ing 5-8% of ethanol. The eluates containing the individual substance were combined and evaporated, and the residue was crystallized from methanol–ether. The crystals obtained (29 mg) with mp 170-172°C, $[\alpha]_D^{20}$ −10° (c 0.1; methanol) were identified as convallatoxin [9].

Methylation of Neoconvallatoxoloside. The glycoside (I) (150 mg) was methylated as described previously [6]. A hydrolyzate of the methylated glycoside was found by paper chromatography in the systems described by Aspinall and Wood [15] to contain 2,3,4,6-tetramethyl-D-glucose and 3,4-dimethyl-L-rhamnose.

SUMMARY

A new cardinolide glycoside has been isolated from the leaves of Convallaria majalis L.; it has been called neoconvallatoxolisode and its structure has been established as strophanthidol 3-O-[O-β-D-glucopyranosyl-(1 → 2)-α-L-rhamnopyranoside].

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ALKALOIDS OF Sophora alopecuroides

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UDC 547.944/945

Previously, from Sophora alopecuroides collected on the banks of the R. Zeravshan in the period of incomplete ripening of the fruit, in addition to known alkaloids, we isolated two new bases 6 and 7 [1, 2]. Base 7 has the composition $C_{15}H_{22}O_2N_2$, mp 68-70°C (from ether), $[\alpha]_D^{25}$ + 27.5° (c 0.75; water). The present paper gives the results of a study of the structure of this alkaloid.

The UV spectrum of base 7 has adsorption in the 253 nm region corresponding to the presence of the chromophore (−CH=CH−CO−). The IR spectrum of the alkaloid lacks the absorption band of a trans-quinolizidine (2800-2700 cm^{-1}). Strong absorption is observed in the 1602 and 1658 cm^{-1} region (−CH=CH−CO−N<), and weak absorption at 970, 950, and 925 cm^{-1}, which is characteristic for a N-oxide group [3].

The mass spectrum of the bases has, in addition to the peak of the molecular ion (M^+ 262) confirming the composition of the alkaloid, the peaks of ions with m/e 246 (M−16; 86%), 245 (M−17; 100%), 217 (8%), 203 (12%), 177 (90%), 150 (72%), 138 (42%), 122 (19%), 96 (68%), which are characteristic for the matrine alkaloids [4-6].

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TABLE 1. Comparative Mass Spectra of Sophocarpine, Lehmannine, and the Deoxy Base 7

Alkaloid	m/e, % intensity											
	M+246	245	231	217	203	188	177	160	150	137	122	96
Sophocarpine	72,8	100	2,7	8,9	19,5	5,6	14	12,3	44	22,5	20	47,4
Lehmannine	100	62	1,5	16	85	9	12	31,5	89	30	34	98
Deoxy base 7	75	100	6,3	9,3	12,5	4	88	10	82,3	14	22,9	70,6

The ions with m/e 217 (M − 29) and 203 (M − 43), differing by two units from the corresponding ions of matrine and its isomers, show the presence of a double bond in ring D [7, 8]. The low intensity of the molecular ion M^+ 262 (7%) [8, 9]; the difference by 16 mass units in the region of high masses as compared with the mass spectra of sophocarpine; the absence of a Bohlmann band in the IR spectrum; and the good solubility in water permit the assumption that base 7 is the N-oxide form of an alkaloid of the matrine series.

In the PMR spectrum of base 7 at 6.42 and 5.88 ppm can be seen the signals of two olefinic protons in the form of a doublet of triplets. The signals of three α-protons are located in the 3.6-4.45 ppm region. The signals of the other protons are found in the 1.3-3.4 ppm region.

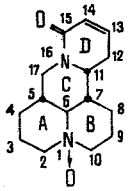
When the deoxybase of compound 7 was obtained by means of zinc dust in an acid medium, two products were formed, with R_f 0.56 and 0.58. It is possible that in addition to the reduction of the N-oxide group hydrogenation of the double bond takes place. To exclude this reaction, base 7 was reduced with sodium hydrosulfite. This gave the deoxybase with R_f 0.58, mp 83-84°C, $[\alpha]_D^{22}$ + 76.8° (c 0.266; ethanol), M^+ 246. The IR spectrum of the deoxybase 7 had absorption bands characteristic for a trans-quinolizidine in the regions of 2795, 2750, 2705, 2690, and 2672 cm^{-1} (Bohlmann band) and 1650 and 1596 cm^{-1} (−CH=CH−CO−N<).

The NMR spectrum of the deoxybase 7 showed signals at 6.24 and 5.74 ppm in the form of a doublet of triplets of two olefinic protons at C_{14} and C_{13}. The signals of the H_{17e} and H_{11} protons are in the 3.66 and 3.24 ppm regions. The signals of the H_{2e}, H_{10c}, and H_{17a} protons are found in the 2.82 and 2.30 region. The signals of the other protons are located in the 2.22-0.8 ppm region.

The mass spectrum of the deoxybase 7 has the peak of the molecular ion with M^+ 246 (75%) and the peaks of ions with m/e 245 (100%), 217, 203, 177, 160, 150, 138, 122, and 96.

A comparative study of the mass spectra of sophocarpine [4], lehmannine [10], and the deoxybase shows that they differ by the intensities of the peaks of the ions of certain fragments (Table 1). These compounds are possibly stereoisomers in the A/B, A/C, and B/C parts of the molecule. Thus, it may be assumed that base 7 is the N-oxide of an unknown alkaloid the molecule of which contains one double bond in ring D as is confirmed by the nature of the mass-spectrometric fragmentation. To establish the structure of the alkaloid definitively, the deoxybase 7 was catalytically hydrogenated over Raney nickel. This gave a crystalline base with mp 108-109°C, $[\alpha]_D^{25}$ −53.4° (c 0.51; ethanol), the IR, PMR, and mass spectra and physicochemical constants of which showed its identity with sophoridine.

On the basis of spectral characteristics and chemical transformations we have put forward as the most probable structure of the new alkaloid that of 13,14-dehydrosophoridine N-oxide:



EXPERIMANTAL

The mass spectra were taken on a MAT-311 instrument, the NMR spectra on a Varian-15 XL-100 instrument with a working frequency of 100 MHz (the chemical shifts are given in the δ scale relative to HMDS), the IR spectra on a UR-10 spectrometer with the substances in the form of thin films, and the UV spectra on a Beckmann instrument.

Filtrak No. 1 paper was used for paper chromatography and type LS 5/40 μm silica gel for thin-layer chromatography. The following solvent systems were used: 1) butan-1-ol–water–hydrochloric acid (100:27:15) and 2) ethyl acetate–isopropanol–25% ammonia (50:35:25). The revealing agents were Dragendorff's reagent and iodine vapor.

Isolation of the Alkaloids. The dry comminuted plant (4.5 kg) was moistened with 10% ammonia and was extracted repeatedly with methanol. The methanolic extract was concentrated, the residue was dissolved in 10% sulfuric acid, and the solution was washed with chloroform. The acid solution of the combined alkalids was made alkaline with 25% ammonia, and the alkaloids were extracted successively with petroleum ether (yield 21.86 g), benzene (yield 44.69 g), and chloroform (yield 14.54 g). The total yield of alkaloids was 81.09 g (1.8% on the weight of the dry plant).

Isolation of 13,14-Dehydrosophoridine N-Oxide. The chloroform-extracted fraction (6 g) was deposited on a column of cellulose (1:100) and was eluted with system 1. The eluates were chromatographed on paper (system 1), and the fractions with the same R_f values were combined and evaporated to dryness in vacuum. The residue was dissolved in 10% ammonia, and the bases were extracted with chloroform. This gave 0.95 g of 13,14-dehydrosophoridine N-oxide, 2.54 g of sophoridine N-oxide, and 0.55 g of cytisine.

13,14-Dehydrosophoridine N-oxide (0.95 g) was dissolved in methanol and 10-mg portions were deposited on a single plate (200 × 200 mm) with a fixed layer of silica gel and were chromatographed in system 2, the spots being revealed with the Dragendorff reagent. The zones corresponding to 13,14-dehydrosophoridine N-oxide were combined, and the base was extracted with methanol. The solvent was evaporated to dryness in vacuum, giving 0.45 g of 13,14-dehydrosophoridine N-oxide with mp 68-70°C (from ether), $[\alpha]_D^{25}$ + 27.5° (c 0.73; water), M^+ 262.

Preparation of 13,14-Dehydrosophoridine. A solution of 120 mg of 13,14-dehydrosophoridine N-oxide in 5 ml of 12% hydrochloric acid was heated at 60-70°C for 30 min in the presence of zinc dust. Then the acid solution was filtered from the zinc dust and made alkaline with ammonia. The base was extracted with benzene. The solvent was evaporated off in vacuum and the residue was transferred to a column of cellulose and was eluted in system 1, giving 60 mg of 13,14-dehydrosophoridine with R_f 0.58 and 15 mg of a base with R_f 0.56. After recrystallization from petroleum ether, the 13,14-dehydrosophoridine had mp 83-84°C, $[\alpha]_D^{22}$ + 76.8° (c 0.266; ethanol), M^+ 246.

Alternative Preparation of 13,14-Dehydrosophoridine. An aqueous solution of 150 mg of base 7 was treated with 200 mg of sodium hydrosulfite. After the mixture had stood at room temperature for 48 h, the base was extracted with benzene. After drying and the distillation of the solvent 120 mg of 13,14-dihydrosophoridine was obtained with mp 83-84°C (from petroleum ether), $[\alpha]_D^{22}$ + 76.5° (c 0.5; ethanol).

Catalytic Hydrogenation of 13,14-Dehydrosophoridine. In the presence of Raney nickel, 100 mg of 13,14-dehydrosophoridine in 10 ml of ethanol was hydrogenated in a current of hydrogen at room temperature with constant stirring. After the end of the reaction, the solvent was evaporated off in vacuum to dryness, and the residue was recrystallized from petroleum ether. This gave 80 mg of a base with mp 107-108°C, $[\alpha]_D^{22}$ −53.4° (c 0.5; ethanol), M^+ 248.

From its physicochemical constants and mass spectrum, the resulting base was identical with sophoridine.

SUMMARY

On the basis of spectral characteristics and chemical transformations, a new alkaloid with the composition $C_{15}H_{22}O_2N_2$ isolated from Sophora alopecuroides has been assigned the most probable structure of 13,14-dehydrosophoridine N-oxide.

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QUINAZOLINES

X. SYNTHESIS OF 6,6'-METHYLENEBISDEOXYVASICINONE AND ITS HOMOLOGS

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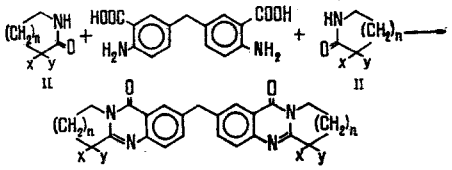
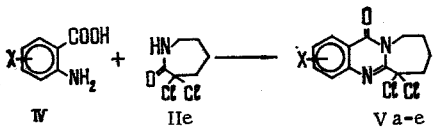
6,6'-Methylenebis(2-methyl-3H-quinazolin-4-one) has been synthesized from methylenebisanthranilic acid [1]. Continuing a study of the chemistry of condensed quinazolines [2-4], in order to synthesize new deoxyvasicinone derivatives we have performed the reaction of methylenebisanthranilic acid (I) with various lactams (γ-butyrolactam, δ-valerolactam, ε-caprolactam, and α-chloro- and α,α-dichloro- ε-caprolactams (IIa-e)). 6,6'-Methylenebisdeoxyvasicinone and its homologs (IIIa-e) were obtained:



a. $x = y = H$, $n = 1$; b. $x = y = H$, $n = 2$; c. $x = y = H$, $n = 3$; d. $x = H$, $y = Cl$, $n = 3$; e. $x = y = H$, $n = 3$.

The reaction took place smoothly when 1 mole of the acid (I) was heated with 3 moles of a lactam (II) in the presence of phosphorus oxychloride in the water bath (see Table 1).

We have also studied the reaction of anthranilic acid and its derivatives (4-nitro-, 5-bromo-, 5-iodo, and 5-nitroanthranilic acids) (IVa-e) with the lactam (IIe). In this way the quinazolinones (Va-e) were synthesized with yields of 46-59% (see Table 1).



a. $x = H$; b. $x = 4 - NO_2$; c. $x = 5 - Br$; d. $x = 5 - I$; e. $x = 5 - NO_2$.

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