

**STRUCTURE OF THE SULFUR-CONTAINING ALKALOID DIPTOCARPAMINE**

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**ANNOTATION**

The article studied the mass spectra of sulfur-containing alkaloids of this type and the products of their chemical transformations. It has been established that their mass spectrometric fragmentation, in addition to simple breaking of ordinary -C-S-, -C-C- and -C-N-bonds, proceeds with the formation of nitrogen- and sulfur-containing heterocyclic ions.

Complete synthesis of the racemic sulfur-containing alkaloids diptocarpamine, diptocarpaine, diptocarpidin, diptocarpylidine and their deoxy derivatives has been carried out.

**Keywords:** Chemistry of organic sulfur compounds, drugs, PMR spectroscopy, NMR, UV spectroscopy, mass spectroscopy.

Organosulfur compounds have a number of valuable properties, which allows them to be used as medicines, pesticides, etc. The great interest in the problems of organic sulfur compounds all over the world is evidenced by the 18 international symposia on the "Chemistry of Organic Sulfur Compounds". In this regard, a special place is occupied by sulfur-containing compounds of plant origin.

The rational use of plant resources as a naturally renewable raw material is one of the main tasks of the economy. Therefore, the chemical study of plants as potential sources of new effective drugs for medicine and agriculture is one of the urgent problems of modern bioorganic chemistry.

This paper discusses the chemical and spectral properties of sulfur-containing alkaloids, which are based on a new structural chain that combines methyl sulfoxide, thiomethyl, and nitrile groups with urea in various forms.

From the empirical formulas of the isolated alkaloids, it follows that the ratio of carbon and hydrogen atoms indicates the fact that these alkaloids are saturated compounds (with the exception of diptocarpylidine and diptocarpinine), do not contain any cycles, and structurally represent an extended chain /90/. The presence of sulfur atoms in the composition of isolated alkaloids is easily determined without the use of analytical methods.

Mass spectrometrically, by the presence of peaks of the isotopic ion of sulfur in the spectrum, one can not only indicate whether the substance contains a sulfur atom or not, but also determine the number of its atoms. In the presence of one sulfur atom, the intensity of the (M+2)<sup>+</sup> peak is 5% of the peak of the molecular ion, which corresponds to the abundance of the S<sup>34</sup> isotope in nature. Moreover, it is possible to differentiate between sulfur-containing and sulfur-free fragments. Determination of the elemental composition of M<sup>+</sup> and fragment ions greatly facilitates the determination of the structures of unknown compounds using HRMS. On the other hand, the mass spectrometric fragmentation of sulfur-containing alkaloids is significantly complicated by the presence of numerous rearrangement ions in the spectrum.

Sulfur in the studied group of compounds is present in the sulfide and sulfoxide groups, as evidenced by the spectral data of these compounds.

The first nine of the sulfur-containing alkaloids presented in the table turned out to be similar in their physicochemical properties. A positive biuret reaction to urea derivatives is noted, which led us to the idea that the isolated alkaloids are probably N-alkyl derivatives of urea. The latter was confirmed spectrally. The UV spectrum contained one maximum at 210 nm. In the IR spectra, absorption bands of active hydrogen, amide carbonyl, C-S bonds, stretching and bending vibrations of the methyl, methylene and methine groups appear. A characteristic feature of alkaloids with a sulfoxide group was the detection of an intense band at 1030-1045  $\text{cm}^{-1}$ , the absence or presence of which indicated the nature of the sulfur atom.

To prove the structure of the isolated alkaloids, the reactions of hydrogenolytic desulfurization (desulfurization) on Raney nickel, reactions for obtaining deoxy derivatives (in the presence of a sulfoxide group), oxidation reactions, etc. were used. synthesis of the original base. In establishing the structures of isolated substances, a comparative study and comparison of the data obtained for all compounds and mutual transitions between alkaloids played an important role, which confirmed the correctness of the proposed structures.

Most sulfur-containing alkaloids turned out to be optically active compounds. The presence of optical activity in these alkaloids and the absence of such activity in the reduction products is explained by the presence of a sulfoxy group in the structure, where the sulfur atom, connected to two nonequivalent radicals and oxygen, having an unbound (free) pair of electrons playing the role of the fourth substituent, is asymmetric. Sulfur and oxygen atoms in sulfoxides are bonded in a semipolar manner, i.e. the pair of electrons by which the bond is carried out belongs to the sulfur atom. Therefore, the molecule has a pyramidal structure, and the lone pair of electrons occupies one corner of the pyramid and plays the role of the fourth substituent, while at the top of a stable pyramid that is not capable of inversion, there is a sulfur atom.

Diptocarpamine is an optically active substance. Based on the data of elemental analysis and mass spectrum, a composition was proposed for it,  $M + 248$ . The alkaloid is resistant to acids and alkalis, gives a positive biuret reaction to urea derivatives, does not contain any cycles in the structure. The foregoing suggests that diptocarpamine is an N-alkyl derivative of urea. Oxidation of I with chromic anhydride in an acid medium gave acetone in the form of its 2,4-dinitro-phenylhydrazone. Therefore, diptocarpamine contains an isopropyl group. The presence of the latter is also confirmed by the PMR spectrum of the alkaloid, where two signals are found in the form of a six-proton doublet at 1.1 ppm. (from gem-dimethyl groups) ( $J = 7 \text{ Hz}$ ) and a one-proton multiplet at 3.76 ppm.  $/\text{N-CH}(\text{CH}_3)_2/$ . It follows from the PMR spectrum data that the isopropyl group is directly bonded to the nitrogen atom. According to the IR spectrum, the alkaloid contains a sulfoxide group ( $1045 \text{ cm}^{-1}$ ), an amide carbonyl ( $1630 \text{ cm}^{-1}$ ), an NH group ( $3330, 3365 \text{ cm}^{-1}$ ). The presence of the latter is also confirmed by the PMR spectrum data: signals at 5.45 and 5.64 ppm. (1H, d,  $J = 6 \text{ Hz}$  and 1H capable of being exchanged for deuterium) are assigned to the protons of two NH groups. This is evidenced by the mass spectrum data of the base. The presence in the spectrum of intense peaks of ions with  $m/z$  58 and 44 is a confirmation of this. These ion peaks are formed as a result of  $\alpha$ - and C-N-breaking of bonds, accompanied by the rearrangement of hydrogen.



The molecular weight of the alkaloid is confirmed by the ion peak with  $m/z$  248, the peak of the  $(M+2)^+$  ion is 5% of the molecular ion peak, which corresponds to the content of one sulfur atom. The spectrum also shows fragmentation peaks of ions with  $m/z$  233  $(M-15)^+$ , 218  $(M-30)^+$ , 190  $(M-58)^+$ , 185  $(M-63)^+$ , 171, 162, 70, 61, 58 (100%), 44.

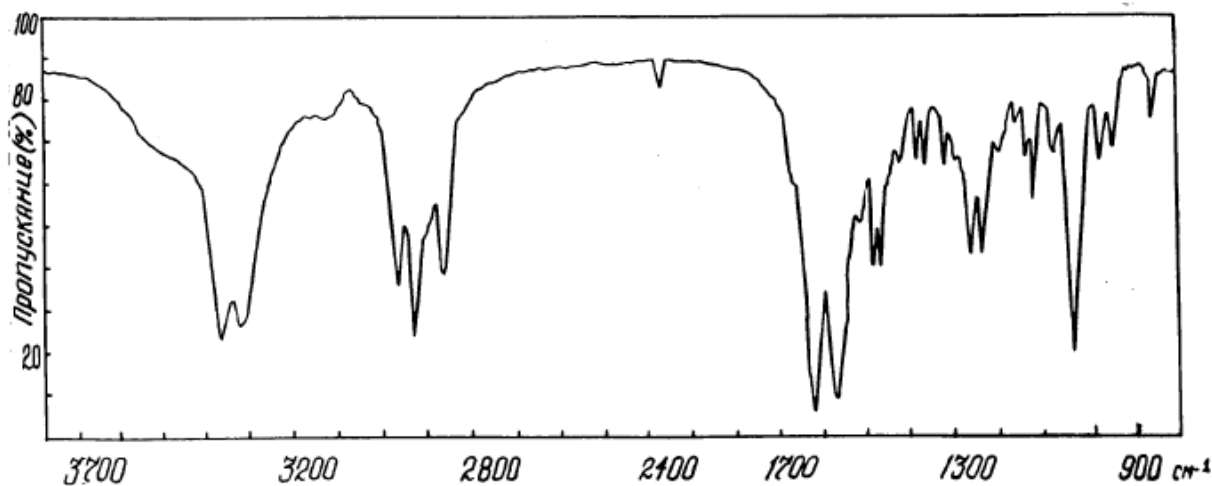
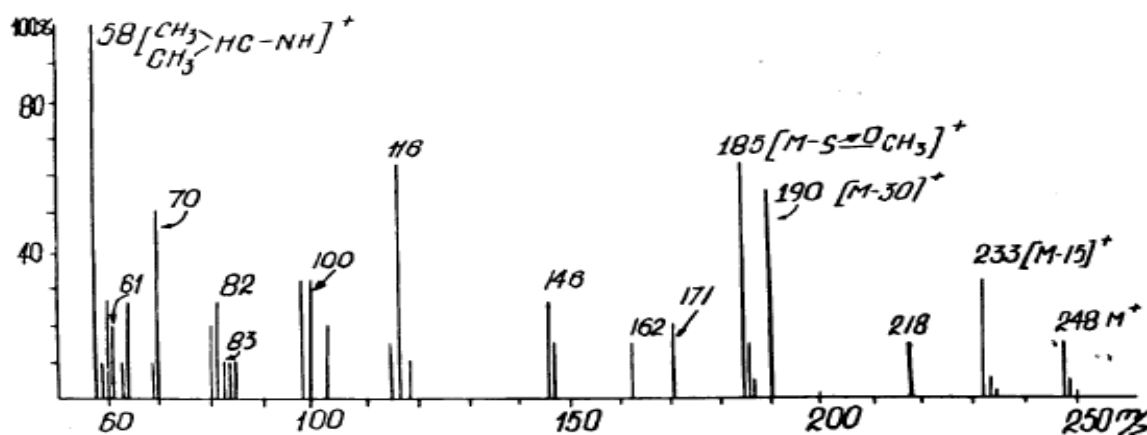


Fig.1. IR spectrum of diptocarpamine



Rice. 2. Mass spectrum of diptocarpamine

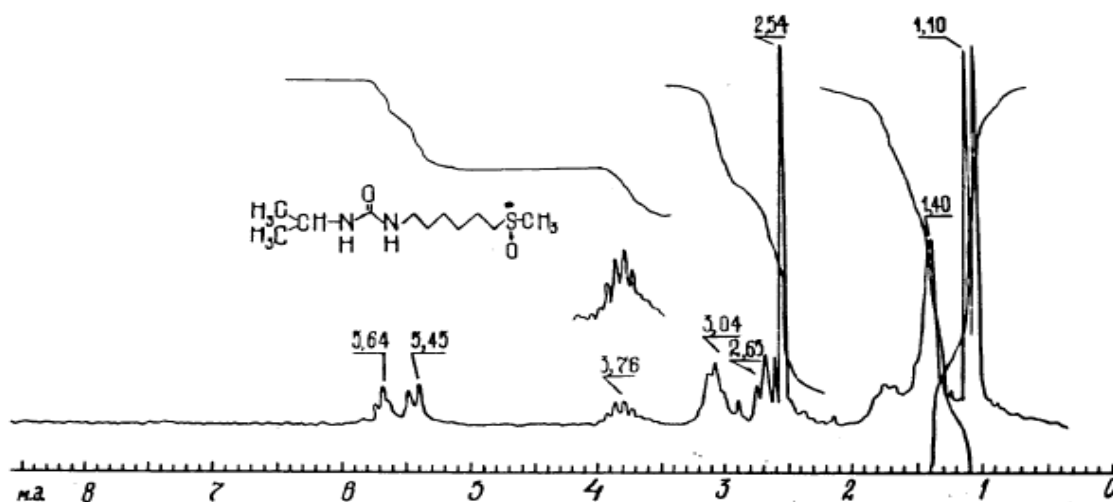


Fig.3. <sup>1</sup>H NMR spectrum of diptocarpamine

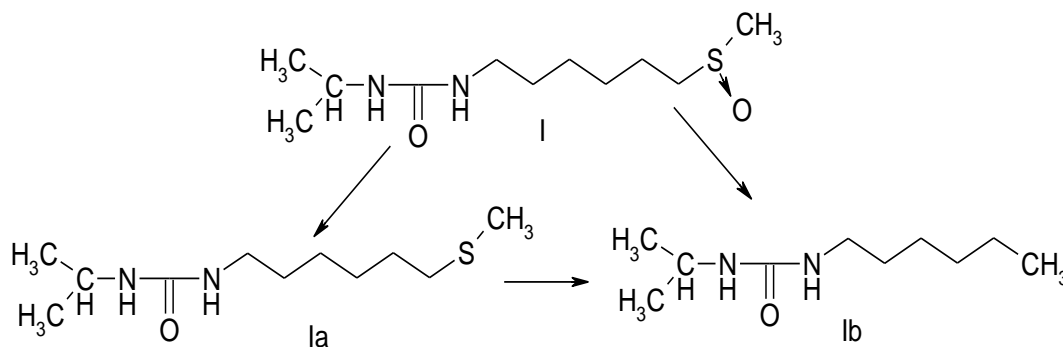
Sulfur in the structure of the alkaloid is represented as a methyl sulfoxide ( $O\leftarrow S-CH_3$ ) group, which appears in the PMR spectrum as a three-proton singlet at 2.54 ppm. On the other hand, the sulfur atom is bonded to the methylene group {quartet at 2.65 ppm. (2H),  $J=8$  Hz}. The PMR spectrum also shows a "methylene hump" at 1.25-2.00 ppm. (8H,  $(CH_2)_4$  and also signal at 3.04 ppm (2H, t,  $-CH_2-N$ ).

Reduction of I with lithium aluminum hydride or zinc in hydrochloric acid gave an optically inactive substance (1a) with m.p. 108-109 °C,  $M+232$ . The difference in molecular weights of the original base and the reduction product by 16 m.u. and the absence of a band at 1045  $cm^{-1}$  in the IR spectrum 1a indicate that the reduction of the  $S\rightarrow O$  group has occurred. Optical activity in diptocarpamine and the absence of such activity in the reduction product are due to the presence of a sulfoxo group in I.

Upon desulfurization of diptocarpamine in the presence of Raney nickel in a stream of hydrogen, the reduction product (1b) was isolated in the form of an amorphous, optically inactive substance with m.p. 79-80°C. The difference in the molecular weights of diptocarpamine and its deiodo product ( $M+186$ ) by 63 m.u. in the mass spectrum is explained by the fact that  $O\leftarrow S-CH_3$ -rpyppa was probably cleaved off with simultaneous restoration of the bond break.

In the NMR spectrum 1b in the high field region ( $\delta$  0.83 ppm), a triplet appears from the proton of the primary methyl group formed at the site of the break and restoration of the C-S bond. Mass spectrum 1b has a molecular ion peak at  $m/z$  186 and ion peaks at  $m/z$  171, 157, 143, 129, 115, 101, 87, 58, 44 (100%), differing by 14 m.u. ( $CH_2$ ), which is typical for a saturated hydrocarbon chain.

PMR spectrum data, as well as the nature of the mass spectrum 1b, namely the presence in the spectrum of a number of gradually decreasing peaks of ions - homologues  $(M-15)^+$ ,  $(M-29)^+$ ,  $(M-43)^+$ ,  $(M-57)^+$ ,  $(M-71)^+$  shows that the second alkyl substituent associated with nitrogen is n-hexyl.



The structure of diptocarpamine (1)

The mass spectra of sulfur-containing alkaloids of this type and the products of their chemical transformations have been studied for the first time. It has been established that their mass spectrometric fragmentation, in addition to simple breaking of ordinary  $-C-S-$ ,  $-C-C-$  and  $-C-N-$  bonds, proceeds with the formation of nitrogen- and sulfur-containing heterocyclic ions.

Complete synthesis of the racemic sulfur-containing alkaloids diptocarpamine, diptocarpaine, diptocarpidin, diptocarpylidine and their deoxy derivatives has been carried out.

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