5. A. Guggisberg, M. Hesse, H. Schmid, H. Bohm, H. Ronsch, and K. Mothes, Helv. Chim. Acta, 50, 621 (1967).
6. M. Maturova, D. Pavlaskova, and F. Šantavý, Planta Medica, 14, 22 (1966).
7. S. Pfeifer and H. Dohnert, Pharmazie, 23, 585 (1968).
8. L. Dolejš and V. Hanuš, Tetrahedron, 23, 2997 (1967).
9. M. Shamma, J. A. Weiss, S. Pfeifer, and H. Dohnert, Chem. Commun., No. 4, 212 (1968).
10. M. Shamma, J. L. Moniot, W. K. Chan, and K. Nakanishi, Tetrahedron Lett., No. 44, 4207 (1971).
11. H. Ronsch, Tetrahedron Lett., No. 43, 4431 (1972).
12. S. Pfeifer and I. Mann, Pharmazie, 23, 82 (1968).
13. I. Lalezari, A. Shafiee, and P. Nasseri-Nouri, J. Pharm. Sci., 62, 1718 (1973).
14. W. Klotzer, S. Teitel, and A. Brossi, Helv. Chem. Acta, 54, 2057 (1971).
15. R. H. F. Manske and R. G. A. Rodrigo, The Alkaloids, Academic Press, New York, Vol. XVIII (1981), p. 257.

ELECTROCHEMICAL EXTRACTION OF ALKALOIDS FROM EPHEDRA HERBAGE

A. M. Gazaliev, S. D. Fazylov, and M. Zh. Zhurinov

UDC 547.944/945 + 541.138

The process of extracting ephedra herbage in a constant electric field has been studied. It has been shown that the application of an electric field considerably accelerates the isolation of the alkaloid molecules from the cellulose of the plant raw material. The main kinetic characteristics of the electroextraction of the total alkaloids as functions of various factors have been obtained.

The existing method of obtaining the alkaloid ephedrine, which is widely used in medical practice, presupposes the extraction of the alkaloids with hot water in a diffusion battery on the countercurrent principle. The disadvantages of this method include its lengthiness, its high temperature, the incomplete extraction of the desired substances, and others.

Our aim was to develop a more effective electrochemical method of extracting medicinal substances from ephedra herbage. Methods of extracting certain natural compounds are known that are based on the principle of the electromigration of polarized molecules. Veratrine is isolated by the electrolysis of an aqueous alcoholic extract of sabadilla seeds [1], "electropium" is isolated from poppy heads, and narcotine and morphine are isolated from opium by electrophoresis [2]. The electrochemical method has permitted a 20% increase in the yield of scopolamine from Datura stramonium and a considerable shortening of the time of extraction [3].

We have investigated the herbage of Mongolian ephedra (Ephedra equisetina Bunge) with a moisture content of 10.6% (alkaloid content 1.72%). For the extraction of the alkaloid, the ephedra was ground to 0.5 and 1-2 mm [4, 5]. As can be seen from the curves of the dependence of the yield of extractable alkaloids on various factors, two periods were observed in the extraction process – fast and slow extraction (Fig. 1). The relative amount of substances obtained in the period of fast extraction (elution coefficient) was 48-49% for particles of raw material with a size of 0.5 mm, and 10-15% for the 1-2 mm fraction. While the rate of the process in the period of rapid extraction depends on the hydrodynamic conditions, in the period of slow extraction it depends on the rate of diffusion of the alkaloids from the cell tissue of the plant raw material. There are a number of factors that increase the rate of diffusion of the substances from the raw material: a rise in the temperature, the use of ultrasound, the addition of surface-active agents, etc. [5].

Institute of Organic Synthesis and Coal Chemistry, Kazakh SSR Academy of Sciences, Karaganda. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 862-864, November-December, 1987. Original article submitted February 25, 1987; revision submitted May 25, 1987.

 0009-3130/87/2306-0718$12.50

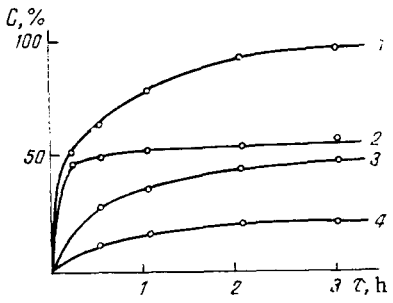

Fig. 1

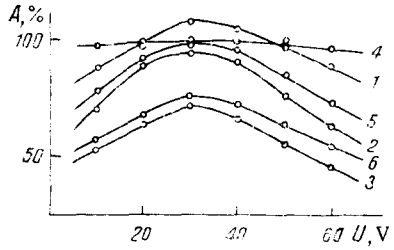

Fig. 2

Fig. 1. Kinetic curves of the passage of the combined alkaloids into an extract: 1, 3) on the imposition of an electric field (U = 30 V); 2, 4) without the imposition of an electric field (U = 0 V). Size of the particles of raw material, mm: 1, 2) 0.5; 3, 4) 1-2. Liquor ratio – 0.05.

Fig. 2. Dependence of the yield of alkaloids (1-3) and of the degree of extraction (4-6) on the voltage for a time of electrolysis of 3 h. Liquor ratio: 1, 4) 0.05; 2, 5) 0.10; 6) 0.20.

Figure 1 shows the curves of the kinetics of the extraction of the total alkaloids of ephedra as a function of the time with the imposition of an electric field and without it. Where an electric field was imposed, the yield of alkaloids rose sharply, and at a given time of extraction it was possible to raise the yield of alkaloids by 20-25%. At the same time, the yield of alkaloids was greatest from the more highly ground raw material. Since the alkaloids, which are present in the plants in the form of salts of various acids, undergo dissociation, in an electric field their migration from the internal pores into the bulk of the solution is considerably accelerated. This can explain the increase in the yield of alkaloids on the imposition of an electric field.

We also studied the influence of a constant electric field on the extraction of the alkaloids from the finely ground raw material (≤0.5 mm – 89-90%). Preliminary experiments had shown that the degree of extraction and the yield of alkaloids were greatly affected by the voltage on the bath, the ratio of raw material to water (liquor ratio), the pH of the medium, and the temperature of the solution. In an investigation of the influence of these factors on the extraction process, extremal relationships were obtained in all cases.

The imposition of an electric field (20-60 V) greatly increased the degree of extraction (from 40-50 to 90-100%). However, when an electroextractor without a diaphragm was used the yield of alkaloids as a function of the conditions of extraction varied between fairly wide limits, apparently because of a transformation and resinification of part of the alkaloids on the electrodes. Furthermore, because of the electrochemical breakdown of the electrodes, particularly the graphite anode, the extract was contaminated. The main series of experiments was therefore performed in an extractor with a ceramic diaphragm impreganted with water glass which practically prevented the passage of the molecules of organic substances to the electrodes.

The results of the investigations (see Fig. 2) showed that at all the values of the liquor ratio that were selected the maximum yield of alkaloids was obtained at a voltage of 25-35 V (which corresponds to i = 0.2-0.5 A/dm^2). In a weaker electric field, the rate of migration of the alkaloid molecules was insufficiently high, and at U > 35 V the yield of alkaloids fell. This was apparently connected with the penetration of the alkaloid molecules into the electrode spaces under the action of the stronger electric field and their electrochemical transformation into other products at the anode. During electrolysis, the layer adjacent to the cathode was enriched with hydroxyl ions, which could cause charge reversal of the alkaloid cation to give an alkaloid anion, and this apparently explains the migration of the alkaloid to the anode.

A rise in the temperature of the solution to 60°C on the whole led to an increase in the yield of alkaloids, but at high temperatures the extract was contaminated with accompanying substances (resins, tannin substances, etc.) which complicated the extraction of the

alkaloids from the solution. The main series of experiments was therefore performed at room temperature. The duration of the electroextraction of alkaloids must be selected experimentally as a function of the degree of grinding of the plant raw material and a number of other factors.

Thus, the optimum conditions for the electrochemical extraction of the ephedra alkaloids – ephedrine and pseudoephedrine – in an electrolyzer with a ceramic diaphragm are the following: potential difference between the electrodes – 30 V; time of electroextraction – 3 h; liquor ratio – 1:15; temperature of the solution – 20-23°C; graphite electrodes.

EXPERIMENTAL

Electrolysis was performed in glass electrolyzers with a capacity of 1-3 liters without a diaphragm and with a ceramic diaphragm. The electrodes were graphite rods with a working surface of 0.6-1.5 dm^2. The electrolyzers were fed from a VSA-111 K rectifier. The raw material was ground in an apparatus of the Ekstsel'sier type. The experiments were performed at a potential difference between the electrodes of from 5 to 70 V in the range of temperatures of 15-50°C. The amount of alkaloids in the extract was determined by Massagetov's method [6].

SUMMARY

1. The alkaloids of ephedra herbage have been isolated by electroextraction. The influence of the conditions of electroextraction on the yield of total alkaloids in the aqueous solution has been investigated.

2. It has been shown that the imposition of an electric field considerably accelerates the migration of the alkaloid molecules from the plant raw material.

LITERATURE CITED

1. H. Auterhoff, Arzreim. Forsch., 3, 530 (1953).
2. E. I. Ginzberg and N. I. Gavrilov, Zh. Prikl. Khim., 20, 120 (1947).
3. L. I. Skorkin and N. G. Bozhko, USSR Inventors' Certificate No. 158281; Byull. Izobr., No. 21, 16 (1963).
4. V. L. Litvinov and P. P. Vetrov, Khim.-farm. Zh., No. 4, 465 (1982).
5. V. D. Ponamarev, The Extraction of Drug Raw Material [in Russian], Meditsina, Moscow (1976), p. 34.
6. P. S. Massagetov, Farmats. Farmakol., No. 6, 17 (1938).