## SUMMARY

Four new cycloartane glycosides have been isolated from a methanolic extract of Thalictrum squarrosum Stephan ex. Willd. The following structures have been established for them: squarroside A1 (I) — (21R, 22S, 23R)-3β-(β-D-glucopyranosyloxy)-21α-methoxy-21,23-epoxycycloart-24-ene-22β,30-diol; squarroside A2 (II) is the (21S)-epimer of compound (I); squarroside B1 (III) is (21R, 22S, 23R)-3β-[O-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyloxy]-21α-methoxy-21,23-epoxycycloart-24-ene-22β,30-diol; and squarroside B2 (IV) is the (21S)-epimer of compound (III).

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# ANODIC BEHAVIOR OF EPHEDRINE AT SOLID ELECTRODES

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The electrooxidation of the alkaloid ephedrine at solid electrodes in a wide range of concentrations and pH values of solutions has been studied by the methods of potentiodynamic voltammetric curves, preparative electrolysis, and quantum-chemical calculations by the SCF MO LCAO method in the MINDO/3 approximation. A quantitative basis has been given for the sequence of stages in the electrooxidation of ephedrine proposed previously by the authors of one of the cited papers. Good agreement has been established between the values found theoretically and experimentally.

In electrochemical methods of extracting alkaloids from plant raw materials [1, 2] a large role is played by the choice of the material of the electrode and the nature of the medium. Continuing investigations on the electrochemistry of ephedrine [3], we have studied its electrochemical oxidation at platinum, graphite, and vitreous carbon in Britton-Robinson aqueous buffer solutions with various pH values [4].

As the results of the experiments have shown, the voltammetric curves of the oxidation of ephedrine have the form of distinctly expressed current maxima, the greatest value of which is observed in an alkaline medium. The nature of the effective oxidation curve depends on the material of the electrode (Fig. 1). The electrooxidation of ephedrine on platinum takes place with greater difficulty than on graphite and on vitreous carbon electrodes. On the voltammetric curves taken in more concentrated solutions of ephedrine ($C > 2 \cdot 10^{-3}$ M) at a graphite electrode a second electrode wave appears (Fig. 1c). This shows the further electrooxidation of the products of the initial oxidation of ephedrine. The treatment of the curves by Semerano's criterion [5] showed in all the solutions studied a linear relationship between the peak current and the square root of the rate of scanning the potential, which is characteristic for diffusion processes. However, such a relationship may also be observed in a number of other cases; for example, on the slow transfer of charge or on desorption of a primary oxidation product [6]. The values of $(\partial \log i/\partial \log v)_{c,T}$ calculated from these

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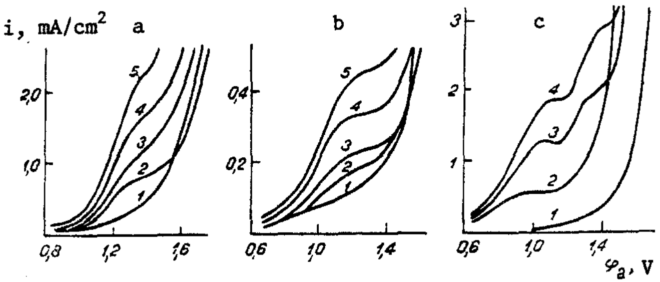


Fig. 1

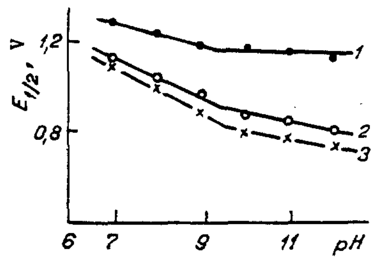


Fig. 2

Fig. 1. Voltammetric curves of the in vitro oxidation of ephedrine in Britton–Robinson universal buffer solution with pH 9.0; a and b) at $C_{eph} = 1 \cdot 10^{-3}$ M and various rates of scanning of the potential, mV/sec: 1, 4) 40; 2) 8; 3) 20; 5) 80; c) at various concentrations of ephedrine, M: 1) 0; 2) $1 \cdot 10^{-3}$; 3) $2 \cdot 10^{-3}$; 4) $5 \cdot 10^{-3}$. Rate of scanning – 40 mV/sec: a) on platinum; b) on vitreous carbon; c) on graphite.

Fig. 2. Dependence of $E_1/_2$ for the oxidation of ephedrine ($1 \cdot 10^{-3}$ M) on the pH of the universal buffer solution. Rate of scanning of the potential 40 mV/sec: 1) on platinum; 2) on vitreous carbon; 3) on graphite.

relationships are in the interval from 0.40 to 0.50 on graphite and vitreous carbon and from 0.75 to 0.80 on platinum. The first case is characteristic for processes with mixed control, i.e., for reactions the rates of which are limited by diffusion and by retarded discharge, while the second (Pt) corresponds to processes with kinetic control. The apparent transfer coefficient β was determined from a graph of the relation E, log $[i/(i_d - i)]$. On platinum it was 0.28, and on graphite and vitreous carbon 0.25 and 0.20, respectively. These results confirm the assumption made above.

Depending on the pH of the solution, alkaloids containing hydroxy and amino groups can exist in it in various forms: as a neutral molecule, a cation, or an anion. In view of this, it may be expected that the potential of the oxidation of ephedrine will depend on the pH of the medium. It can be seen from Fig. 2 that with a rise in the pH of the medium $E_{1/2}$ shifts into the cathodic region of potentials. In the pH range of 6 to 9, this relationship has a linear nature with slopes of 50, 80, and 90 mV/pH for platinum, vitreous carbon, and graphite, respectively. This shows the potential-determining role of the deprotonation of the ephedrine after the abstraction of the first electron.

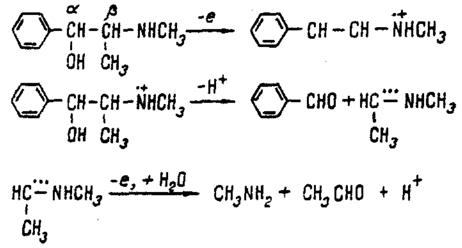
In order to establish the theoretically possible direction of the electrooxidation process, we made a quantum-chemical calculation of the ephedrine molecule with the partial optimization of the geometry of the molecule of the initial alkaloid by the MINDO/3 program [7]. Conformational analysis of the molecule under investigation permitted its spatial structure to be refined and information to be obtained on the distribution of reaction centers in it.

Below, we give the bond orders in the molecule and in the radical cation of ephedrine (not all the values of the bond orders are given but only those that determine the occurrence of the process):

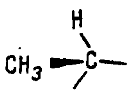
| Bond | Molecule | Radical cation |
|---|---|---|
| $C_\alpha - C_\beta$ | 0.914 | 0.748 |
| $C_\alpha - O$ | 0.993 | 1.028 |
| $O - H$ | 0.878 | 0.849 |
| $C_\beta - N$ | 0.956 | 1.046 |

Thus, it follows from the results of the calculations that the weakest carbon-carbon bond in the ephedrine molecule is the $C_\alpha - C_\beta$ bond (bond order 0.914), which should become the main reactive fragment of the molecule in the electrooxidation process. This hypothesis was confirmed by an analysis of the results of quantum-chemical calculations of the radical cation formed in the first stage of the electrooxidation of the ephedrine molecule by the detachment of an electron from the nitrogen atom [8]. This led to a considerable weakening of the $C_\alpha-C_\beta$ bond in the radical cation (bond order 0.748), while the $C_\alpha-O$ and $C_\beta-N$ bonds became stronger (bond orders 1.028 and 1.046, respectively).

Thus, on the basis of theoretical calculations of the ephedrine molecule and the corresponding intermediates of the first act of electrooxidation it is possible to suggest the following scheme of the process:



The intermediates formed as the results of the cleavage of the $C_\alpha-C_\beta$ bond then lead to benzaldehyde and a biradical. As calculation showed, the formation of the singlet biradical is energetically more favorable ($\Delta H_f$ = 225.586 kcal/mole, while $\Delta H_f$ for the triplet state is 242.920 kcal/mole). From the values of $\Delta H_f$ given for the biradical its low stability is obvious. If an electron is removed from the system it undergoes considerable stabilization ($\Delta H_f$ = 44.169 kcal/mole). Then, from the molecule of the intermediate amine are formed particles



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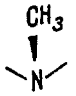

which interacting with $H^+$ and $OH^-$ in an aqueous medium form the products $CH_3CHO$ and $CH_3NH_2$.

For an experimental conformation of this scheme we carried out preparative electrolysis at a controlled anodic potential with identification of the final products. It was established that in all media the main products of the electrooxidation of ephedrine were benzaldehyde, methylamine, and acetaldehyde with various yields depending on the conditions of electrolysis.

## EXPERIMENTAL

The voltammetric curves were taken on a P-5827 M potentiostat with automatic recording. The working electrodes consisted of wires or disks with a diameter of 1-2.5 mm fused into glass or molded into Teflon. The ephedrine used in our work was obtained from technical ephedrine hydrochloride and was subjected to vacuum redistillation ($T_b$ = 130°C/0-3 mm Hg). Reagents of kh. ch. ["chemically pure"] grade and double-distilled water were used for preparing the solutions. Electrolysis was performed in a thermostated glass electrolyzer with a ceramic diaphragm. The experiments were conducted at 25°C, and the potentials given have been recalculated on the hydrogen scale. Universal buffer solutions were prepared as described in [4].

## SUMMARY

1. An investigation of the electrooxidation of ephedrine by electrochemical and quantum-chemical methods has shown good agreement between the values obtained experimentally and theoretically.

2. A quantitative interpretation of the mechanism of the electrooxidation of ephedrine has been given.

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# REACTIONS OF LYCOCTONINE ALKALOIDS CONTAINING A 7,8-METHYLENEDIOXY GROUP WITH Na IN LIQUID AMMONIA

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The reactions of 6-dehydroeldelidine and 6-dehydrodelcorine with sodium in liquid ammonia have been studied. Structures have been put forward for the compounds obtained. Features of the fragmentation of these compounds under electron impact are discussed.

One of the problems in the chemistry of the C-19 diterpene alkaloids is the elimination of oxygen functions and, in particular, the passage from the alkaloids of the lycoctonine type to alkaloids of the aconitine type. In this paper, we discuss the results obtained in the reactions of 6-dehydroeldelidine (I) and 6-dehydrodelcorine (II) with sodium in liquid ammonia.

In the first case, eldelidine (III) and two other products — (IV) and (V) — were obtained.

Product (IV), $M^+$ 435, $C_{24}H_{37}NO_6$. The IR spectrum of (IV) contained the absorption band of a carbonyl group in a 5-membered ring (1740 $cm^{-1}$), and its NMR spectrum the signals of these methoxy groups but no signal of a methylenedioxy group. The position in the PMR spectrum of the H-14β signal at 4.09 ppm (1H, triplet, J = 4.5 Hz) showed that the hydroxy group at C-10 had been retained [1]. An intense peak of a $(M - 49)^+$ ion showed the presence of a hydroxy group at C-8 [2]. On the basis of what has been said above, this product had the structure (IV) and this was confirmed by the results of x-ray structural analysis (Scheme 1).

Product (V), $M^+$ 419, $C_{24}H_{37}NO_5$, differed from the initial compound by a $CO_2$ group. Its mass spectrum was characteristic for C-19 diterpene alkaloids, and the maximum peak, $(M - OCH_3)^+$, showed the presence of a methoxy group at C-1 [2]. According to its PMR spectrum, the molecule of compound of (V) contained three methoxy groups (3.23, 3.26, and 3.27 ppm, singlets, 3H each), and there were no signals of olefinic protons or of a methylenedioxy group. The IR spectrum retained the absorption band of a carbonyl group in a five-membered ring (1745 $cm^{-1}$). On the basis of the facts given, for product (V) it is possible to suggest a structure differing from (IV) by the absence of one hydroxy group. The presence in the PMR spectrum of product (V) of a one-proton triplet at 3.94 ppm with J = 5 Hz due to a β-proton geminal to an α-methoxy group at C-14 is evidence in favor of the retention of the hydroxy group at C-10 [1]. Thus, the product under consideration may have structure (V) (see Scheme 1).

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