QUANTITATIVE DETERMINATION OF ANABASAMINE BY A CHROMATOPOTENTIOMETRIC METHOD

A. M. Saiitkulov, A. M. Maksudov,
A. I. Ishbaev, and K. Kh. Kholmatov

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The alkaloid anabasamine [1], obtained from the wastes of the manufacture of anabasine – the high-boiling fraction (HBF) of the combined alkaloids of *Anabasis aphylla* – possesses valuable pharmacological properties [2].

In the present paper a method for the quantitative determination of anabasamine is considered.

A benzene solution of the HBF of the total alkaloids (1-4%, 0.5 ml) was deposited on the starting line of a thin nonfixed layer of alumina on a glass plate with dimensions of 20 × 12 cm.

The mixture of alkaloids was chromatographed by the ascending method in the chloroform–ether (50:20) system, and the substances were revealed with iodine vapor. The spot with R_f 0.35 was accurately removed from the sorbent and was eluted four times with 15 ml of hot methanol each time. It was established experimentally that under these conditions the anabasamine is desorbed almost quantitatively, the treatment with iodine vapor having no effect on the accuracy of the determination. The substance in the eluate was determined by the method of potentiometric titration on a pH-340 instrument using a measuring glass electrode of the ÉSL-41G-04 type and a flow-through ÉVL-1M3 silver chloride comparison electrode. The titrant was a $3.25 \cdot 10^{-3}$ N solution of HCl in methanol. The equivalence point was determined from the jump in potential on the alkaloid-titration curves.

The accuracy of the method and the optimum amount of substance necessary for chromatography were determined on experiments performed with a 0.1374 N solution of anabasamine in methanol prepared from the sample with mp 65-66°C [1]. The results showed that the mean relative error does not exceed 0.5% and the method possesses adequate reproducibility.

The percentage content of anabasamine in the HBF of the total alkaloids of *A. aphylla* was calculated from the formula

$$G = \frac{M \cdot 10}{n} \cdot \frac{N\ V}{V_0\ P}\ \frac{V_{HCl}}{V'_{HCl}}\ .$$

where M is the molecular weight of anabasamine; n is the number of nitrogen atoms in the anabasamine molecule; N is the normal concentration of the standard solution of anabasamine; V is the volume of standard solution of anabasamine taken in titration, ml; V_{HCl} is the volume of HCl solution consumed in the titration of the standard solution of anabasamine, ml; V_{HCl} is the volume of HCl solution consumed in the titration of alkaloid in the eluate, ml; V_0 is the volume of the solution of HBF deposited on the TLC; and P is the percentage of HBF in the solution.

In our experiments, V = 1 ml, V_{HCl} = 1.2 ml.

Below we give the results of a quantitative determination of anabasamine in the HBF of the total alkaloids of *A. aphylla*.

Expt.	*P*, %	V_0, ml	V'_{HCl}, ml	*G*, % (mean of two measurements)
1	1.0	0.5	0.12	23.16
2	2.0	0.5	0.24	23.16
3	4.23	0.5	0.51	23.27
4	4.23	0.5	0.51	23.27

$G_{av} = 23.21$

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ALKALOIDS OF *Diptychocarpus strictus*

O. Abdilalimov, S. F. Aripova,
and S. Yu. Yunusov

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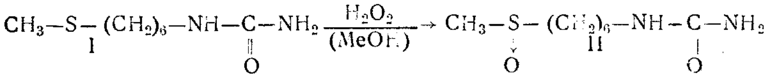
Continuing a study of the alkaloid composition of the seeds of *Diptychocarpus strictus* collected in the territory of the Chimkent oblast (September, 1976), by the usual chloroform extraction we obtained 0.13% of total alkaloids. On separating these alkaloids by polybuffer distribution, from the pH 2.2 fraction we isolated a new crystalline base with mp 118-119°C (acetone—MeOH) with the composition $C_8H_{18}N_2OS$ (I). The IR spectrum of (I) showed absorption bands at 3220, 3390 cm^{-1} (stretching vibrations of a NH bond) and 1660 cm^{-1} (amide carbonyl).

The NMR spectrum of the base (C_5D_5N) was characterized by the following signals (ppm): 1.10-1.42 (8 H, m, methylene protons); 1.18 (3 H, s, $S{-}CH_3$), and 2.20 (2 H, t, $S{-}CH_3$). The mass spectrum of (I) contained, in addition to the peak of the molecular ion with m/e 190, strong peaks of ions with m/e 175 $(M-15)^+$, 143 $(M-57)^+$, 119, 73, 61, and 44.

In a comparative study of the mass spectra it was found that base (I) and diptocarpaine (I) contain the same set of peaks, with the exception of the peaks of the molecular ions, which differ by 16 m/e. The IR spectrum of one differs from the spectrum of diptocarpaine by the absence of the absorption band of an S—O bond.

On the basis of what has been said above, we assumed that base (I) is a deoxy product of diptocarpaine. In fact, when base (I) was oxidized with hydrogen peroxide we obtained a product the spectral (IR, mass, and NMR) characteristics of which proved to be identical with those of diptocarpaine (II). Thus, base (I) is 6-thiomethyl-N-n-hexylurea:



$$\underset{\text{I}}{CH_3{-}S{-}(CH_2)_6{-}NH{-}\underset{\underset{O}{\Vert}}{C}{-}NH_2} \xrightarrow[(MeOH)]{H_2O_2} \underset{\text{II}}{CH_3{-}\underset{\underset{O}{\downarrow}}{S}{-}(CH_2)_6{-}NH{-}\underset{\underset{O}{|}}{C}{-}NH_2}$$

The epigeal part of the plant collected in the Dzhizak oblast (April, 1976) contained 0.1% of combined alkaloids from which by separation of a column of alumina we isolated a base with the composition $C_4H_{10}N_2O$ (III), mp 157-158°C.

IR spectrum (cm^{-1}): 3230 and 3360 (NH, NH_2), 1660 (amide carbonyl), and 1605, 1555 (amide II bands). The NMR spectrum showed the signals of the protons of an isopropyl group with δ 1.08 (6 H, d, J = 6 Hz, $-HC\begin{smallmatrix}CH_3\\ CH_3\end{smallmatrix}$, 3.32 ppm (1 H, m, >CH), and the signals of NH and NH_2 groups at 4.41 ppm.

The mass spectrum of the base showed the peak of the molecular ion with m/e 102 and the peaks of ions with m/e 87 $(M-15)^+$, 58, and 44 (100%).

The mass spectrometric fragmentation of (III) was similar to that of N,N'-diisopropylurea [2], isolated previously from this plant. The difference of 42 m/e in the molecular weights shows that base (III) contains one isopropyl group. This was also confirmed by the NMR spectrum, which had a signal in the 1.1 ppm in the form of a doublet (6 H) from one isopropyl group.

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