STRUCTURE OF ARGENTAMINE

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Argentamine (I), isolated from the epigeal part of Ammodendron argenteum O. Ktze, is a ditertiary monoacid crystalline base (mp 203° C) with the composition $C_{15}H_{20}N_2O_2$ [1]. It gives a series of crystalline monoacid salts: perchlorate with mp 245–246° C, hydrochloride with mp 298° C, and picrate with mp 230° C.

The UV absorption spectrum of the base has the two maxima at 232 and 308 mμ (log ε 4.31 and 4.41) which are characteristic for an α-pyridone fragment [2].

The IR spectrum of argentamine has bands at 3260 cm^{-1} (broad)and 1045 cm^{-1} relating to the stretching vibrations of O—H and C—O bonds, respectively, which shows the presence in the substance of a hydroxyl group involved in a hydrogen bond. The presence of an α-pyridone fragment in argentamine is confirmed by absorption in the 3040, 1640, 1560–1540, and 802 cm^{-1} regions. Furthermore, the IR spectrum of argentamine clearly shows the band of a trans-quinolizidine (2810–2675 cm^{-1}).

On catalytic hydrogenation over a nickel catalyst, argentamine absorbs two moles of hydrogen, forming tetrahydroargentamine (II), $C_{15}H_{24}N_2O_2$, with mp 210° C (decomp.), $[\alpha]_D$ −37° (in ethanol).

The IR spectrum of II lacks the bands characteristic for the α-pyridone fragment, and the band due to the absorption of the lactam group is shifted in the low-frequency direction, which shows the presence of an α-piperidone nucleus.

The reduction of argentamine in solution in 2 N hydrochloric acid with platinum oxide gave deoxohexahydroargentamine (III), $C_{15}H_{26}N_2O$. The IR spectrum of substance III had no absorption bands characteristic for double bonds and lactam groups, and in place of these the strong band of a trans-quinolizidine (2835-2690 cm^{-1}) appeared, which shows the reduction of the α-pyridone fragment, and the absorption band of the hydroxyl group was shifted somewhat (3380 cm^{-1}). This excludes the α-position of the hydroxyl group with respect to the second nitrogen [3-4].

The presence of a hydroxyl group in argentamine (I), tetrahydroargentamine (II), and deoxohexahydroargentamine (III) is confirmed by the M — 17 peaks in their mass spectra (Figs. 1 and 2).

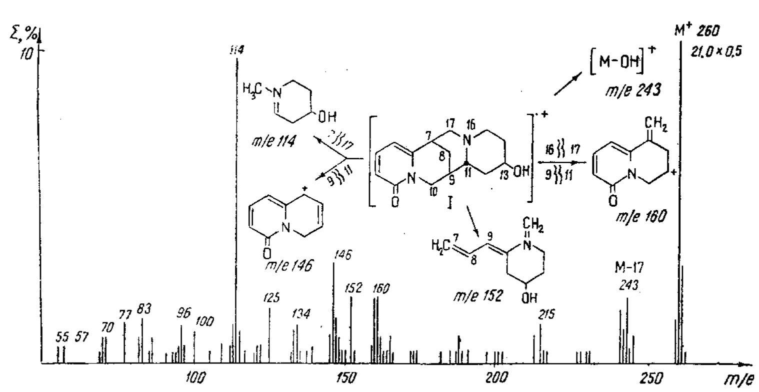


Fig. 1. Mass spectrum of argentamine.

The results of a study of the mass spectra of I and II (see Figs. 1 and 2) and of a comparison of the mass spectra of I and of anagyrine [5], and also the complete identity of the mass spectra of III and of 13-hydroxysparteine

[6] showed that I is based on the heterocyclic skeleton of sparteine in which a hydroxyl group is present in ring D, namely in position 13. The dehydration of the hydroxyl group in substance III by a known method [7] and subsequent hydrogenation gave α-isosparteine (IV), which likewise confirms the heterocyclic skeleton of argentamine.

The empirical composition of substance I, and also the features of its UV, IR, and mass spectra show that it is a diastereoisomer of baptifoline [8].

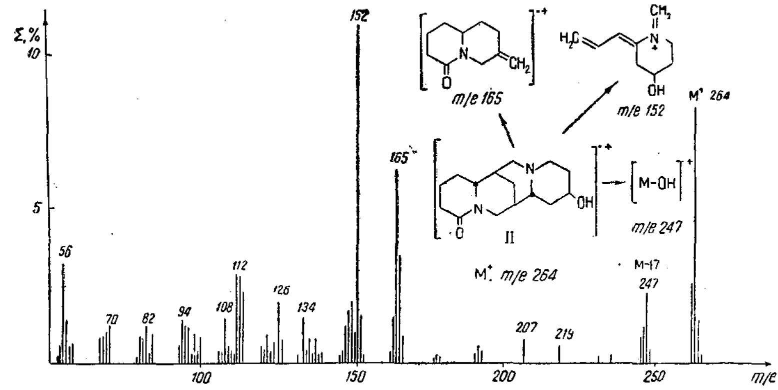
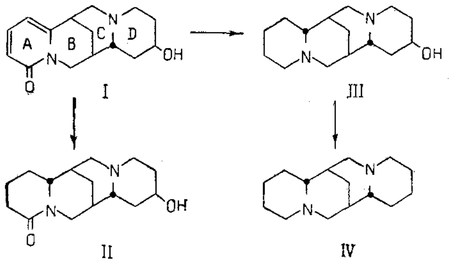


Fig. 2. Mass spectrum of tetrahydroargentamine.

The IR spectrum of I differs from the latter by the presence of the trans-quinolizidine band; in addition, III proved to be identical with 13-hydroxy-α-isosparteine [9], which shows the trans-linkage of rings C and D in the structure of I and the position of the hydroxyl group at C_{13}.



Consequently, substance I has the structure of (—)-13-hydroxythermopsine, and argentamine and baptifoline are epimeric at C_{11}. Argentamine is the first hydroxyl derivative of thermopsine found in nature. The chemical conversions of argentamine can be represented by the above scheme.

EXPERIMENTAL

The UV spectra were taken on an SF-4 instrument, the IR spectra on a UR-10 instrument (tablets with KBr or in $CHCl_3$), and the mass spectra on a MKh-1303 instrument fitted with a system for the introduction of the sample directly into the ion source at an ionizing voltage of 70 V and inlet temperatures of 130° C (for III) and 180° C (for I and II).

Paper chromatography was carried out on chromatographic paper of Leningrad No. 2 Mill (fast). The solvent system was butan-2-ol–water–HCl (100 : 27 : 15). Radial chromatography was used with Dragendorf's reagent for revealing the substances. The analytical data for all the compounds correspond to the calculated figures.

Argentamine. Isolated from the perchlorate [1] by treatment with ammonia and extraction with chloroform, mp 203° C (from benzene), $[\alpha]_D$ —142.3° (c 2.04; ethanol), R_f 0.23, insoluble in petroleum ether and ether, sparingly soluble in benzene and acetone, readily soluble in chloroform and ethanol. Mol. wt, 260 (mass spectrometry). Mass spectrum: main peaks of ions with m/e 260 (M^+), 243 (M — 17), 160, 152, 146, 114.

The hydrochloride was obtained by the addition of a saturated solution of hydrogen chloride in dry acetone to an acetone solution of the base, mp 298° C (from a mixture of ethanol and acetone).

Picrate. Mp 230° C (from ethanol).

Tetrahydroargentamine. A mixture of 0.2212 g of argentamine and 3 ml of nickel catalyst in 5 ml of ethanol was shaken in an atmosphere of hydrogen for 15 hr; 55 ml was absorbed. Yield 0.2250 g, mp 210° C (decomp., from acetone), $[\alpha]_D$ −37° (c 1.44; ethanol), R_f 0.42; mol. wt. 264 (mass spectrometry).

IR spectrum: 3380 cm^{-1} (—OH), 2815–2670 cm^{-1} (trans quinolizidine), 1615 cm^{-1} ($>$CO—N$<$). Mass spectrum: main peaks of ions with m/e 264 (M^+), 247 (M − 17), 165, 152.

Deoxohexahydroargentamine (13-hydroxy-α-isosparteine). 0.120 g of argentamine hydrochloride in 5 ml of 2 N hydrochloric acid was hydrogenated for 10 hr with 0.150 g of platinum oxide previously reduced in 2 N hydrochloric acid solution. 65 ml of hydrogen was absorbed. After the removal of the catalyst, the acid solution was neutralized with potassium carbonate and the reaction product was extracted with ether. The deoxohexahydroargentamine, $C_{15}H_{25}N_2O$, had mp 147° C (from petroleum ether, $[\alpha]_D$ +45° (c 3.45; ethanol), R_f 0.38, mol. wt. 250 (mass spectrometry).

α-Isosparteine. To 0.150 g of deoxohexahydroargentamine in 50 ml of xylene was added 2.5 g of P_2O_5, and the mixture was boiled for 10 hr. After the decomposition of the P_2O_5 and the removal of the xylene, the aqueous layer was made alkaline with ammonia and extracted with ether. The mixture was chromatographed on a column of alumina. The column was eluted successively with petroleum ether and with acetone. The petroleum ether eluate contained a base with R_f 0.53, and the acetone eluate substances with R_f 0.53 and 0.38 (deoxohexahydroargentamine).

The residue after the evaporation of the petroleum ether eluate (0.045 g) was dissolved in 3 ml of ethanol and hydrogenated with 1 ml of nickel catalyst in an atmosphere of hydrogen, and 45 ml of hydrogen was absorbed. The hydrogenated product proved to be identical with α-isosparteine.

CONCLUSIONS

On the basis of chemical transformations and the UV, IR, and mass spectra of argentamine, isolated from the epigeal part of Ammodendron argenteum O. Ktze, the structure of (—)-13-hydroxythermopsine has been proposed as the the most probable one for it. It has been shown that argentamine and baptifoline are epimeric at C_{11}.

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