STRUCTURE OF DIPTOCARPILIDINE

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Diptocarpilidine (bp 193-194° (4 mm)) has been isolated from the epigeal part and seeds of *Diptychocarpus strictus* (Fisch) Trautv., and its structure has been established as 1-cyano-6-methylsulfinylhexane.

Previously, from the epigeal part and seeds of *Diptychocarpus strictus* (Fisch.) Trautv., an optically active liquid base was isolated [1], which was called diptocarpilidine and had the composition $C_8H_{15}NO$ (I), bp 193-194°C (4 mm), readily soluble in acetone, chloroform, acetone, and ethanol and less readily in hexane and petroleum ether.

UV spectrum of (I): $\lambda_{max}^{C_2H_5OH}$ 206 nm (log ε 3.15). The IR spectrum showed absorption bands due to the vibrations of nitrile (2255 cm^{-1}) [2] and sulfoxide (1030 cm^{-1}) groups. The NMR spectrum of (I) showed the signal from the following protons (ppm): 1.20-1.85 (8H, m, methylene protons); 2.28 (2H, t, $N\equiv C-CH_2$); 2.51 (3H, s, $O \leftarrow S-CH_3$); 2.65 (2H, q, J = 6 Hz, $O \leftarrow S-CH_2$).

The mass spectrum of (I) contained the peaks of the following ions: 174 [M + 1 (6%)$^+$], 158 (77), 156 (36), 110 (98), 93 (40), 81 (52), 69 (100), 55 (64), 41 (94). The formation of the ion $(M + 1)^+$ is due to the high tendency of the diptocarpilidine molecule to undergo protonation.

On the basis of spectral characteristics, the developed formula $(N\equiv C-CH_2-)$, $-(CH_2)_4-$, $(-CH_2-\overset{\nearrow O}{S}-CH_3)$ may be proposed for diptocarpilidine.

The reduction of (I) with zinc in hydrochloric acid led to an optically inactive oxygen-free oily substance (II) with a molecular weight of 157. To prove the presence of a nitrile group diptocarpilidine was subjected to alkaline hydrolysis, which yielded a white crystalline substance (III) of acid nature with mp 60-62°C (M^+ 192). The IR spectrum of (III) showed the absorption bands of hydroxy (3300-3500 cm^{-1}) and carbonyl (1720 cm^{-1}) groups. A comparative study of the IR spectrum of the initial base (III) showed that in the hydrolysis product the absorption band of a nitrile group had disappeared and that of a carboxy group had appeared. The difference in the molecular weights of (I) and of the hydrolysis product of 19 m/z confirmed that an acid group had been formed in the hydrolysis product. Its methylation with diazomethane yielded the methyl ester of (III) with a molecular weight of 206 (IV).

The hydrogenation of (III) with Raney nickel in order to eliminate the sulfur led to an acid which was identified by TLC as enanthic (V). Methylation of the latter with diazomethane gave the methyl ester (VI), with M^+ 144. The formation of enanthic acid showed that between the nitrile and methylsulfinyl groups there was an unbranched chain consisting of six carbon atoms.

On the basis of the chemical transformations performed and spectral characteristics, the structure of 1-cyano-6-methylsulvinyl-n-hexane is proposed for diptocarpilidine.

Let us consider the mass spectra of (I) and the products of its transformation, since here certain features are observed in the mass-spectrometric fragmentation which are connected with the structures of these compounds. In the mass spectra of (III), (IV), and (V) the peaks of the M^+ ions appeared clearly, and in the spectrum of (I) in place of M^+ the protonated form of the molecular ion appeared, which is due to the high tendency of the dipto-

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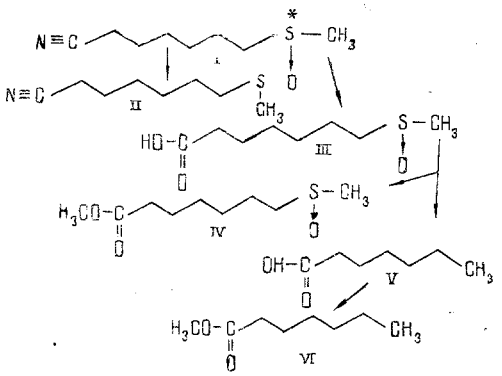
carpilidine molecule to undergo protonation. However, such an effect was lacking in the spectra of the derivatives in the molecules of which one of the terminal functional groups had lost its nature. Thus, in the spectra of (II), (III), and (IV) the peaks of ions characteristic for methylsulfinyl and methylthio derivatives of urea [3] appeared. A peak with m/z 175 in the spectrum of (III) could be formed only by the ejection of OH from the carboxy group or by the elimination of the oxygen of the sulfoxide group in the form of OH. This was confirmed by the appearance in the spectrum of the methyl ester (IV) of the peaks of ions with m/z 189 $(M - OH)^+$ and 175 $(M - OCH_3)^+$.



The loss of the methylsulfinyl group led to the appearance of a strong peak of an ion with m/z 110 in the spectrum of (I). Other fragmentation pathways were followed with the cleavage of ordinary bonds, accompanied by the migration of the two hydrogen atoms to the charged part of the molecule. Thus, in the spectrum of (I) from the part of the molecule containing the nitrile group ions with m/z 41, 55, 69, and 83 were formed which were possibly stabilized in the form of heterocyclic rings. These ions were also characteristic for the spectrum of (III). From the other part of the molecule of (II), sulfur-containing ions characteristic of the spectra of methylsulfinylhexylureas [3] were formed.

The pharmacological properties of diptocarpilidine have been studied in the department of experimental cardiology of the Uzbek Scientific-Research Institute of Cardiology of the Ministry of Health of the Uzbek SSR. As a result it was found that diptocarpilidine has a pronounced antihypoxic activity.

The antihypoxic activity of (I) was studied on mice and rats using the most important experimental models of hypoxic hypoxia — normobaric (brought about in a sealed chamber) and hypobaric (brought about in an altitude chamber). The results of the experiment showed that diptocarpilidine considerably prolongs life with both types of hypoxia.

EXPERIMENTAL

Diptocarpilidine (I) was isolated in the form of an oil with $[\alpha]_D$ −49.23° ($CHCl_3$), bp 193-194°C (4 mm). TLC in systems 1) benzene—chloroform—methanol (5:3.5:1.5) and 2) chloroform—methanol (9:1): R_{f_1} 0.91; R_{f_2} 0.85.

Reduction of Diptocarpilidine. In portions, 0.7 g of zinc dust was added to a solution of 50 mg of (I) in 10 ml of 20% hydrochloric acid in methanol, and the mixture was heated on the boiling water bath under reflux for 4 h. The catalyst was filtered off from the reaction mixture with suction and was washed with methanol, and the solvent was driven off in vacuum. The mass, concentrated to a volume of 2 ml, was made alkaline with 25% ammonia solution and extracted with chloroform, after which concentration of the chloroform extract yielded 35 mg of (II) in the form of an oil, M^+ 157, $[\alpha]_D$ ±0°, R_f 0.80 (system 1).

Alkaline Hydrolysis of Diptocarpilidine. A solution of 0.2 g of the base in 10 ml of 40% KOH solution was heated in the water bath for 3 h. Then the reaction mixture was cooled and extracted with chloroform. The concentrated chloroform extracts yielded 35 mg of the initial substance. Then the alkaline solution was acidified with 20% of sulfuric acid and extracted with chloroform to give 0.15 g of (III) in the form of crystals with mp 60-62°C, M^+ 192, R_f 0.89 (system 1).

Preparation of the Methyl Ester of the Hydrolysis Product of (I). A solution of 30 mg of the substance with mp 60-62°C in 3 ml of absolute methanol was treated with 3 ml of an ethereal solution of diazomethane. After two hours the solvent was driven off in vacuum. The residue consisted of (IV) in the form of an oil with R_f 0.95 (system 1), M^+ 206.

Desulfuration of the Hydrolysis Product of Diptocarpilidine. A mixture of 0.05 g of (I) and 1 g of Raney nickel in 5 ml of methanol was shaken on a mechanical shaker for 3 h. Then the catalyst was filtered off with suction and the solvent was distilled off. As a result of the hydrogenation, a colorless oily substance with R_f 0.90 (system 1) was isolated, and this was identified as enanthic acid.

SUMMARY

From the epigeal part and seeds of *Diptychocarpus strictus* has been isolated a new base — diptocarpilidine — which possesses antihypoxic activity and for which, on the basis of spectral characteristics and chemical transformations the structure of 1-cyano-6-methylsulfinylhexane has been established.

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NEW SPECIES OF LECTIN-CONTAINING PLANTS

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151 species of plants of the flora of Central Asia have been studied. Lectins have been found in 23 of them. The immunochemical specificities of the extracts have been determined, and for some types of plants also the carbohydrate-binding specificities.

Lectins, or carbohydrate-containing proteins, are widely represented in the animal and vegetable kingdoms. The presence of this class of proteins was known about a century ago [1], but their all-sided study began only in the sixties. The achievements in the field of lectin chemistry leave something better to be desired. At the present time, the industries of foreign countries are marketing a number of lectin preparations that are used in medicine and biology. In our country, the Biokhimreaktiv Amalgamation (Olaine) is producing a single lectin preparation.

In the USSR, investigations to find new plant lectins were first begun by M. I. Potov [2] and were continued by M. D. Lutsik [3]. We have begun a search for lectin-containing plants of the flora of Central Asia. The great diversity of the flora is opening up broad possibilities for the search for lectins in various vegetative organs and a comparison of their amounts and properties according to the vegetation period and the growth site. A hereditary capacity for synthesizing lectins with a definite specificity in the seeds is characteristic of a number of plants of one and the same genus [4], and therefore we took for the search seeds and other organs of the plants of those families in some of the species of which lectins had been detected previously.

150 species of plants of the families *Cruciferae*, *Leguminosae*, *Labiatae*, and one genus — *Datura* — from the *Solanaceae* family have been tested for the presence of hemagglutinins. The search was carried out on extracts or partially purified fractions with the aid of agglutination reactions of the erythrocytes of various human blood groups. The results are presented in Table 1.

The carbohydrate-bonding specificities of the lectins were studied by the inhibited hemagglutination reaction with the aid of the following sugars: L-fucose, D-galactose, N-

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