## SPECIFIC ROTATION OF ANABASINE

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It is known that the specific rotation of anabasine depends on the method of its isolation:  $[\alpha]_D - 82.88^\circ$ (benzoylation) [1],  $-81.10^\circ$  (via the fluosilicic salt) [1],  $-72.59^\circ$  (from tobacco, via the picrate) [2],  $-82.45^\circ$ (resolution of racemic anabasine) [3],  $-47.0^\circ$  [1] and  $-59.60^\circ$  [4] (nitroso method),  $-56.20^\circ$  (sulfuric acid method) [5],  $-92.01^\circ$  [6], and  $-83.1^\circ$  (polybuffer separation) [7, 8].

Anabasine, isolated from technical anabasine sulfate by two different methods, has identical physicochemical constants and the corresponding derivatives differ only in the  $[\alpha]_D$  values (Table 1). The IR and NMR spectra of the different anabasine preparations and their derivatives are identical.

As early as 1935 [8] it was established that the iodomethylation of N-benzoylanabasine yields two isomeric methiodides: (I), with mp 230-231° and  $[\alpha]_D$  0, and (II), with mp 108-109° and  $[\alpha]_D$  -116°:



However, data are lacking in [8] on the optical purity and the method used to isolate the starting anabasine from the mixture of Anabasis aphylla alkaloids.

We also obtained two products, with the same constants as given in [8], when we subjected N-benzoylanabasine to iodomethylation. Since the methylation was run at 20°C, the possibility of racemization was very slight. Consequently, the fact that two products were obtained can be explained by a partial racemization of the N-benzoylanabasine. In order to confirm this assumption we took anabasine with  $[\alpha]_D$  $-62.0^\circ$  and subjected it to racemization as described in [1], and the thus obtained dl-anabasine was converted to the N-benzoyl derivative, the constants of which agreed with those given in [1]. The iodomethylation of dl-N-benzoylanabasine gave one product, which in the melting point and the IR and NMR spectra was identical with product (I). It is possible to assume that, depending on the isolation method, the anabasine that is isolated from technical anabasine sulfate contains various amounts of l- and dl-anabasine.

## EXPERIMENTAL METHOD

Anabasine, with  $[\alpha]_{D} = 62.0^{\circ}$ , was obtained from technical anabasine sulfate by the nitrosation method and subsequent decomposition of the nitrosoanabasine with hydrochloric acid [1]. Anabasine, with  $[\alpha]_{D} = 72.0^{\circ}$ , was obtained from technical anabasine sulfate by the sulfuric acid method and subsequent purification via anabasine hydriodide [5]. The N-methyl-, N-acetyl- and N-benzoylanabasines, and also their methiodides, were obtained as described in [8-10].

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TABLE 1. Properties of Anapasine Derivative	TABLE 1.	Properties	of	Anabasine	Derivative
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Derivative	Anabasine with $[\alpha]_D^{25} - 62.0^\circ$								
	Bp,°C (p, mm			$\left[\alpha\right]_{D}^{25}^{\dagger}$	Methiodide				
	of Hg) or mp, °C	Yield,%	$R_{f}^{*}$		Mp,°C	$[\alpha]_D^{25}$			
N-Methyl N-Acetyl N-Benzoyl	78—80 (0,8) 162—163 (0,8) 72—73	85 72 78	0,85 0,84 0,87	81,25° 113,46° 108,84°	227—228 113—114 229—230 (I) 103—104 (II) Con	+15,65° -95,42° 0.1.1 -108,84° atinued			
, , , , , , , , , , , , , , , , ,	Anabasine with $[\alpha]_D^{25} - 72.0^{\circ}$								
Derivative	Bp, °C (p, mm of Hg) or mp, °C	Yield,%	R <sub>f</sub>	$[\alpha]_D^{25}$	Methiodide				
					Mp,°C	$[\alpha]_D^{25}$			
		1	1			1			

N-Benzóyl 80 0,87 128.21 102--103 (II) \*Support = Al<sub>2</sub>O<sub>3</sub> (II activity, system: 24 : 1 chloroform - methanol).

0,85

0,84

228 .990 112-

229.230

-113

91,42°

-93,75°

O. H.

90

85

†C 0.2, alcohol.

N-Methyl

N-Acetv]

**‡O.** L = optically inactive.

<u>dl-Anabasine</u>. A sulfuric acid solution of anabasine, with  $[\alpha]_{D}$  -62.0°, was heated in an autoclave at 200° for 200 h. After the appropriate workup we obtained d*l*-anabasine, the constants of which coincided with the data given in [1].

 $d_{l-N-Benzoylanabasine}$  Methiodide. To 2 g of  $d_{l-N-benzoylanabasine}$  in 10 ml of methanol was added 2 g of CH<sub>3</sub>I. The next day the obtained pale yellow crystals were suction-filtered and dried in vacuo; yield 2.2 g (80%). The compound is optically inactive. After two recrystallizations from water, mp 231-232°.

## CONCLUSIONS

The iodomethylation of N-benzoylanabasine gave two isomeric products, one of which is dl-N-benzoylanabasine methiodide, while the other is the methiodide that is formed from the pure *l*-N-benzoylanabasine.

## LITERATURE CITED

- A. P. Orekhov, Chemistry of Plant Alkaloids of the USSR [in Russian], Nauka (1965). 1.
- O. A. Nelson, J. Am. Chem. Soc., 56, 1989 (1934). 2.
- E. Spath and F. Kesziler, Ber., 70, 70 (1937). 3.
- M. Ehrenstein, Arch. Pharm., 269, 628 (1931). 4.
- O. S. Otroshchenko, A. S. Sadykov, and Kh. A. Akbarov, Zh. Obshch. Khim., 29, 2441 (1959). 5.
- R. Lukeš, A. A. Arojan, J. Kovař, and K. Blaha, Collection Czech. Chem. Commun., 27, 751 6. (1962).
- L. I. Brutko and L. N. Utkin, in monograph: "Synthesis of Natural Compounds and of Their Analogs 7. and Fragments" [in Russian], Nauka (1965); L. I. Brutko, L. S. Massagetov, and L. N. Utkin, Rastitel'nye Resursy, 4, No. 3, 336 (1968).
- A. P. Orekhov, G. P. Men'shikov, and A. G. Grigorovich, Khim.-Farm. Prom., No. 2, 94 (1935). 8.
- A. S. Sadykov, Chemistry of Alkaloids [in Russian], Izd. Akad. Nauk Uzbek SSR, Tashkent (1956). 9.
- O. S. Otroshchenko and A. S. Sadykov, Zh. Obshch. Khim., 24, 1885 (1954). 10.