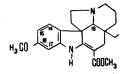
15 or 16. A comparison of the UV spectrum of dihydroervinceine with those of 7-methoxytetrahydrocarbazole and of dihydroervincinine [3, 4] showed that the methoxy group in ervinceine is possibly in position 16.

On the basis of what has been stated, the following structure, isomeric with 16-methoxyvincadifformine, is proposed as the most probable for ervinceine



The isolation of a new alkaloid herbavinine from <u>Vinca herbacea</u> has been reported. A comaprison of the properties of herbavinine and majdine [6, 7] and of their IR and NMR spectra has shown that these alkaloids are identical.

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## ALKALOIDS OF GALANTHUS CAUCASICUS

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From 1700 g of the plant <u>G. caucasicus</u> (Bak) Grossh., collected in the flowering period near Tblisi, by dichloroethane extraction we have isolated 7.3 g of total alkaloids (1.01% of the weight of the dry plant). Their separation yielded 4.5 g of lycorine, 6.3 g of galanthine, 3.6 g of tazettine, 0.4 g of galanthamine [1,2], and 0.5 g of a base  $C_{II}H_{19}O_4N$  with mp 214° C (water),  $[\alpha]_D^{20}$  +94.3° (c 0.71; methanol); mol. wt. 301 (mass spectroscopy); UV spectrum:  $\lambda_{max}$  228, 269, 210 mµ (log  $\varepsilon$  4.32, 3.91, 2.72). The IR spectrum of the base has absorption bands at 1700 (>CO) and 3400-3200 cm<sup>-1</sup> (OH).

The NMR spectrum of the compound has signals of the protons of an aromatic ring at 2.54, 2.99 ppm and of an olefinic proton at 4.54 ppm. The signal of an OCH<sub>3</sub> group is found at 6.16 ppm and that of a N-CH<sub>3</sub> group at 8.02 ppm.

The mass spectrum of the base has peaks of the ions  $M^+$  301, 109 (100%), 108, 96, 94, and 82 m/e. This is characteristic for alkaloids of the lycorenine type [3, 4].

These results permitted us to consider that the alkaloid isolated is not demethylhomolycorine [5].

The NMR spectrum was taken on a JNM-4H-100/100 MHz instrument in deuterochloroform with HMDS as internal standard ( $\tau$  scale) and the mass spectrum on a MKh-1303 instrument with a glass inlet system at an energy of the ionizing electrons of 40 eV and a temperature of 125° C.

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# COMPARATIVE CHARACTERISTICS OF THE MASS SPECTRA OF ISOMERS OF MATRINE

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The mass spectra of matrine (I) [1], leontine (II), sophoridine (III), and isosophoridine (IV) are characterized by high intensities of the peaks of the ions  $M^+$  and  $(M - 1)^+$ .

In matrine, the maximum peak is that of the  $M^{+}$  ion and in the others it is that of the  $(M - 1)^{+}$  ions which are formed mainly by the detachment of H' from C6. If one connects the stability of the system only with the intensity of  $M^+$ , all the isomers have approximately the same stability with a slight increase in the case of II and IV. However, if one considers the sum of the  $\Sigma$ % values for the ions with m/e 248 and 247, this sum is greatest for leontine (38.7%) which is in agreement with the least strain of the (trans-AB, BC, AC, CD) system. The matrine molecule is characterized by the the lowest value (22.2%), which corresponds to the presence of a strained (cis-AC, BC) system. At the same time, the intensities of the peaks of the fragments with m/e 247, 219, 206, 205, 192, and 162, formed by the splitting off of the elements of rings A and B and, in particular, C (rupture of a C-C bond adjacent to the asymmetric centers at  $C_5$  and  $C_7$ ), are considerably greater for I than for the other isomers. However, if one sums the  $\Sigma\%$  value of all the groups of peaks mentioned above, we obtain extremely close values for all the isomers (I, 33.3%; II, 32.4%; III, 31.4%; IV, 31.5%) (table). The combined probabilities of the expulsion of small fragments close to the center of ionization coincide for all the isomers. Almost all the fragments contained in the elimination of rings D and C pass through the stage of the  $(M-1)^{\dagger}$  ion, and the rupture of the  $C_7 - C_{11}$  bond is approximately equally probable, and therefore the  $\Sigma \%$  values of the ions with m/e 150 and below are comparable for all the isomers. The only displacement is found for the ions with m/e 137 and 136 in the spectrum of I. This fact shows that the ion with m/e 137 is formed directly from  $M^+$  by  $\beta$ -cleavage and the ion with m/e 136 from the  $(M - 1)^{T}$  ion.

With the exception of the above-mentioned differences in the intensities of the  $M^+$ ,  $(M - 1)^+$ , 137, 136 amu. peaks, the spectra of I and III are similar. This confirms the fact that matrine differs from sophoridine in the configuration at C<sub>6</sub> and also emphasizes that the main fragments are formed via the  $(M - 1)^+$  ion. The spectra of II and IV are also similar. In the molecule of IV the A and B rings have a cis linkage, while A-C and B-C are trans-linked [2]. Since in the spectrum of IV the intensity of the ion with m/e 138 is far higher than in the other spectra, it may be concluded that this process takes place with the rupture of the  $C_7 - C_{11}$  and  $C_5 - C_{17}$  bonds and the migration of hydrogen from  $C_2$ to  $C_5$  and from  $C_{12}$  to  $C_7$ . This can take place easily with a cis-AC linkage. Experimental conditions: MKh-1303 instrument, temperature  $80-100^{\circ}$  C, ionizing voltage 40V.

Sub- stance	248	247	219	206	205	192	177	162	150	138	137	136
(1) (11) (111) (111) (11)	12.3 14.1 11.6 14.5	9.9 24.6 15.0 21.3	1.6 0.6 1.3 0.7	$2.6 \\ 0.4 \\ 1.4 \\ 0.7$	$5.5 \\ 1.0 \\ 3.5 \\ 1.2$	2.2 0.3 1.4 0.6	1.5 8.6 2.8 2.2	$1.5 \\ 0.8 \\ 1.3 \\ 0.6$	4.0 6.7 6.0 5.5	1.3 0.4 1.2 2.7	3.3 1.1 1.7 1.1	$1.8 \\ 2.8 \\ 2.4 \\ 2.5$

Values of the  $\Sigma$ % in the Mass Spectra of I-IV.