

the sixth no longer contained pachycarpine, while the other alkaloids (N-methylcytisine, thermopsine, etc.) continued to be extracted. At the stage of the adsorption of the alkaloids by KU-2 ion-exchange resin, after "breakthrough", with a qualitative analysis of the solution issuing from the column every hour, almost all the main alkaloids present in the extract were detected, but the investigation of this process is continuing. At the stage of the desorption of the alkaloids from the sorbent by alkaline methanol, the qualitative composition of the alkaloids in the eluates taken every hour was again checked. In this case, the cytisine was extracted far more rapidly, i. e., it could no longer be detected by the method used even in the seventh sample of eluate. Analysis of the subsequent sample showed that the remaining alkaloids and small traces of pachycarpine were continuing to pass into the eluting solution.

No.	System	Cytisine	N-Methyl- cytisine	Ther- mopsine	Pachycarpine	
1	Benzene-methanol (1 : 1)	0.24	0.57	0.66	0.12	* }
2	Ethanol-chloroform (1 : 5)	0.23	0.46	0.65	0.13	
3	Acetone-ethanol (1 : 2)	0.18	0.37	0.59	0.05	
4	Isopropanol-chloroform (5 : 2)	0.14	0.27	0.61	0.06	** }
5	Benzene-methanol (8 : 1)	0.38	0.61	0.80	0.21	
6	Acetone-water-ethyl acetate-benzene (6 : 1 : 2 : 2)	0.22	0.54	0.71	0.50	
7	Ethyl acetate-benzene-methanol (4 : 5 : 1)	0.31	0.81	0.90	0.41	
8	Cyclohexane-ethanol (5 : 1)	0.10	0.25	0.40	0.42	

*Silica gel-gypsum (9 : 1). **Alumina-gypsum (9 : 1)

Thus, the use of thin layer chromatography for the qualitative monitoring of the stages of the industrial process for the production of alkaloids from Th. alterniflora permits the optimum conditions for the performance of the industrial operations to be selected.

REFERENCES

1. K. A. Sabirov, T. T. Shakirov, and M. R. Shamsutdinov, KhPS [Chemistry of Natural Compounds], 2, 443, 1966.
2. E. Stahl, Dünnschichtchromatographie [Russian translation], Moscow, p. 15, 1965.

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ALKALOIDS OF HAPLOPHYLLUM DUBIUM ACCOMPANYING FOLIOSIDINE

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From the epigeal part of H. dubium collected at the end of August 1967, in the flowering stage in the Surkhan Dar'ya region of the Uzbek SSR we have isolated by chloroform extraction 0.75% of total alkaloids (of the weight of the dry plant), and by their separation we have obtained eight alkaloids.

By chromatography on alumina of the nonphenolic fraction we obtained dubamine, haploperine, foliosine [1], foliosidine, and dubinidine, and from the phenolic fraction we obtained haplopine [2], robustine [3], and folifidine [4].

The phenolic alkaloids, and also foliosidine, were obtained from the epigeal part of H. dubium for the first time.

Technical foliosidine [5] was heated in water (1 : 20) at 60-70° C and the solution was separated from the resinous residue and filtered hot. On cooling, a mixture of foliosidine and skimmianine deposited. On repeated crystallization, the sparingly soluble skimmianine was separated from the foliosidine.

The yield of pure foliosidine amounted to 35% and that of skimmianine 45% of the technical product.

REFERENCES

1. S. A. Sultanov, V. I. Pastukhova, and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], 3, 355, 1967.

2. G. P. Sidiyakin and S. Yu. Yunusov, DAN UzSSR, no. 4, 39, 1962.
3. I. M. Fakhruddinova, G. P. Sidiyakin, and S. Yu. Yunusov, Uzb. khim. zh., no. 4, 41, 1963.
4. Z. Sh. Faizutdinova, I. A. Bessonova, and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], 3, 257, 1967.
5. L. Avazmukhamedov and T. T. Shakirov, Uzb. khim. zh., no. 5, 75, 1967.

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ALKALOIDS OF LEONTICE DARVASICA

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From the epigeal part of *L. darvasica*, family Berberidaceae, collected in the flowering stage in the western Gissars range we have obtained 1.1% of total alkaloids by chloroform extraction. From them we have isolated thaspine [1], and from the mother liquor of the latter in the form of perchlorates N-methylcytisine and a new alkaloid darvasine with mp 145° C (ether) $[\alpha]_D^{20} -183^\circ$ (c 1; ethanol), having the composition $C_{15}H_{22}N_2O$. Darvasine forms crystalline mono salts: perchlorate with mp 250° C (ethanol), picrate with mp 231° C (decomp., ethanol), and methiodide with mp 262° C (acetone). The IR spectrum of the alkaloid has absorption bands characteristic for the carbonyl of a six-membered lactam and a double bond (1670 w, 1645 cm^{-1}) and the UV absorption spectrum shows that these groups are conjugated in the form of the $-\overset{|}{C}=\overset{|}{C}-\overset{|}{N}-\overset{|}{C}=O$ chromophore (λ_{max} 244 m μ , log ϵ 4.3).

A study of the mass spectrum of darvasine (taken on a MKh-1303 mass spectrometer at an energy of the ionizing electrons of 40 V and a temperature of 85° C) has shown that it belongs to the matrine group of alkaloids with one double bond in ring C. The fragments formed by the elimination of the methyl and ethyl radicals from rings A and B are analogous to those of matrine and sophocarpine; however, the ions arising as a result of the degradation of ring C differ markedly from those of matrine and sophocarpine [2]. The peaks of the ions in the region of lower mass numbers are displaced by one or two atomic units, as in leontalbine. The spectra of darvasine and leontalbine differ in the intensity of several peaks, which is explained by steric factors. The dehydrogenation of darvasine using palladized asbestos (260-270° C, 30 min) gave hexadehydrodarvasine, identical with octadehydromatrine [3].

The NMR spectrum of the alkaloid shows, in addition to complex signals of protons of various methylene and methine groups, the signal of an isolated olefinic proton present in the α -position to a heteroatom (τ 3.19), which corresponds to a position of the double bond at C_5-C_{17} . The IR spectrum of darvasine lacks a trans band [4]. Consequently, the base is the first representative of the matrine alkaloids of the cis series and has the structure of 5,17-dehydroisomatrine.



REFERENCES

1. S. Iskandarov, R. N. Nuriddinov, and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], 3, 26, 1967.
2. S. Iskanderov and S. Yu. Yunusov, KhPS [Chemistry of Natural Compounds], 4, 106, 1968.
3. E. Ochiai, S. Okuda, and H. Minato, J. Pharm. Japani, 72, 781, 1952.
4. F. Bholmann, Ber., 91, 2157, 1958.

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