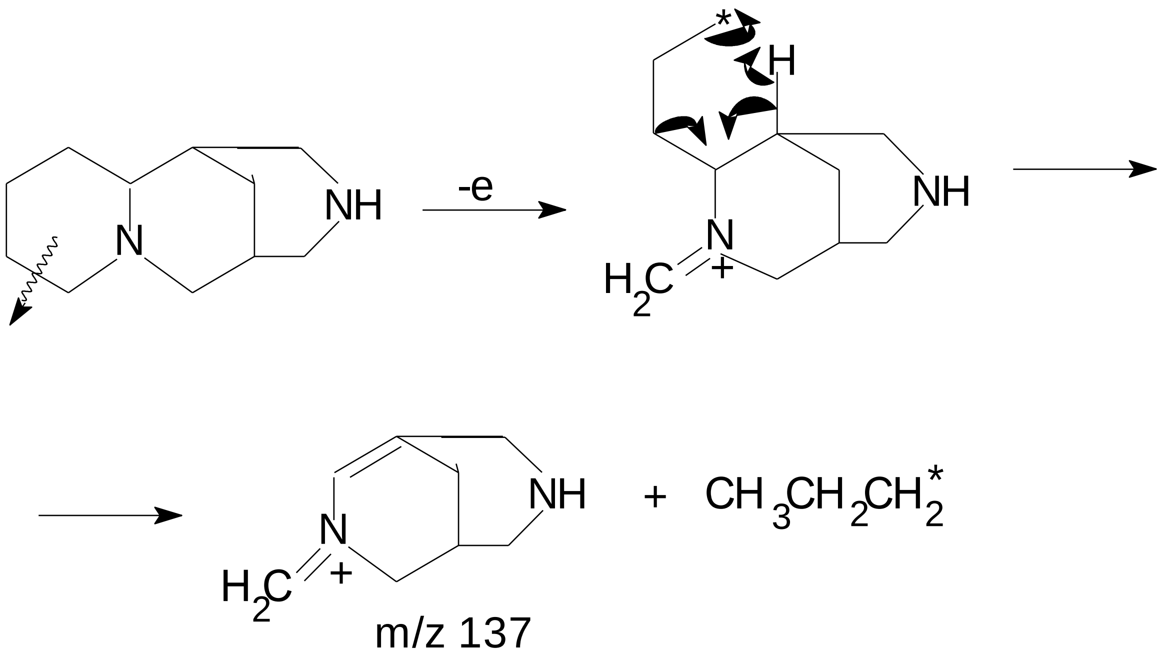




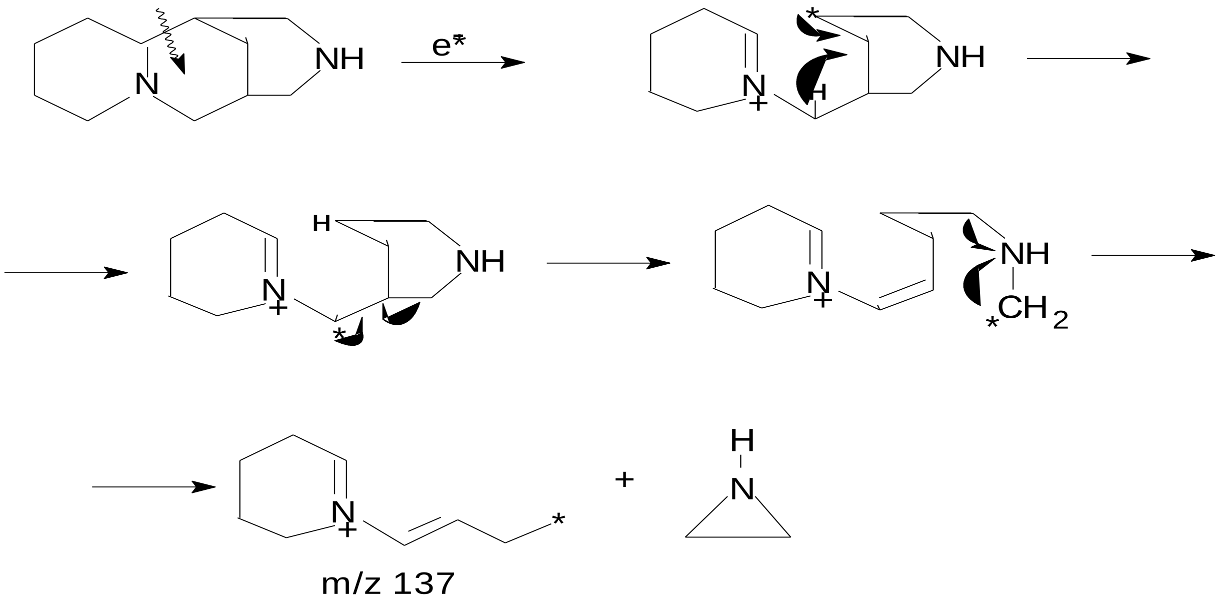
A 137-mass fragment can also be formed in two ways:

1. Under the influence of an electron impact, the bond between S2 and S3 is broken and a radical ion is formed. As a result of separation of propyl radical and

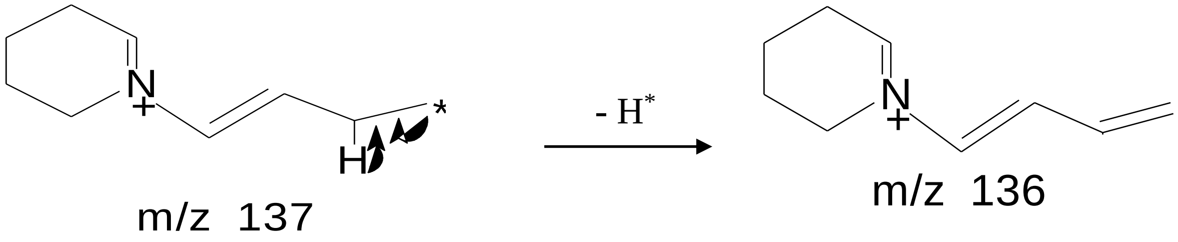
displacement of hydrogen from it, m/z 137 ion is formed:



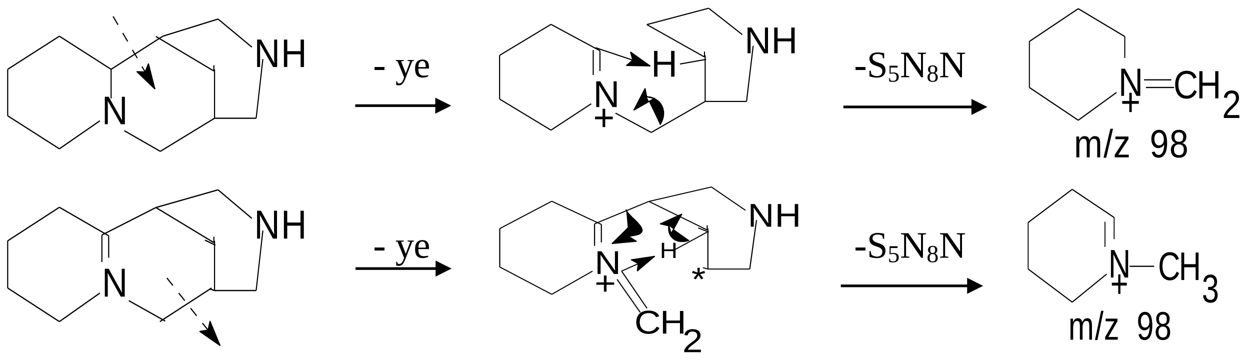
2. This ion can also be formed from the separation of ethyleneimine:



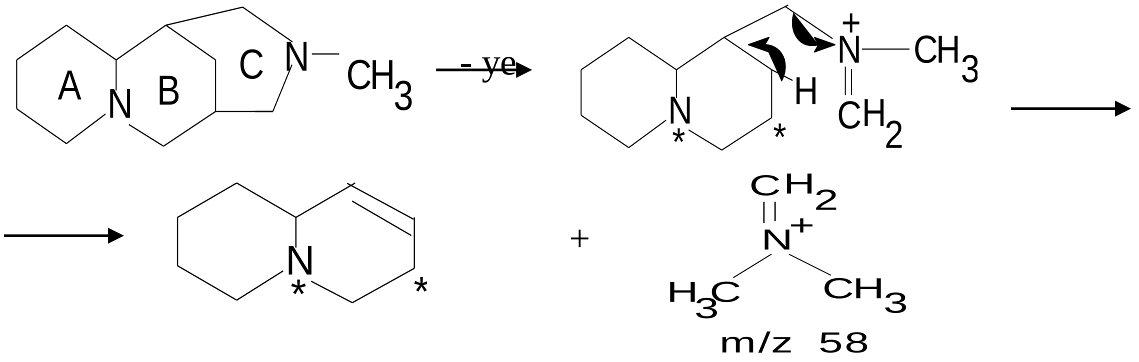
As a result of the separation of a hydrogen atom from a fragment with a mass of 137, an ion with a mass of m/z 136 is formed: [7]



The peak of the 98 mass ion is the most intense. It is formed by breaking the bond between S6 and S7 or S9 and S10, followed by regrouping of the hydrogen:

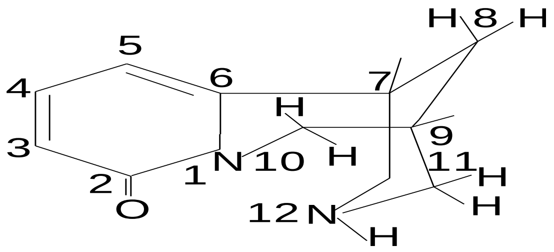


Along with the characteristic peaks mentioned above in the mass spectrum of tetrahydrodexo-N-methylcytisine, the peak of the m/z 58 ion is formed from the S ring:



Along with foreign scientists, Academician Sodikov O.S. The service of the scientific school [51] is noteworthy. They studied the PMR spectra of cytisine and its derivatives.

Weak field signals corresponding to α, β, γ protons of α-pyridone are observed in the PMR spectrum of cytisine. 7.33 m. h. signals in the field (J β,α = 7.5 ga and J β, $_{\gamma}$ = 9 ga) and the α - and γ- protons belonging to the β-proton are 6.05 and 6.47 m, respectively. h. appear in the field in the form of fragmented doublets: [8]



Axial and equatorial protons in the S10 state are 3.6–4.4 m. h. gives a complex signal in the field. In this case, the equatorial proton moved to a weaker field compared to the axial proton.

Signals of four protons bound to S11 and S13 and a tertiary proton bound to S7 (total of five protons) are 3 m. h. observed in the field.

The broad signal of the tertiary proton bound to S9 is 2.34 m. h. And the signal of N – H – proton is 1.50 m. h. is observed in the form of a singlet.

The two tertiary protons in the S7 and S9 states of cytisine are not equivalent to each other. Due to the fact that the proton in the S7 state is in the α-position relative to the double bond, it is shifted to a weak field in the PMR-spectrum compared to the proton in the S9 state.

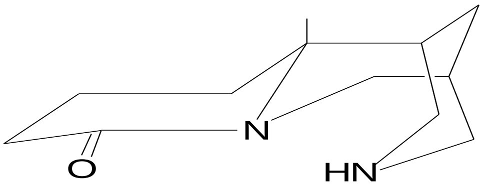
In N-methylcytisine, the general character of the α-pyridone part of the PMR spectrum is the same as that of cytisine. 3.6 - 4.4 m of protons in the S10 state in PMR spectra of N-methylcytisine and cytisine. h. the nature of the signals in the field is almost the same.

In the PMR-spectrum of N-methylcytisine, the doublet signal of α-equatorial protons in the S11, S13 positions, as well as the signal of the equatorial proton in the S9 position is 2.55-3.10 m. h. is observed at

A comparison of the spectra of cytisine and some of its derivatives shows that the character of the chemical shift of the signals of the axial protons in the S11 and S13 states is not the same. Because the non-generalized electron pair of the N12 atom, which occupies an equatorial position in cytisine, becomes axial when the hydrogen atom is exchanged for a more complex radical. [9]

PMR spectra of hydrogenated cytisine derivatives are very complex. But in the spectra of these compounds 4.5 - 5.00 and 3.00 - 3.50 m. h. is characterized by the presence of two doublets. These signals correspond to equatorial and axial protons bound to S10, respectively.

The location of these signals in the PMR-spectra of hydrogenated products indicates the formation of a trans-quinolizidine nucleus with a lactam group:



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