direct introduction of the sample at 90-100°C and at an ionizing voltage of 40 V. The accurate masses of the ions were measured on a Varian MAT-311 mass spectrometer.

Isolation and Separation of the Combined Alkaloids. The combined ether-soluble alkaloids [3] were chromatographed on a column of silica gel (1:20). Elution of the alkaloids with petroleum ether yielded 75 mg of phenyl-β-naphthylamine and a red mixture of two bases. A benzene–chloroform (1:1) eluate yielded 0.16 g of cinnamamide. The mixture of two bases was separated by preparative TLC on a fixed layer of silica gel in the benzene–chloroform (5:3) system, giving 16 mg of (II) with mp 185-186°C and 13 mg of (III) with mp 177-179°C.

SUMMARY

The qualitative and quantitative changes in the composition of the combined bases in *Reseda luteola* during the vegetation periods have been studied. From the epigeal part of the plant we have isolated cinnamamide and two new alkaloids: lutine and lutinine. A study of the spectral characteristics and the mechanism of fragmentation has shown that lutine has the structure of 2-anilino-1,4-naphthoquinone and lutidine that of 4-anilino-2-phenylamino-1,2-dihydronaphthalen-1-one.

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THE ELECTROCHEMICAL EXTRACTION OF ALKALOIDS OF THE PYRROLIZIDINE SERIES FROM PLANT RAW MATERIAL. I

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UDC 547.944/945+541.138

The alkaloids of the pyrrolizidine series — platyphylline, seneciphylline, and their N-oxide forms — consist of complex cyclic diesters of the bicyclic base heliotridane and dicarboxylic acids and are widely represented in various species of Cruciferae [1].

As pharmacological and clinical investigations have shown, platyphylline possesses valuable atropine-like properties, and it is used as a spasmolytic and hypotensive agent. Seneciphylline can be used for the synthesis of curaremimetic compounds [2].

A characteristic feature of alkaloids of the pyrrolizidine series is the presence in the plant raw material of the N-oxide forms, the amounts of which in different species of *Senecio* depend on the growth site and the date of collection and range between 80 and 93% [3]. The isolation of the N-oxide alkaloids and their conversion into the reduced form is an important step in the production of the alkaloids, since this considerably raises the yield of the main product.

At the present time, the optimum conditions for the isolation of the N-oxide alkaloids of *Senecio* are connected with the process of their extraction by dichloroethane in the presence of glucose and with the process of the reduction of a sulfuric acid or hydrochloric acid

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Zaporozh'e Medical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 831-834, November-December, 1977. Original article submitted July 5, 1977.

0009-3130/77/1306-0699$07.50

extract with zinc dust [4]. Furthermore, the possibility has been investigated of investigating redox polymers for the reduction of the N-oxides of the alkaloids of an ethanolic eluate from *Senecio platyphylloides* [5].

We have studied the possibility of the electrochemical isolation of the alkaloids of the pyrrolizidine series from plant raw material. We have investigated tinctures and extracts of the epigeal part of *Senecio platyphylloides*, family Compositae.

The amounts of alkaloids in the initial tincture and extract were determined by acid–base titration after the reduction of the N-oxide forms with zinc dust in sulfuric acid. The total alkaloid content in a tincture was 1.1 g/liter (0.11%) and in an extract 5.4 g/liter (0.54%).

The catholyte obtained after the electrodialysis of an infusion of the herb *Senecio platyphylloides* formed a clear liquid, and that obtained after the electrodialysis of an extract formed a liquid with a faint yellowish tinge. Qualitative reactions for alkaloids with a 2% solution of tungstosilicic acid gave a voluminous reaction for alkaloids. The results of the thin-layer chromatography of the catholyte obtained showed the presence of two distinct spots identical in chromatographic behavior and coloration with those of platyphylline and seneciphylline ($R_{f_{\text{plat}}}$ 0.45, $R_{f_{\text{senec}}}$ 0.57). No other spots were observed on a thin-layer chromatogram.

In a quantitative determination of the alkaloids in the catholyte, zinc dust was not used in the course of the analysis, since electrodialysis led not only to the isolation of the alkaloids but also to the reduction of their N-oxide forms in the electrode process. There were no N-oxide forms of the alkaloids in the catholyte.

The amount of alkaloids in the catholyte was determined by thin-layer partition chromatography followed by the spectrophotometric analysis of the eluate at λ 218 nm [6].

Experiments on the electrodialysis of an infusion and extract of the herb *Senecio platyphylloides* were performed in several series according to the magnitude of the current, the time of electrodialysis, and the pH of the catholyte. The experimental results on the influence of the current on the degree of isolation of the alkaloids are given below (volume of the catholyte 50 ml, temperature 25°C; catholyte a 2% solution of H_2SO_4):

	Current density, A/m^2	Amount of alkaloids in the initial material, g/liter	Time of electrodialysis hours	Degree of isolation of the alkaloids, %
Tincture	200	1,1	5	68,0
	400	1,1	2,5	74,1
	800	1,1	1,25	84,0
Extract	200	5,4	5	65,4
	400	5,4	2,5	72,0
	800	5,4	1,25	82,0

Thus, the amount of alkaloids in the catholyte rises with an increase in the current. However, performing the process at higher current densities causes the overheating of the electrolyte, leading to the necessity for controlling the temperature conditions. The time of the process for a given current was determined experimentally from the results of a study of the dependence of the amount of total alkaloids isolated on the time (Fig. 1). It corresponded to a negative reaction of the dialyzate with a 2% solution of tungstosilicic acid. The amount of electricity necessary for the complete extraction of the alkaloids was 1 A • h; for example, at a current of 0.4 A the time of electrolysis was 2.5 h and the degree of isolation of the alkaloids was 74.1%.

As observed previously [6], during electrodialysis the catholyte becomes alkaline through the electrode reaction and the accumulation of the alkaloids, and therefore the process was performed at a controlled pH not exceeding 5.5 in order to prevent the precipitation of the alkaloids.

Thus, the optimum parameters for obtaining the combined alkaloids (platyphylline and seneciphylline) from the herb *Senecio platyphylloides* under the conditions of electrodialysis are a current strength of 0.8 A (current density 800 A/m^2), a time of electrodialysis of 1 h

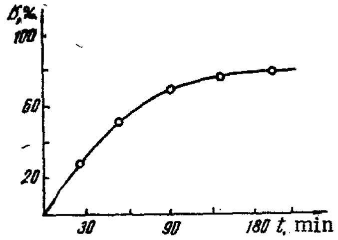

Fig. 1. Dependence of the degree of isolation of the total alkaloids on the time of electrodialysis (tincture of the herb *Senecio platyphylloides*); current 0.4 A, catholyte a 2% solution of sulfuric acid: B) degree of isolation, %; t) time of electrodialysis, min.

25 min (amount of electricity 1 A • h), and a catholyte consisting of a 2% solution of sulfuric acid.

EXPERIMENTAL

Preparation of the Tincture. The air-dry comminuted herb collected in the flowering phase (200 g) was covered with 70% ethanol (2 liters) and steeped at room temperature for 2 days. The extract obtained was poured off, and the raw material was pressed out and washed with 70% ethanol until the total volume of tincture was 2 liters. The tincture was left for a day and was then filtered, after which it was used for electrodialysis.

Preparation of an Extract. The air-dry plant raw material (100 g) was exhaustively extracted with 70% ethanol (1:10); the 300 ml of ethanolic extract obtained was filtered and evaporated in vacuum to a volume of 250 ml. This extract was used for dialysis.

Electrodialysis. The process was performed in a three-chamber cell by a method that we have described previously [6]. The source of constant current was a type VSA-5A selenium rectifier, and the current strength was 0.20-0.80 A. The current density, calculated from the visible surface of the cathode, was 200-800 A/m^2. The time of electrodialysis was determined from the negative reaction of the dialyzate with a 2% solution of tungstosilicic acid. The pH of the catholyte was monitored by a type LPM-60M pH-meter.

Chromatographic Investigations. For thin-layer chromatography we used type KSK domestic silica gel previously washed free from iron salts. A thin layer of a suspension consisting of 5.2 g of silica gel, 0.3 g of medicinal gypsum, and 13 ml of distilled water was deposited on a degreased 20 × 15 cm glass plate. The plates with the deposited silica gel layer were first dried in the air for 12 h and then, to activate the surface, in a drying chest at 100 ±0.02°C for 2 h.

The following solvent systems were used: benzene—ethyl acetate—diethylamine (70:20:10), and chloroform—acetone—diethylamine (80:20:5). The length of run of the solvent from the starting line was 10 cm. The chromatograms were revealed with modified Dragendorff reagent, aqueous and ethanolic solutions of platyphylline, seneciphylline, and sarracine being used as "markers" [8].

QUANTITATIVE DETERMINATION. A 50-ml sample of the tincture was evaporated to dryness in vacuum, the residue was dissolved with heating in 15 ml of distilled water, and 5 ml of 5% sulfuric acid and 0.5 g of zinc dust were added. Reaction was performed for an hour with periodic stirring, and then the mixture was filtered and was brought to pH 9 with a 25% solution of ammonia. The combined alkaloids were extracted with chloroform until the reaction with 2% tungstosilicic acid was negative. The chloroform extracts were dried over anhydrous sodium sulfate, filtered, and evaporated to dryness. The residue was dissolved in 10 ml of ethanol, 10 ml of a 0.02 N solution of hydrochloric acid was added, and the excess of acid was back-titrated with a 0.02 N solution of caustic soda (with Methyl Red as indicator).

SUMMARY

1. Alkaloids of the pyrrolizidine series (platyphylline and seneciphylline) have been isolated by an electrochemical method from the herb *Senecio platyphylloides*. The amount of alkaloids extracted into the catholyte depends on the current strength and the time of electrodialysis.

2. It has been established that the N-oxide forms of the alkaloids are reduced during the dialysis process.

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ALKALOIDS OF *Corydalis gortschakovii*

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UDC 547.943

Continuing the separation of the combined alkaloids of *Corydalis gortschakovii* collected in the upper reaches of the R. Pskem in the flowering period, by chloroform extraction we have obtained 0.66% (0.59% of ether fraction and 0.07% of chloroform fraction) of combined alkaloids. Protopine, d-bicuculline, *l*-adlumine, sendaverine, and isocorydine have previously been isolated from this plant collected at the same site [1]. The combined ether-soluble alkaloids were separated into phenolic and nonphenolic fractions. The nonphenolic fraction of the total alkaloids yielded isocorydine, corydine, *l*-adlumidine, and d-bicuculline. The mother liquor after the separation of these alkaloids was chromatographed on a column of silica gel. Elution with benzene and with benzene–methanol yielded isocorydine, d-bicuculline, stylopine, protopine, *l*-adlumine, and gortschakoine [2].

The combined ether-soluble phenolic bases were separated according to basic strength into 13 fractions. The first fraction by chromatography on a column of silica gel yielded juziphine [3] and a base with mp 215-216°C, and the second fraction gave a base with mp 197-198°C; fractions 6-10 yielded sendaverine. The phenolic chloroform-soluble alkaloids were chromatographed on a column of silica gel, and domesticine and isoboldine were isolated. On treatment with methanol, the combined chloroform-soluble bases yielded corytuberine.

The base with mp 215-216°C, composition $C_{18}H_{21}NO_4$, is sparingly soluble in organic solvents. UV spectrum: λ_{max} 232, 284 nm (log ε 4.28, 4.04). The mass spectrum shows a weak peak of the molecular ion with m/e 315, and also the peaks of ions with m/e 299, 298, 297, 178, 150, 135, 121 (100%), and 107. The NMR spectrum of the base has the following signals: two three-proton singlets at 3.50 and 3.55 ppm from two methoxy groups, one-proton singlets at 6.29 and 6.43 ppm (para aromatic protons), and two-proton doublets at 6.70 and 7.09 ppm (J = 8 Hz, two pairs of equivalent ortho aromatic protons). There are a two-proton singlet at 4.41 ppm, one-proton doublets at 4.15 and 4.35 ppm (J = 14 Hz), and also two two-proton multiplets at 3.61 and 2.93 ppm. The spectral characteristics given permit this base to be assigned to the benzyltetrahydroisoquinoline alkaloids of the sendaverine type. The poor solubility of the base in organic solvents, the low intensity of the peak of the molecular

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Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 834-836, November-December, 1977. Original article submitted August 23, 1977.

0009-3130/77/1306-0702$07.50