J_{AB} from the remaining spectrum – a quartet with its center at about 7.20 ppm. The X part of the ABX spectrum (signal of the proton geminal to the OH group at C_3) appears in the form of a one-proton triplet at 6.20 ppm with $^1/_2[J_{AX} + J_{BX}] = 5.0$ Hz.

A characteristic feature of the NMR spectrum of folifine is that with a rise in the temperature the difference in the CSs of the signals of the protons of the methyls of the gem-dimethyl group decrease: at +45°C this difference $\Delta\nu = 15.0$ Hz at +60°C $\Delta\nu = 12.8$ Hz. Furthermore, the AB part (quartet) of the folifine spectrum (Fig. 1a) is converted, with a rise in the temperature, into a doublet with its center at 7.15 ppm, J=5.0 Hz, i.e., on heating, the protons of the methylene group at C_4 become magnetically equivalent and together with the H_X-C_3OH proton they form a spin system of the A_2X type with $J_{AX} = 5.0$ Hz (Fig. 1b).

Thus, the observed temperature dependence of the CSs of the protons of the gem-dimethyl groups and the SSCC of $\underline{H}_X-COH$ and CH_2 show that with a rise in the temperature the rate of conversion of the dihydropyran ring C from one half-chair conformation (Scheme II, A) to the other (B) rises. With the rapid conversion of ring C, of course, reorientation of the hydroxy group and the proton geminal to it from the equatorial (A) to the axial (B) orientation takes place, which, in its turn, leads to the magnetic equivalence of the protons of the methylene group and to the equalization of the SSCCs of the $\underline{CH}_2-\underline{H}_X-COH$ protons.

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THE STRUCTURE OF DIPHTHOCARPAMINE

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Continuing an investigation of the alkaloids of Diphthychocarpus strictus, we have studied the structure of diphthocarpamine (I) with mp 100-101°C, $[\alpha]_D^{26}$ –58.21° [1].

On the basis of the results of elementary analysis and mass spectroscopy, the composition $C_{11}H_{24}N_2O_2S$, M^+ 248 has been proposed for (I), and it has Rf value 0.40 in a thin layer of silica gel in the chloroform–methanol (9:1) system.

The alkaloid is stable to the action of acids and alkalis and is not reduced by the Adams method, since the sulfur present in the base poisons the catalyst. The base gives a positive biuret reaction for urea derivatives. The oxidation of (I) with chromium trioxide in an acid medium gave acetone in the form of its 2,4-dinitrophenylhydrazone. Consequently, diphthocarpamine contains an isopropyl group.

The IR spectrum of (I) shows the absorption band of active hydrogen (3365 and 3330 cm^{-1}), the band of an amide carbonyl (1630 cm^{-1}), and an intense band at 1045 cm^{-1} (S → O).

The NMR spectrum (JNM-4H-100/100 MHz in $CDCl_3$ with HMDS as internal standard) shows a doublet at δ 1.1 ppm [6H, $-HC(CH_3)_2$], a singlet (3H) from a $S-CH_3$ group at 2.5 ppm, a quartet (2H; $CH_2-N=$) at 3.04 ppm, a multiplet (1H) from $=CH-N=$ at 3.76 ppm, and a one-proton doublet and a triplet from two NH groups capable of undergoing deuterium substitution at 5.64 and 5.45 ppm.

Mass spectrum: m/e 248 (M^+), 233 $(M-15)^+$, 218 $(M-30)^+$, 190 $(M-58)^+$, 185 $(M-63)^+$, 171, 162, 61, 58, 44.

The reduction of (I) with lithium tetrahydroaluminate or with zinc in hydrochloric acid gave an optically inactive substance (II) with mp 108-109°C, M^+ 232.

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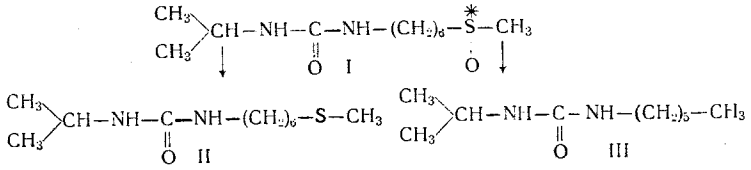
The difference in the molecular weights of the initial base and of the reduction product of 16 m/e and the absence from the IR spectrum of (II) of the band of 1045 cm^{-1} shows that reduction of the S → 0 group has taken place. The optical activity in diphthocarpamine and its absence in the reduction product show the presence of a sulfoxy group in (I) [2].

When diphthocarpamine was desulfurized in the presence of Raney nickel in a current of hydrogen, the reduction product (III) was isolated in the form of an amorphous optically inactive substance with mp 79-80°C.

The difference in the molecular weight of diphthocarpamine and its dethio product (M^+ 186) by 63 m/e in the mass spectra is due to the fact that a O ← S−CH_3 group was probably split out with the simultaneous reduction of the position of bond cleavage.

In the NMR spectrum of (III) in the strong-field region (δ 0.83) a triplet appears from the protons of a primary methyl group formed at the position of the cleavage and reduction of the C−S bond. At 3.76 ppm there is a multiplet at (A) corresponding to the proton of a methine proton attached to nitrogen (similar to the spectrum of diisopropylurea), which shows the presence in (I) of a $(CH_3)_2CH$−NH grouping. This is also indicated by the mass spectrum of (III), in which the peaks of ions with m/e 58 and 44 are the strongest (as in diisopropylurea) [1]. The mass spectrum of (III) has the peak of the molecular ion with m/e 186 and the peaks of ions with m/e 171, 157, 143, 129, 115, 101, 87, 58, 44 (100%), corresponding to the successive splitting out of 14 m/e CH_2).

Thus, on the basis of spectral characteristics and some chemical reactions we propose (I) as the most probable structure for diphthocarpamine:



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UMBROSINE − A NEW ALKALOID FROM Aconitum umbrosum

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From the roots of the previously unstudied species Aconitum umbrosum collected in the flowering period in the environs of Utkura (Sikhoté-Alin' range) we have isolated lycaconitine, anthranoyllycaconitine, ajacine, and a new base with the composition $C_{24}H_{39}NO_6$, mol. wt. 437.2738, mp 150-151°C (hexane), which we have called umbrosine (I).

According to its NMR spectrum ($CDCl_3$, δ scale), the alkaloid contains a methyl group (105 ppm, 3H, triplet) and three methoxy groups (3.33, 3.28, and 3.26 ppm, 3H each). Its composition and spectral characteristics permit the conclusion that umbrosine is based on a lycoctonine skeleton, and the subsequent chemical reactions of (I) confirmed this hypothesis.

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