LITERATURE CITED

1. L. D. Yakhontova, M. N. Komarova, M. E. Perel'son, K. F. Blinova, and O. N. Tolkachev, Khim. Prirodn. Soedin., 624 (1972).
2. G. Nonaka and J. Nishioka, Chem. Pharm. Bull., 23, No. 2, 294 (1975).

THE STRUCTURE OF ANHYDROLUPININE

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UDC 547.944.6

The product of the dehydration of lupinine — anhydrolupinine — obtained by various methods [1-6] has widely differing specific rotations. This has led to the assumption that anhydrolupinine may exist in the form of two structural isomers readily changing into one another (I and II).

The anhydrolupinine obtained by heating lupinine with a mixture of sulfuric and glacial acetic acids [6] is a very unstable substance which rapidly oxidizes in the air. Judging from the fact that the product obtained is optically inactive, structure (II), having no asymmetric carbon atoms, has been proposed for it. In the separation of the alkaloids of *Anabasis aphylla* by the sulfuric acid method, we observed that the hydrolysis of lupinine sulfate formed a secondary product identical with the anhydrolupinine obtained by the method described by Willstätter and Fourneau [6].

The IR spectrum of the base taken immediately after its isolation showed a low-intensity absorption band in the 2800-2700 cm^{-1} region (trans-quinolizidine), a band in the 1650-cm^{-1} region, and a less intense band in the 1730-cm^{-1} region. The spectrum of the anhydro product that had been allowed to stand for a day retained the trans band, but the bands in the 1650- and 1730-cm^{-1} regions had acquired equal intensities, Apparently, anhydrolupinine consists of a mixture of two α,β-unsaturated isomeric compounds differing by the position of the double bond. At the moment of isolation, in all probability, one of them is present in predominating amount, and after a day an equilibrium is set up between these forms. On the basis of the characteristics of the IR spectra, it may be assumed that the isomeric mixture consists of forms (II) and (III).

The NMR spectrum, taken in benzene, of the anhydrolupinine obtained showed the following signals doublet at 1.07 ppm and singlets at 1.7 and 4.5 ppm. The doublet at 1.07 ppm is due to the protons of a methyl group bound in the form of >CH–CH_3, and the singlet in the weaker field at 1.7 ppm is due to the protons of a methyl group on an unsaturated carbon atom. The ratio of the intensities of the signals of the two methyl groups shows that the substance consists of the two isomers (II and III) in a ratio of 7:3, and the downfield shift of the singlet signal is caused by the anisotropic influence of the double bond on the protons of the methyl group. The upfield shift of the signal of the proton on the double bond may be due to the delocalization of the electrons of the unshared pair of the nitrogen into the π-orbital of the double bond. The signals of the protons of a $=CH_2$ group are not observed in the NMR spectrum, which shows the absence of form (I).

On analyzing the IR and NMR spectra, it may be concluded that anhydrolupinine is a mixture of two isomers (II) and (III) which can pass into one another, form (I) being completely absent from the mixture and form (II) amounting to about 70%. The production of these two forms in the dehydration of lupinine by the method of Willstätter and Fourneau [6] can be explained by the following scheme:

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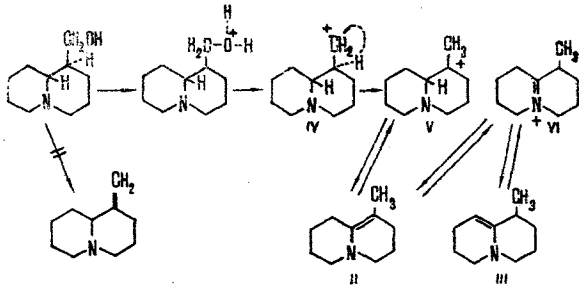
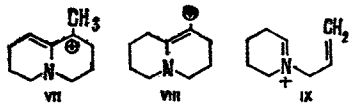


The carbonium ion (IV) formed has a tendency to undergo rearrangement. In this case, apparently, ionization is accompanied by the migration of hydrogen from the α- to the β-carbon atom (with respect to the alcohol group) with the formation of the more stable tertiary ion (V) which, by splitting off a proton, is converted into anhydrolupinine. The presence of concentrated sulfuric acid in excess leads to the existence of the reaction product in the protonated form (VI), which, on alkalinization with caustic potash may be converted either into (II) or into (III).

A confirmation of what has been said is provided by the mass spectrum of **anhydrolupinine**, in which there is the peak of the molecular ion with m/e 151 (M). In addition, the peaks of intense ions are observed with m/e 150 (M − 1) and 136 (M − 15) and a weaker peak with m/e 122 (M − 29), and also peaks of low intensity corresponding to m/e 55, 67, 66, 68, 77, 79, 97, 108, 109, and others, which are characteristic for quinolizidine derivatives. It can be seen from the empirical formula ($C_{10}H_{17}N$) of anhydrolupinine and its mass spectrum that the main fragments with m/e 150, 136, and 122 can correspond to formulas (VII), (VIII), and (IX), respectively, (VII) apparently being formed from the isomer (III), and (VIII) and (IX) from the isomer (II).



EXPERIMENTAL

The IR spectra were taken on a UR-10 instrument in carbon disulfide solution, and the PMR spectra on a Hitachi H-60 instrument at a resonance frequency of 60 MHz, using 10-15% solutions of the compounds under investigation in benzene with HMDS as internal standard. The mass spectra were taken on an MKh-1303 instrument.

Isolation of Anhydrolupinine in the Sulfuric Acid Method of Separating Lupinine and Anabasine. Concentrated sulfuric acid was added with constant stirring to the mixture of anabasine and lupinine obtained from anabasine sulfate. The mixture formed was heated at 100°C for 8 h. After cooling and careful dilution with water, the reaction mixture was made strongly alkaline with caustic soda and was exhaustively extracted with benzene (separation of anabasine). The alkaline mother solution containing lupinine sulfate was neutralized with concentrated hydrochloric acid and, after further acid had been added in a volume equal to that consumed in neutralization, the reaction mixture was heated at 100°C for 50-60 h. After hydrolysis the base was extracted with benzene. The benzene extract contained lupinine and a small (~5%) amount of anhydrolupinine. The anhydrolupinine, which was isolated from its mixture with lupinine by elution from Al_2O_3 with the petroleum ether–diethyl ether (1:1) system, consisted of an oily product undergoing rapid change in the air.

Anhydrolupinine [6]. A solution of 10 g of lupinine in 12 g of glacial acetic acid was treated with 25 g of concentrated sulfuric acid and the mixture was heated at 180°C for 8 h. Then, with ice cooling, the reaction mixture was carefully neutralized with 40% caustic soda solution. After this, an excess of potassium carbonate was added and the product was extracted with ether. The ethereal solution was dried over calcined potassium carbonate in a flask filled with nitrogen. After the rapid filtration of the solution, the ether was distilled off in an atmosphere of nitrogen. The residue, consisting of 8.72 g of a light

yellow oil with a sharp smell, was distilled under reduced pressure in a current of nitrogen. This gave a clear yellow oil (7.5 g), which rapidly became red in the air and even on storage under nitrogen.

SUMMARY

It has been shown that the anhydrolupinine obtained from lupinine by the action of water-abstracting agents is a mixture of two isomers differing by the position of a double bond in the ring system of the molecule.

LITERATURE CITED

1. G. Clemo and P. Raper, J. Chem. Soc., 1927 (1929).
2. P. Karrer and A. Vogt, Helv. Chim. Acta, B, 1073 (1930).
3. E. Whitte, New Zealand, J. Sci. Technol., B, 33, 47 (1951).
4. Heterocyclic Compounds [in Russian], Vol. 3, Moscow (1954), p. 314.
5. G. Clemo and G. Ramage, J. Chem. Soc., 437 (1931).
6. R. Willstätter and E. Fourneau, Ber., 35, 1910 (1902).

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

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UDC 547.944/945+541.138

Electrodialysis is an extremely promising method of isolating alkaloids from plant raw material, since it leads to the isolation of a purified product, avoids the use of organic solvents, and shortens the technological process [1]. The aim of the present work was to investigate further the conditions for extracting alkaloids of the tropane group from acid aqueous extracts of the leaves of *Atropa belladonna* (Z.).

To study the conditions of isolating the alkaloids we used model systems with concentrations of aqueous solutions of atropine sulfate approximately equal to the amount of the alkaloids in the plant raw material. The use of model systems permitted the influence of the impurities present in acid extracts of belladonna on the process of electrodialysis to be excluded. In addition to traditional methods [2], the possibility has been considered of using conductometric and photonephelometric methods for determining the concentration of atropine sulfate in model systems. The amounts of atropine salt in the initial solutions and the catholyte were determined from the characteristic inflection on the conductometric titration curve (Fig. 1). In the photonephelometric method, the optical densities of the solutions were measured at a wavelength of 430 nm, gelatin being used as a stabilizer for the system.

The experimental results show that the size of the current has a fundamental influence on the process of extracting atropine into the catholyte when using model systems. Thus, for example, at an initial concentration of atropine salt of $0.6 \cdot 10^{-3}$ kmole/m^3 the amount of alkaloid that passed into the catholyte in the first 10 min of the experiment was $0.08 \cdot 10^{-3}$ kmole/m^3 at 0.1 A and $0.24 \cdot 10^{-3}$ kmole/m^3 at 0.5 A. With a further increase in the current, the amount of alkaloid fell because of a sharp rise in the temperature of the solution (to 60°C) and its boiling, while small currents caused a considerable lengthening of the electrodialysis process. In view of this, we checked the dependence of the degree of isolation of the alkaloid on the time of electrodialysis at an optimum current of 0.5 A.

Zaporozh'e State Medical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 497-500, July-August, 1976. Original article submitted December 23, 1975.