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ALKALOIDS OF FOUR SPECIES OF Argemone

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The alkaloid compositions of four species of plants of the genus Argemone (A. mexicana L., A. alba L., A. platyceras Link et Otto., and A. hybrida) collected in the flowering phase in the Tashkent Botanical Garden have been studied. They have yielded 16 alkaloids. Corydine and isocorydine have been detected in plants of this genus for the first time, and O-methylplatycerine has been found in nature for the first time.

Plants of the genus Argemone (family Papaveraceae) are widely distributed in North America [1]. These plants do not grow wild in the Soviet Union and Europe but they are widely cultivated. At the present time, about 40 alkaloids belonging to six groups of isoquinoline bases have been isolated from plants of the genus Argemone [1-22].

We have studied the alkaloid compositions of the epigeal parts of four species of Argemone: A. mexicana L., A. alba L., A. platyceras Link et Otto., and A. hybrida collected in the flowering phase in the Tashkent Botanical Garden. This has led to the isolation of 16 alkaloids, of which O-methylplatycerine has been isolated from a plant for the first time and corydine and isocorydine have been isolated from this genus for the first time; the total yields of alkaloids from the species mentioned as percentages of the weights of the air-dry raw material were 0.49, 0.3, 0.33, and 0.38%, respectively.

Alkaloid	A. mexicana	A. alba	A. platyceras	A. hybrida
Protopine	+	+	+	+
α-Allocryptopine	+		+	+
Scoulerine	+	+		+
Sanguinarine		+	+	+
Cheilanthifoline	+			+
Stylopine α-methiodine			+	
Chelerythrine		+		
Reticuline	+	+	+	+
Berberine	+	+	+	+
Corydine				+
Isocorydine	+			
Magnoflorine			+	
Munitagine			+	+
Platycerine			+	
O-Methylplatycerine			+	
Argemonine			+	

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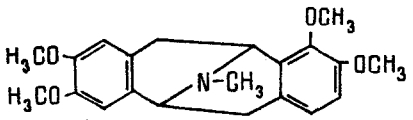
O-Methylplatycerine is an amorphous optically active base with the composition $C_{21}H_{25}NO_4$. Its UV spectrum has one absorption maximum, at 282 nm (log ε 3.84). Its mass spectrum shows the peaks of ions with m/z 355 (M^+] and 204 (100%). Its PMR spectrum shows signals from a N-methyl group at 2.48 ppm and from four methoxy groups at 3.66, 3.70, 3.74, and 3.83 ppm. In the aromatic region of the spectrum there are one-proton singlets at 6.30 and 6.46 ppm and a two-proton singlet at 6.57 ppm. Broadened one-proton doublets with J ∿ 5 Hz appear at 4.24 and 3.89 ppm and a multiplet corresponding to four protons at 2.60-3.60 ppm.

A comparison of our base with the pavine alkaloid O-methylplatycerine [22] obtained by the methylation of platycerine showed their identity.



EXPERIMENTAL

Type KSK silica gel was used for chromatography and, in the case of TLC, the following solvent systems: 1) benzene–ethanol (9:1), and 2) chloroform–ethanol (9:1). UV spectra were taken on a Hitachi spectrometer in ethanol; PMR spectra in a JNN-100/100 MHz instrument in $CDCl_3$ with HMDS as standard (δ scale); mass spectra on a MKh-1303 mass spectrometer; and IR spectra on a UR-20 instrument (tablets with KBr).

Isolation and Separation of the Alkaloids. The air-dry plant A. mexicana (1845 g) was extracted with ethanol. Eight extractions were made. The ethanolic extract was concentrated to give a resinous mass, and this was triturated with 10% sulfuric acid solution. The acid solution was washed with ether and, with cooling, it was made alkaline with 25% ammonia solution and the alkaloids were extracted successively with ether and with chloroform. The chloroform extract was evaporated to dryness, giving 2.75 g of total chloroform alkaloids. The ethereal extracts, after concentration, were treated with a 4% solution of caustic potash. The ethereal layer was dried with anhydrous sodium sulfate and evaporated, giving 5.35 g of total ether-extracted nonphenolic material.

The caustic potash solution, after being acidified to pH 5-6, was made alkaline with 25% ammonia and was shaken with ether. The solvent was distilled off to give 0.94 g of ether-extracted phenolic material.

The aqueous alkaline solution after the extraction of the tertiary alkaloids was acidified with 10% sulfuric acid to pH 3-4, and then a saturated solution of potassium iodide was added and it was extracted with chloroform. The solvent was evaporated off to give a fraction of iodides of quaternary bases (0.36 g).

The ether-extracted nonphenolic material was treated with methanol, which led to a crystalline mixture of bases (4.41 g) from which protopine (1.31 g) and allocryptopine (2.03 g) were isolated by fractional crystallization from methanol–chloroform. The ether-extracted phenolic material was chromatographed on a column of silica gel (1:30). Mixtures of benzene and ethanol, in various ratios were used as eluents. The benzene–ethanol (99:1) fractions yielded 0.08 g of cheilanthifoline and 0.14 g of scoulerine, and the (96:4) fractions yielded 0.07 g of isocorydine and 0.14 g of reticuline. By treatment with methanol 1.52 g of berberine was isolated from the chloroform-extracted material.

The air-dry plant A. hybrida (1050 g) was extracted with ethanol. The extraction and the isolation of the combined alkaloids were carried out by the methods described above, and 0.35 g of ether-extracted phenolic, 1.5 g of ether-extracted nonphenolic, and 1.63 g of chloroform-extracted alkaloids and 0.51 g of iodides of quaternary bases were obtained. The combined nonphenolic material was treated with ethanol to give a crystalline mixture of bases (1.28 g) from which 0.65 g of allocryptopline and 0.35 g of protopine were isolated by fractional crystallization from ethanol–chloroform. The mother solution was chromatographed on a column of silica gel (1:30). The alkaloids were eluted with chloroform and with mixtures of chloroform in methanol in various ratios. The chloroform fraction yielded 0.04 g of sanguinarine, and the fractions eluted by chloroform–ethanol (99:1) 0.08 g of corydine. The ether-extracted phenolic material was chromatographed on a column of silica gel (1:30). The fractions eluted by benzene–ethanol (99:1) yielded cheilanthifoline (0.014 g), scoulerine (0.071 g), and munitagine (0.03 g), and the (98:2) fraction gave

0.034 g of platycerine. Elution with the (95:5) mixture gave 0.014 g of reticuline. From the chloroform-extracted material 0.95 g of berberine was obtained.

The plant A. alba (610 g) was extracted with ethanol. Six extractions were made. The concentrated ethanolic extract was evaporated, and the residue was dissolved in 10% sulfuric acid. The acid solution was washed with ether, and the total alkaloids were isolated by the method described above. This gave 0.12 g of ether-extracted phenolic, 0.23 g of ether-extracted nonphenolic, and 0.39 g of chloroform-extracted alkaloids and 0.06 g of iodides of quaternary bases. The ether-extracted nonphenolic and phenolic materials were separated by chromatography on a column of silica gel (1:30) as described above. The nonphenolic material yielded 0.12 g of protopine, 0.014 g of sanguinarine, and 0.011 g of chelerythrine, and the phenolic material 0.045 g of scoulerine and 0.014 g of reticuline. The chloroform-extracted material gave 0.11 g of berberine.

The air-dry plant A. platyceras (900 g) was extracted with ethanol. The combined alkaloids were isolated by the method described above. This gave 1.37 g of ether-extracted phenolic, 1.14 g of ether-extracted nonphenolic, and 0.51 g of chloroform-extracted alkaloids, and also 0.32 g of iodides of quaternary bases. The combined alkaloids were separated in a similar manner to those from A. mexicana and A. hybrida. From the ether-extracted nonphenolic material were isolated 0.14 g of allocryptophine, 0.21 g of cryptopine, 0.03 g of sanguinarine, 0.084 g of argemonine, and 0.062 g of O-methylplatycerine, and the phenolic material gave 0.35 g of munitagine, 0.24 g of platycerine, and 0.42 g of reticuline. The chloroform-extracted alkaloids, on treatment with ethanol, gave 0.11 g of berberine. Fractional crystallization of the iodides of the quaternary bases from methanol provided 0.05 g of stylopine methiodide and 0.065 g of magnofluorine.

O-Methylplatycerine. $[\alpha]_D$ − 285° (c 0.8; chloroform).

Methylation of Olatycerine. An ethereal solution of diazomethane was added to a solution of 25 mg of platycerine in 5 ml of absolute methanol. After a day, the solvent was distilled off to give O-methylplatycerine identical with the base isolated from the plant (IR spectrum, TLC).

SUMMARY

From four species of plants of the genus Argemone 16 alkaloids have been isolated of which corydine and isocorydine have been detected in this genus for the first time, while this is the first time that O-methylplatycerine has been found in nature.

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ALKALOIDS OF THE EPIGEAL PART OF Aconitum karakolicum

STRUCTURE OF KARASAMINE AND OF 1-BENZOYLKARASAMINE

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The known alkaloids phenyl-β-naphthylamine, karakoline, neoline, delsosine, monticamine, songorine, napelline acetylnapelline, napelline-n-oxide, and isoboldine and two new alkaloids, which have been called karasamine (I) and 1-benzoylkarasamine (II), have been isolated from the epigeal part of Aconitum karakolicum Rapaics. The structure of the new alkaloids have been shown by the preparation of the mono- and triacetates (IV) and (VI) of karasamine and its carbinolamine derivative (V), and also by the direct passage from karakoline (III) to karasamine (I) and 1-bezoylkarasamine (II) and by a study of their spectral characteristics.

We have investigated the alkaloids of the epigeal part of Aconitum karakolicum Rapaics collected in the valley of the R. Irisu, Kirghiz SSR in the budding period. The total alkaloid content amounted to 1.06% on the weight of the dry plant. Separation of the combined alkaloids yielded phenyl-β-naphthylamine [1] karakoline, neoline, delsoline, monticamine, songorine, apelline, acetylnapelline [2, 3], napelline N-oxide [4], the aporphine alkaloid isoboldine, and two new alkaloids which have been called karasamine (I) and 1-benzoylkarasamine (II) [5].

Karasamine (I) has the composition $C_{23}H_{37}NO_4$ (M^+ 391.2764 HRMS), mp 110-112°C (acetone). Its IR spectrum has absorption bands of hydroxy groups at 3180 and 3590 cm^{-1} and of ether bonds at 1100 cm^{-1}. According to the NMR spectra, the alkaloid contains a N-ethyl, a tertiary C-methyl, and two methoxy groups. Acetylation showed the presence of two hydroxy groups. The spectral characteristics of the alkaloid are close to those of the diterpene alkaloid karakoline (III), and a comparison of developed formulas showed that karasamine differed from karakoline by the presence of a methoxy group in place of a hydroxy group. In the mass spectrum of karasamine, the maximum peak was that of the $M^+ - 17$ ion, which shows the presence of a hydroxy group at C-1 [6]. When (I) was acetylated with acetic anhydride in the presence of pyridine, a monoacetyl derivative (IV) was obtained in the NMR spectrum of which there was a one-proton quartet at 4.82 ppm J_1 = 10 Hz, J_2 = 7 Hz, which is characteristic for a proton geminal to a C-1 acetoxy group [7, 8]. In the mass spectrum of (IV) the maximum peak was that of an ion $M^+ - 59$, which indicated that the acetoxy group was present at C-1 [7].

When (I) was oxidized with potassium permanganate in aqueous acetone, an anhydroepoxy derivative (V) was formed. These results indicate the presence in karasamine of α-oriented hydroxy group at C-1. The acetylation of karasamine with acetic anhydride in the presence of p-toluenesulfonic acid led to the diacetate (VI). The maximum peaks in the mass spectrum of the diacetate were those of the ions $M^+ - 59$ (100%) and $M^+ - 59 - 60$ (93%), arising on the successive ejection of an acetoxy radical from C-1 and of a molecule of acetic acid at the expense of the acetoxy group at C-8 [7].

The facts given permit us to consider that the additional methoxy group in karasamine is located at C-14. To confirm this, we methylated karakoline (III) with methyl iodide in dioxane and obtained the C-14 monomethyl ether of karakoline, which was identical with karasamine according to a mixed melting point with an authentic sample and to the results

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