

separating the alkaloids according to their solubility in organic solvents and also on a column of alumina, we have isolated protoprine, cryptopine, d-bicuculine, γ -adlumine, a base with mp 158–159° C, fumaridine, and fumaramine [2].

The authenticity of the γ -adlumine was shown by its oxidation with potassium permanganate to a 3,4-methylenedioxy dicarboxylic acid and m-hemipinic acid and the identity of its physical properties with literature data [3].

The base with mp 158–159° C, $[\alpha]_D^{25} +127.7^\circ$ (c 1.1; chloroform) had R_f 0.79 on chromatography in a thin layer of silica gel [chloroform–methanol (8:2)] and R_f 0.73 on a paper chromatogram [1-butanol–acetic acid–water (100:5:100)].

The IR spectrum of the base had absorption bands at 940 cm^{-1} , 1035 (CH_2O_2), 1505, 1610 (aromatic ring), and 1760 cm^{-1} ($=\text{CO}$), and the UV spectrum had λ_{max} 296 $\text{m}\mu$ ($\log \epsilon$ 3.90). The NMR spectrum had a singlet at $\tau = 7.55$ ($\text{N}-\text{CH}_3$), two singlets at $\tau = 6.10$, 6.23 (2 OCH_3), and a quadruplet at $\tau = 4.30$ (CH_2O_2), two one-proton doublets at $\tau = 2.92$, 2.68 (ortho aromatic protons), and two singlets at $\tau = 3.43$, 3.70 (para aromatic protons). Oxidation of the base with dilute nitric acid gave hydrastinine and hemipinic acid. All this permits the conclusion that our base is d- α -hydrastine [4], which we have found in this plant for the first time. From *Fumaria vaillantii* Loisl, collected in the Tashkent Oblast on 3–5 May 1965 in the period of vegetation and incipient fruit-bearing, we obtained 0.54% of total alkaloids by chloroform extraction. Separation of the mixture of alkaloids yielded protopine, d- α -hydrastine, fumaridine, and fumaramine.

The NMR spectra were taken by M. R. Yagudaev on a JNM-4H-100/100 MHz instrument in deuteriochloroform with HMDS as internal standard.

REFERENCES

1. T. R. Govindachari, K. Nagarajan, B. R. Pai, and S. Rajappa, C. A., 18674, 1958.
2. G. F. Platonova, P. S. Massagetov, A. D. Kuzovkov, and L. M. Utkin, ZhOKh, 26, 173, 1956.
3. H. G. Boit, Ergebnisse der Alkaloid-Chemie bis 1960, Akademie-Verlag, Berlin, 356, 1961.
4. Michitoshi Ohta, Hideo Tani, and Sekiko Morozumi, Chem. Pharm. Bull., 12, 1072–1080, 1964.

23 November 1967

Institute of the Chemistry of Plant Substances AS UzSSR

UDC 547.944/945

THE ALKALOIDS OF PEDICULARIS

A. Abdusamatov, S. Khakimdzhanov, and S. Yu. Yunusov

Khimiya Prirodnikh Soedinenii, Vol. 4, No. 3, p. 195, 1968

We have studied the alkaloids of the epigeal part of four species of *Pedicularis*. The results can be seen from the following table.

Species	Place and time of collection (year, date)	Vegetation period	Total alkaloids, % by weight of the raw material
<i>P. dolichorhiza</i> Schrenk.	Basin of the R. Talas, KirgSSR, 24 June 1966	Flowering	0.29
<i>P. olgae</i> Rgl.	Chimgan, Tashkent Oblast, 27 March 1967	Incipient bud formation	0.70
<i>P. macrochila</i> Vved.	Kungei Ala-Tau, KazSSR, 15 June 1967	End of flowering	0.31
<i>P. olgae</i> Rgl.	Sarydasht, TadzhSSR, 20 June 1967	Flowering	0.80

We investigated the alkaloids of *P. dolichorhiza* in more detail. By chloroform extraction, *P. dolichorhiza* yielded 0.18% of combined ethereal bases and 0.11% of combined chloroform bases. From the ethereal fraction by treatment with acetone, we isolated a base with mp 218–220° C (acetone), $[\alpha]_D^{25} +38^\circ$ (c 0.315; methanol) identical with the plantagonine from *P. olgae* [1].

The mother liquor was separated with respect to basicity into five fractions. The 3-rd and 4-th fractions yielded

a picrate with mp 127-128° C (water), $C_{14}H_{23}ON \cdot C_6H_8O_7N_3$ the properties of which agreed with those of the picrate of indicamine from *Plantago indica* [2].

From the chloroform fraction by treatment with a mixture of ethanol and petroleum ether (1:5) was isolated a base with mp 136-138° C, $[\alpha]_D^{25} -168.2^\circ$ (c 0.215; ethanol). By comparative paper chromatograms and a mixed melting point, this alkaloid was shown to be identical with an authentic sample of N-methylcytisine [1].

REFERENCES

1. Kh. Ubaev, P. Kh. Yuldashev, and S. Yu. Yunusov, Uzb. khim. zh., no. 3, 33, 1963.
2. A. V. Danilova and R. A. Konovalova, ZhOKh, 22, 2237, 1952.

28 November 1967

Institute of the Chemistry of Plant Substances AS UzSSR

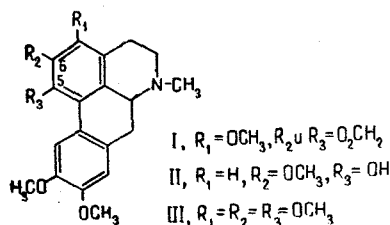
UDC 547.944/945+543.51

MASS SPECTROMETRIC DATA FOR THALICMINE, THALICMIDINE, AND THALICSIMIDINE

Z. F. Ismailov and S. Yu. Yunusov

Khimiya Prirodnikh Soedinenii, Vol. 4, No. 3, p. 196, 1968

We have studied the mass spectra of the alkaloids thalicmine (I), thalicmidine, (II), and thalicsimidine (III).



Characteristic features of these alkaloids are the maximum intensities of the peaks of the molecular ions and the considerable intensities of the peaks of the $(M - 1)^+$ ions.

Substance	m/e and relative intensity, %							
	M^+	a	b	c	d	$(M-1)^+$	$(M-15)^+$	$(M-31)^+$
(I)	369(100)	326(15)	311(16)	295(21)	—	368(94)	354(22)	338(21)
(II)	341(100)	298(50)	283(11)	267(57)	236(21)	340(92)	326(36)	310(28)
(III)	385(100)	342(33)	327(17)	311(33)	280(26)	384(74)	370(50)	354(21)

The results of the fragmentation of the molecular ions of the alkaloids (I)-(III) agree mainly with literature data [1]. The mass spectra of these alkaloids contain fragments with m/e 43 ($H_2C=N-CH_3$) and $a(M - 43)^+$. The intensity of the ion a is from 15 to 50% of the maximum peak. When the ion a loses a methyl group, ion b is formed, and when it loses a methoxy group it forms ion c. The further loss of a methoxy group by ion c in the alkaloids (II) and (III) leads to the appearance of ion d.

The peaks of the ions $(M - 1)^+$, $(M - 15)^+$, and $(M - 31)^+$ are found in the spectra of all three compounds and are formed by the loss of hydrogen, methyl, and methoxy radicals from the molecular ion. The results of our study of the mass spectra of (I)-(III) are given in the table.

The transitions $a \rightarrow b$, $a \rightarrow c \rightarrow d$ are shown by the presence of the following metastable peaks in the mass spectra:

- (I), $m^* = 311^2/326 = 296$ (calc. 296.6); $m^* = 295^2/326 = 267$ (calc. 266.9);
 (II), $m^* = 283^2/298 = 269$ (calc. 268.7); $m^* = 267^2/298 = 239$ (calc. 239.2);
 $m^* = 236^2/267 = 208$ (calc. 208.5);
 (III), $m^* = 327^2/342 = 312$ (calc. 312.6); $m^* = 311^2/342 = 283$ (calc. 282.8);
 $m^* = 280^2/311 = 252$ (calc. 252).