ELECTOROXIDATION OF THE ALKALOIDS ANABASINE, CYTISINE, AND LUPININE AT A PLATINUM ELECTRODE IN ACETONITRILE

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The anodic behavior of anabasine, cytisine, and lupinine at a platinum electrode in anhydrous acetonitrile has been investigated and the basic kinetic parameters of their oxidation have been established.

The alkaloids anabasine, cytisine, and lupinine have limited use in medical practice because of their high toxicity and narrow spectrum of bioactivity [1]. Continuing investigations on the electrochemical modification of industrially available alkaloids [2-4], in the present paper we give the results of a study of the anodic behavior of the alkaloids anabasine, cytisine, and lupinine at stationary and rotating-disk platinum electrodes against a background of 0.1 M solutions of $NaClO_4$ and $LiClO_4$ in anhyrous acetonitrile.

It has been established that the alkaloids anabasine and lupinine are oxidized with the formation of one, and cytisine with the formation of two, oxidation waves (Figs. 1 and 2). The magnitude of the current corresponding to the plateau on the volt-ampere curve for the oxidation of the alkaloids is directly proportional to the concentration of the substrates up to values of $1 \cdot 10^{-2}$ M. To determine the nature of the electrode process and the type of limiting current we investigated the potentiodynamic curves at a rotating-disc electrode at various rates of scanning of the potential. A linear dependence of the maximum oxidation current of the alkaloids on the rate of imposition of the polar voltage was established (Fig. 2), which is characteristic for diffusional processes [5]. The calculated values of $(\log i/\log v)_{s.t.}$ were in the range of 0.70-0.78, which corresponds to processes taking place with adsorption complications [6]. At low speeds of rotation of disc electrode a linear dependence of i_{max} on the rate of rotation of the electrode was observed on the volt-amperograms of anabasine and lupinine, while at high speeds of rotation the form of the relationship was characteristic for mixed difffusional-kinetic control (Fig. 1). It must be mentioned that in the case the alkaloid cytisine the limiting current did not depend on the speed of rotation of the rotating disc electrode.

The dependence of the height of the wave on the temperature is an important diagnostic criterion in determining the nature of an electrode process. A rise in the temperature of the solution led to an increase in the rate of oxidation of the alkaloids. From a graph of the dependence of the limiting currents on the reciprocal temperature we determined the values of the activation energy, which were 7.33 and 8.12 kJ/mole for lupinine and anabasine, respectively. In the case of the electrooxidation of cytisine, the use of the temperature-kinetic method was difficult because of the simultaneous occurrence over the whole range of potentials investigated of processes involving the oxidation of the substrate and of the background solution, i.e., in this case the oxidation of cytosine was limited by the discharge of the molecules at the electrode.

From the slope of the polarization curves in the coordinates $\varphi, \lg \frac{i_{lim.} - i}{i}$, the latter, in accordance with the equation

$$\varphi = \varphi_{1/2} + 2,3 \frac{RT}{\beta_t \cdot F} \lg \frac{i_{lim} - i}{i}$$

being equal to

$$\Delta\varphi / \Delta \lg \left[(i_{lim} - i)/i \right] = 2,3 \frac{RT}{\beta_t \cdot F} \simeq \frac{0,059}{\beta_t},$$

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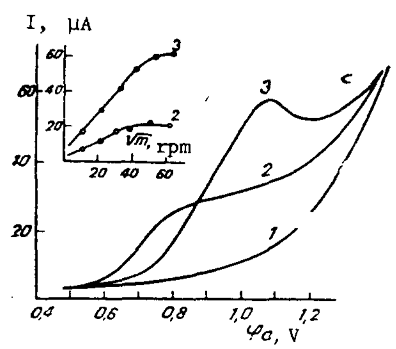

Fig. 1

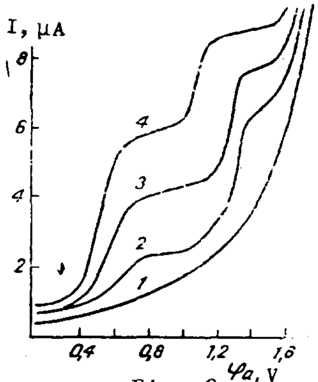

Fig. 2

Fig. 1. Volt-amperograms of the oxidation of anabasine (curve 2, background – 0.1 M $NaClO_4$) and lupinine (curve 3, background – 0.1 M $LiClO_4$) at a platinum electrode in acetonitrile, $C_{alk} = 5\cdot10^{\cdot}$ M, m = 500 rpm, V = 40 mV/s: 1) Background curve. At the top is given the dependence of the maximum current for the oxidation of the alkaloids on the rate of rotation of a disc electrode.

Fig. 2. Volt-amperograms of the oxidation of cytisine ($1\cdot10^{-2}$ M) at a platinum electrode in acetonitrile on a background of 0.1 M $NaClO_4$ at various rates of scanning of the potential (mV/s): 1) 40; 2) 20; 3) 40; 4) 80.

TABLE 1. Electrochemical Characteristics of the Alkaloids Anabasine, Cytisine, and Lupinine in Acetonitrile at a Platinum Electrode on a Background of a 0.1 M Solution of Na or Li Perchlorate at $C_{alk} = 5\cdot10^{-3}$ M

Alkaloid	Background	$E_{1/2}$, V	Order of the reaction	Apparent transport coefficient
Anabasine	$NaClO_4$	0,87	0,55÷0.60	0,30÷0.33
Lupinine	$LiClO_4$	0.68	0,58÷0,65	0,20÷0.25
Citisine	$NaClO_4$	0,50 (0,85)*	0.60÷0,65	0,25÷0,38

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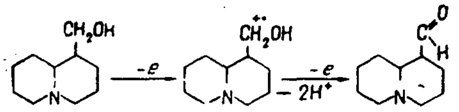
*The value of $E_{\frac{1}{2}}$ for the second wave is given in parentheses.

we determined the apparent transfer coefficient B_t, while the order of the alkaloid oxidation reaction was determined by the method described in [7] (Table 1).

The frational values of the parameters mentioned, which are preserved withina considerable interval of concentrations of the reacting substances, are characteristic for heterogeneous catalytic purposes taking place in adsorption layers on an inhomogeneous surface [8].

The preparative electrolysis at a platinum anode of acetonitrile solutions of anabasine and cytisine took place with the formation on the surface of the electrode of viscous resin-like products of undetermined structure, while the product of the electrooxidation of the alkaloid lupinine was lupinal, formed by the following scheme:



EXPERIMENTAL

Volt-ampere curves were taken on PU-1 and P-5827 M instruments with automatic recording. The working electrodes were wires or discs with a diameter of 1-1.5 mm fused into glass or pressed into Teflon. A platinum plate with an area of 1 cm^2 was used as the auxiliary electrodes.

All the potentials are given relative to a $Ag/AgNO_3$ (0.01 M) comparison electrode in acetonitrile. Reagents of kh.ch. ["chemically pure"] grade were used for preparing the working slutions; the cytisine and lupinine were purified by recrystallization from acetone and petroleum ether, and anabasine by vacuum distillation.

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ALKALOID SPECIOSEINE FROM Colchicum speciosum

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The fraction of weak bases from Colchicum speciosum Stev. (family Liliaceae) has yielded a new compound – specioseine. The structure of 10-demethylspeciosine has been established for this base by chemical and spectral methods.

The main alkaloids of the bulbs of showy autumn crocus are colchisine and colchamine, while the amount of speciosine is far smaller [1]. Among the minor alkaloids, 2-demethylcolchicine (alkaloid E), 3-methylcolchisine (C), N-formyl-N-deacetylcolchicine (B), 2-demethylcolchamine (S) [2, 3], colchameine [1], γ-lumicolchicine (J), N-methylcolchamine, 3-demethylcolchamine [4], and speciosamine [5] have been isolated. In addition, the presence of an unknown alkaloid with mp 215-217°C [1] and of unidentified minor alkaloids with a tropolone ring and without it have been reported [2, 4].

By the chromatographic separation of the alkali-soluble part of the weak-base fraction of the autumn crocus we have succeeded in isolating, together with speciosine, a new compound for which, on the basis of the results of a study of spectral characteristics and chemical transformations,. the structure of 10-demethylspeciosine has been established. By analogy with other alkaloids of autumn crocuses with an unmethylated tropolone hydroxy group (colchiceine, colchameine, etc.) we have called it speicoseine.

Specioseine, with the composition $C_{27}H_{29}O_6N$, mp 169-171°C and $[\alpha]_D$ – 78° (c 1.01; $CHCl_3$) has in its UV spectrum absorption maxima at 247 and 348 nm (log ε 4.51 and 4.39), which are characteristic for the tropolone alkaloids of autumn crocuses [6, 7]. Its IR spectrum contains absorption bands of a tropolone carbonyl group (1612 cm^{-1}), of tropolone and aromatic rings (1590 and 1495 cm^{-1}, respectively), of methylene and methoxy groups (1450, 2840, 2950, and 3000 cm^{-1}) and of hydroxy groups (3380-3530 cm^{-1}), which are characteristic of the cholchicine alkaloids [8].

With ferric chloride, aqueous and alcoholic solutions of specioseine gave an olive green coloration which did not change on acidification. This showed the presence of a free tropolone hydroxy group in it [9].

The PMR spectrum of specioseine showed the signals of all the aromatic and aliphatic protons and also those of the N-methyl and methoxy groups that are characteristic of speciosine [10], with the exception of one methoxy group.

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