THE ELECTROCHEMICAL EXTRACTION OF ALKALOIDS OF THE TROPANE GROUP FROM PLANT RAW MATERIAL

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UDC 547.944/945+541.138

Investigations have appeared in the literature on the electrochemical isolation of alkaloids from nux-vomica seeds, ipecacuanha root, thermopsis foliage, and cinchona bark [1]. "Electroopium" has been extracted by electrophoresis from poppy heads, and also narcotine and morphine from opium [2]. The electrolysis of aqueous alcoholic extracts has yielded veratrine from sabadilla seeds [3] and water-soluble alkaloids from the roots of valerian, mountain tobacco, and white mistletoe [4]. Seneciphylline has been obtained from mixed alkaloids, and tomatine from plant raw material [5, 6].

We have investigated the possibility of isolating alkaloids of the tropane group from aqueous and acid extracts of the leaves of Atropa belladonna (Z.), Datura stramonium (Z.), and Scopolia carniolica (obreru).

The amount of alkaloids in the extract and in the catholyte was determined by Khandsuren's method [7] by their extraction with dichloroethane from an alkaline medium and the subsequent conversion of the bases obtained into the hydrochlorides, which were back-titrated in the form of the free bases with hydrochloric acid using Methyl Red as indicator. In addition, the amounts of alkaloids in the catholyte were monitored spectrophotometrically [8] at λ_{max} 257 nm, the concentrations being found from a calibration curve.

The electrolysis of extracts from the leaves of belladonna and datura and from the roots of scopolia led to the separation in the catholyte of the tropane alkaloids, to the alkalization of the cathode space, and to a sharp change in the pH of the catholyte from 6 to 11 (Fig. 1). This pH change of the alkaloids may be considered an indirect indication of the passage of the alkaloids into the catholyte, as was confirmed by qualitative reactions for alkaloids.

The change of the pH of the catholyte in the alkaline direction opposes the accumulation of the alkaloids in the catholyte, and therefore to extract the alkaloids we used acidified solutions. No passage of the alkaloids into the catholyte without the use of electric current (dialysis) was observed, the reaction for alkaloids being negative.

The amount of alkaloids in the catholyte depends on the time of electrolysis and the current density. Experiments to investigate the influence of the current density on the degree of extraction of the alkaloids were performed in several series, solutions of sulfuric acid of various concentrations being used as the catholyte and the anolyte. Thus, the influence of the current density on the degree of isolation in the electrolysis of a belladonna extract (catholyte 2% H_2SO_4, temperature 20°C, graphite electrodes) was as follows:

Current density $D_c = A/m^2$	Amt. of alkaloids in extract, %	Deg. of extraction of alkaloids into catholyte, %
10	0.12	86
30	0.12	75
100	0.12	60

The experimental results show that with an increase in the current density the amount of alkaloids in the catholyte decreases. At high current densities the alkaloids are found to accumulate not only in the

Zaporozhe State Medical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 334-336, May-June, 1972. Original article submitted October 31, 1971.

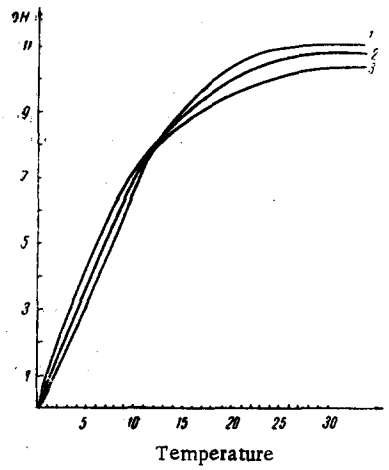

Fig 1

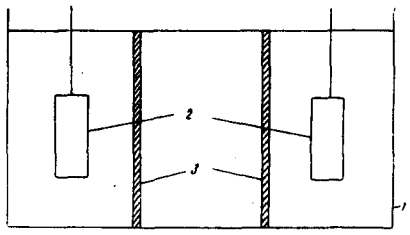

Fig. 2

Fig. 1. Dependence of the pH of the catholyte on the time of electrolysis at $D_C = 10$ A/m^2: 1) belladonna extract; 2) datura extract; 3) scopolia extract.

Fig. 2. Sketch of the electrodialyzer: 1) cell; 2) electrodes; 3) semipermeable membranes.

catholyte but also in the anolyte during electrolysis. In the plants, the alkaloids are present mainly not in the form of the bases (in the free state) but in the form of salts with various organic acids. The salts of the alkaloids, which are monoacid bases, dissociate electrolytically as binary electrolytes. This explains the considerable rate of separation of the alkaloids into the catholyte under the action of a direct electric current. However, in the electrolysis of aqueous solutions of various salts and alkaloids the cathode layer is enriched in hydroxyl ions, which may cause a reversal of the charge of the alkaloid cation to form an alkaloid anion, which apparently explains the migration of the alkaloid to the anode.

Consequently, the extraction of alkaloids takes place at low current densities of from 10 to 30 A/m^2 with the simultaneous acidification of the cathode space.

With an increase in the time of electrolysis, the amount of alkaloids in the catholyte increases; thus, the amount of alkaloids extracted at a current density of 30 A/m^2 during each successive hour from the beginning of the experiment was 40.5, 68, and 86%. A similar relationship was obtained in the isolation of the alkaloids from the datura and scopolia extracts.

The alkaloids of the tropane group isolated into the catholyte at high current densities do not undergo chemical changes. Control experiments were performed on the electrolysis of pure solutions of atropine sulfate and scopolamine hydrobromide under the conditions of a three-chamber cell with various current densities. The results of paper chromatography showed the presence of a single spot, the chromatographic behavior of which (R_f 0.69 and coloration) was identical with that of atropine sulfate and scopolamine hydrobromide.

EXPERIMENTAL

Electrolysis was performed in a 300-cm^3 three-chamber cell with separation of the cathode and anode spaces (Fig. 2). The extract under investigation was placed in the central part of the cell, the cathode and anode spaces being separated from it by a parchment semipermeable membrane and being filled with solutions of sulfuric acid (from 0.5 to 4%) or distilled water. The electrodes were lead and graphite plates with a surface of 100 cm^3. The source of direct current was a type VSA-5A selenium rectifier. The pH values were measured by a type LPM-60 pH-meter. The experiments were performed at a current density of from 10 to 100 A/m^2, a voltage of 10-35 V, and a temperature of 20°C.

The presence of alkaloids in the catholyte was determined by the usual alkaloid reagents (the Wagner and Dragendorff reagents, and a 2% solution of tungstosilicic acid). The qualitative composition of the alkaloids was studied by paper chromatography with the butan-1-ol–acetic acid–water (4 : 1 : 2) system as

the mobile phase. The descending method was used on Filtrak No. 1 paper at 20°C. The chromogenic reagent was modified Dragendorff's reagent. Aqueous solutions of atropine sulfate and scopolamine hydrobromide were used as "markers."

SUMMARY

1. Alkaloids of the tropane group have been isolated from Atropa belladonna, Datura stramonium, and Scopolia carniolica by the electrochemical method.

2. The amount of alklaloids passing into the catholyte depends on the pH of the catholyte, the current density, and the time of electrolysis.

LITERATURE CITED

1. S. Kh. Babich, Zh. Prikl. Khim., 20, 652 (1947).
2. E. I. Ginzburg and N. I. Gavrilov, Zh. Prikl. Khim., 20, 120 (1947).
3. H. Auterhoff, Arzneimittel. Forsch., 3, 530 (1953).
4. G. K. Nikonov, Aptechnoe Delo., 1, 3 (1955).
5. T. P. Dorosh and V. S. Alekseev, Farm. Zh., 1960, No. 6, 44.
6. T. P. Dorosh and E. A. Tukalo, Farm. Zh., 1961, No. 1, 44.
7. S. Khandsuren, B. V. Nazarov, and V. V. Petrenko, Farmatsiya, (1971).
8. F. E. Kagan and G. A. Vaisman, Farm. Zh., 1971, No. 1, 32.