A POLAROGRAPHIC INVESTIGATION OF THE ALKALOIDS OF Ungernia

A. D. Volodina, E. K. Dobronravova,
and T. T. Shakirov

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We have previously [1] reported the use of the polarographic waves of galanthamine and narwedine for the quantitative determination of these alkaloids in plant material. In the present paper we give the results of a further study of the electrochemical properties of nine alkaloids of Ungernia [2] in order to determine the interrelationship between polarographic behavior and structure.

Characteristic of all the alkaloids studied is the formation of catalytic hydrogen waves (see Table 1), the limiting current of which is proportional to the concentration within certain limits and can be used for analytical purposes. Thus, for galanthamine a linear dependence of the current on the concentration was found in the range from $4 \cdot 10^{-4}$ to $1 \cdot 10^{-5}$ M in 0.01 N $(C_2H_5)_4NOH$ and from $1 \cdot 10^{-4}$ to $1 \cdot 10^{-6}$ M in 0.01 N $(C_2H_5)_4NI$. The nature of the "current versus concentration" curve showed that the catalyst was adsorbed on the mercury drop. With a rise in the concentration of the supporting electrolyte, a fall in the catalytic current was observed which is probably due to the displacement of the alkaloid from the surface of the electrode by the surface-active tetraalkylammonium molecules [3]. With a rise in the concentration of the organic solvent (ethanol), the limiting catalytic current decreases. By varying the conditions of polarography we found the optimum conditions for the quantitative determination of alkaloids from the catalytic current [1]. We consider this direction to be promising, particularly for those alkaloids the molecules of which contain no polarographically active groups.

In addition to catalytic waves, some Ungernia alkaloids showed diffusion waves.

Of the alkaloids of the galanthamine group we studied narwedine and galanthamine (see Table 1). The similarity of the chemical properties of the alkaloids of this group to those of the morphine group [4] enabled us to compare their electrochemical properties. Galanthamine, which has an isolated double bond that is readily hydrogenated in the presence of a platinum catalyst, like morphine and codeine [5], is not reduced at a dropping mercury electrode. Synthetic dihydrogalanthamine, like galanthamine itself, catalyzes the liberation of hydrogen at the cathode. Narwedine forms a distinct diffusion wave (see Table 1). By polarographic microcoulometry [6] we found that the number of electrons involved was two. Consequently, only the carbonyl group undergoes polarographic reduction and the reaction product is the corresponding carbinol. The correctness of this scheme was confirmed by a study of the UV spectrum of the product of the electrolysis of narwedine at a controlled potential: its spectrum showed a maximum at 289 nm which is characteristic for the UV spectra of galanthamine. The polarographic reduction of an oxo group conjugated with a double bond, as in narwedine, is also characteristic of sinomenine [7], thebainone, and hydroxythebainone [5]. The four-electron reduction (carbonyl group and double bond) observed for codeinone and hydroxycodeinone is possible only if the oxo group is conjugated with a double bond and the oxygen bridge between rings A and C [5]. The absence of such conjugation in narwedine is responsible for the reduction of the carbonyl group alone.

Of the alkaloids of the lycorenine group, hippeastrine, ungerine, and unsevine showed diffusion waves (see Table 1). By the microcoulometric and pilot-ion method [8] we found the numbers of electrons taking part in the reaction was found for hippeastrine and ungerine and two for unsevine. In view of the chemical properties of these alkaloids [9], it was assumed that the reduction takes place to tetrahydro derivatives and is accompanied by the cleavage of the δ-lactone ring. In actual fact, the UV spectrum of the product of electrolysis of hippeastrine at a controlled potential showed, instead of the three maxima at 226, 268, and 306 nm, only one at 280 nm. The mechanism of the electrode reaction was confirmed by comparison with the spectrum of synthetic tetrahydrohippeastrine.

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TABLE 1. Polarographic Indices of Ungernia Alkaloids and Their Derivatives

Name	C =0.01M in 0.1 N $(C_2H_5)_4NOH$; 80 % C_2H_5OH		C = 0.001 M, 0.01 N $(C_2H_5)_4NOH$; 10 % C_2H_5OH	
	diffusion wave		catalytic wave	
	$E_{1/2}$, V	I_d, μA	$E_{1/2}$, V	I, μA
Galanthamine	—	—	—2,05	18,83
Dihydrogalanthamine	—	—	—2,10	26,31
Lycorine	—	—	—2,00	1,31
Dihydrolycorine	—	—	—2,10	37,70
Narwedine	—1,6	0,75	—2,05	18,85
Pancratine	—	—	—2,05	1,09
Tazettine	—	—	—1,96	1,74
Hordenine	—	—	—2,75	38,50
Hippeastrine	—1,4	1,54	—2,30	1,60
Ungerine	—1,4	1,50	—2,30	1,60
Unsevine	—1,4	0,75	—2,30	1,60
Hexahydroungerine	—	—	—2,60	11,60

EXPERIMENTAL

The experiments were performed on an LP-55A polarograph. The characteristics of the capillary at b_{Hg} 50 cm were: m 1.03 mg · sec^{-1}, t = 4.0 sec in 1 N KCl. An electrolyzer with an internal anode was used and the temperature of the determinations was 25 ±0.5°C. The support was $(C_2H_5)_4NI$ purified as described by Supin [10], $(C_2H_5)_4NOH$, and Britton–Robinson buffer solutions. Electrolysis at a controlled potential was performed by Lingane's method [11].

SUMMARY

In the investigation of the polarographic behavior of nine ungerine alkaloids, it was found that the reduction of narwedine forms the corresponding carbinol, while the reduction of hippeastrine, ungerine, and unsevine forms the corresponding tetrahydro derivatives. The catalytic hydrogen waves that all the ungerine alkaloids form can be used for analytical purposes.

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