SUMMARY

The new base convoline has been isolated from the epigeal part of *Convolvulus krauseanus* Regel. et Schmalh., and its structure has been established from spectral characteristics and some chemical transformations.

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ALKALOIDS OF *Glaucium corniculatum*

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The alkaloids from the epigeal part of the wild blackspot horn poppy have been studied. Twelve alkaloids have been isolated of which one — norbracteoline — proved to be new. Its structure has been established. Dehydrocorydine, predicentrine, glaufidine, thalicmidine, reticuline, and stylopine α-methohydroxide have been isolated from this plant for the first time.

From the cultivated plant *Glaucium corniculatum* (L.) J. Rudolf have been isolated 13 alkaloids belonging to four groups of isoquinoline bases [1]. Three alkaloids have been found in the wild blackspot horn poppy: protopine, allocryptopine, and corydine [2]. We have studied the epigeal part of *G. corniculatum* collected in the Georgievsk region of Stavropol'krai at the end of flowering-beginning of fruit-bearing.

Ethanolic extraction yielded 1.36% of combined alkaloids. The nonphenolic fraction of this combined material contained sanguinarine, dehydrocorydine, predicentrine, isocorydine, corydine, protopine, and allocryptopine. From the combined phenolic alkaloids we isolated predicentine, isocorydine, corydine, glaufidine, thalicmidine, reticulin, and new base (I), from chloroform — dehydrocorydine, isocorydine, corydine, thalicmidine, protopine, and allocryptopine. From the quaternary fraction we isolated stylopine α-methohydroxide in the form of the iodide. The known alkaloids were identified by direct comparison with authentic samples [3-5, 9]. The UV spectrum of the amorphous optically active base (I) is characteristic for 1,2,9,10-tetrasubstituted aporphine alkaloids (λ_{max} 220, 280, 310 nm) [6]. The IR spectrum of (I) shows absorption bands at (cm^{-1}) 3285 (NH), 3400 (OH), and 1520 (aromatic rings). The mass spectrum contains the peak of the molecular ion with m/z 313, a strong peak of the $(M - 1)^+$ ion, and also the peaks of ions with m/z 298 $(M - 15)^+$, 296 $(M - 17)^+$, 284 $(M - 29)^+$, 282 $(M - 31)^+$, and 156.5 (M^{++}). This pattern of the spectrum confirms that the base belongs to a 1,2,9,10-tetrasubstituted aporphine alkaloid [7].

The PMR spectrum of (I) showed signals in the form of singlets from two methoxy groups at 3.83 ppm and from three aromatic protons at 6.43, 6.66, and 7.97 ppm, and also multiplets in the 2.5-4.0 ppm region from seven protons. The absence of the signal of a N-methyl group from the NMR spectrum and also the presence of the peak of the $(M - 29)^+$ ion in the mass spectrum showed the secondary nature of the nitrogen atom.

The spectral characteristics permit the base (I) to be assigned to noraporphine alkaloids of the type of glaucine with two methoxy groups and two hydroxy groups.

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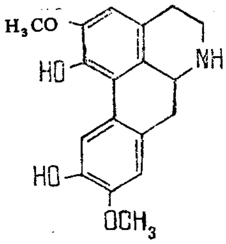
In actual fact, the Craig methylation of (I) led to a product identical with bracteoline [8]. Consequently, (I) is norbracteoline and has the following structure:



EXPERIMENTAL

Chromatography was carried out on KSK silica gel. For TLC we used the solvent systems: 1) benzene—ethanol (95:5); 2) chloroform—ethanol (9:1). UV spectra were taken on a Hitachi spectrophometer (ethanol), IR spectra on a UR-20 (in tablets with KBr), mass spectra on a MKh-1303, and NMR spectra on a JMN-4M-100/100 MHz (internal standard HMDS, δ scale, solvent $CDCl_3$).

Isolation and Separation of the Combined Alkaloids. The comminuted air-dry epigeal part of the plant *G. corniculatum* (1.15 kg) was extracted with ethanol at room temperature. Eight changes of solvent were made. The ethanol was distilled off in vacuum. The concentrated syrupy residue was dissolved in 10% sulfuric acid, and the solution was washed with ether and made alkaline with concentrated ammonia solution. The alkaline solution was shaken first with ether and then with chloroform. From the concentrated ethereal extract by the usual method [9] were obtained 2.20 g of combined phenolic alkaloids (1.97 g of ether fraction and 0.23 g of chloroform fraction), and 5.11 g of combined ether-soluble nonphenolic alkaloids. Evaporation of the chloroform extract to dryness gave 8.33 g of combined chloroform-extracted alkaloids. The remaining alkaloid solution was acidified to pH 3-4 with 10% sulfuric acid, a saturated solution of potassium iodide was added, and it was shaken with chloroform. The combined chloroform extracts were dried with sodium sulfate and evaporated to dryness. This gave the combined iodides of tertiary bases (0.5 g).

Treatment of the nonphenolic combined ether-extracted material with acetone yielded 3.94 g of a mixture of crystals from which 2.45 g of allocryptopine and 0.98 g of protopine were isolated by fractional crystallization from ethanol—chloroform. The mother liquor (1.17 g) was chromatographed on a column of silica gel. The alkaloids were eluted with benzene and benzene—ethanol mixtures of different polarities.

The benzene eluates yielded 45 mg of sanguinarine. The fractions eluted by mixtures with ratios of 99:1 and 98:2 gave 42 mg of dehydrocorydine and 53 mg of predicentrine, and the (97:3), (96:4), and (95:5) fractions yielded 73 mg of isocorydine and 85 mg of corydine. From the subsequent fractions ((9:1) and (4:1)) were isolated 123 mg of protopine and 273 mg of allocryptopine.

The combined phenolic alkaloids were also chromatographed on a column of silica gel using as eluents chloroform and chloroform—ethanol. The first chloroform fractions yielded predicentrine (49 mg), isocorydine (44 mg), and corydine (38 mg). The (99.5:0.5) and (99:1) fractions gave an additional amount of corydine (35 mg) and glaufidine (125 mg). Elution with the (98:2) and (97:3) mixtures gave 66 mg of thalicmidine and 58 mg of norbracteoline. The (95:5) and subsequent fractions led to the isolation of reticulin (41 mg).

The combined chloroform-extracted alkaloids were separated similarly, to give 28 mg of dehydrocorydine, 134 mg of isocorydine, 217 mg of corydine, 18 mg of thalicmidine, 1.75 g of protopine, and 4.16 g of allocryptopine.

Treatment of the combined iodides (0.5 g) with ethanol led to the isolation of 0.12 g of stylopine α-methohydroxide.

Norbracteoline, $[\alpha]_D$ +41° (c. 0.4; methanol).

Methylation of Norbracteoline. A solution of 15 mg of norbracteoline in 2 ml of Craig's mixture (0.25 mg of 25% CH_2O and 25 ml of CH_3OH) was stirred for 1.5 h. Then 0.22 g of sodium tetrahydroborate was added to the solution and stirring was continued for another hour. The solution was evaporated to dryness, the residue was dissolved in 10% sulfuric acid, the solution was made alkaline with concentrated ammonia, and the reaction product was extracted with ether. This gave a product identical with bracteoline according to TLC, melting point, and IR spectrum.

SUMMARY

Twelve alkaloids have been isolated from the epigeal part of wild *Glaucium corniculatum* (L.) J. Rudolf, one of them — norbracteolin — proving to be new.

Dehydrocorydine, predicentrine, glaufidine, thalicmidine, reticulin, and stylopine α-methohydroxide have been isolated from this species for the first time.

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CRYSTALLINE AND MOLECULAR STRUCTURES OF THE ALKALOID DELCOSINE

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The molecular and crystalline structures of the diterpene alkaloid delcosine (iliensine) have been investigated by x-ray structural analysis. It has been confirmed that the OH group in ring A is located at C(1) and has the α orientation. The rings in the molecule have the following conformations: A, B, and D — boat; C and F — envelope; E — chain. The ring linkages are: A/B — trans; A/E — cis; B/C — cis; B/D — cis; B/F — cis. The conformations and linkages of the rings are identical with those observed in lycoctonine.

In order to determine fully and unambiguously the spatial structure of the diterpene alkaloid delcosine (iliensine) (I) isolated from the plant *Delphinium biternatum* Huth., belonging to the family Ranunculaceae [1], we have performed an x-ray structural analysis.

The structure of the molecule of (I) projected onto the (010) crystallographic plane is shown in Fig. 1. The shapes and conformations of the rings can be judged from the figures of Table 1, which gives the coefficient of the equations of the main planes and the deviations of the atoms from them. The cyclohexane ring A (the C(1)C(2)C(3)C(4)C(5)C(11) atoms) has the boat conformation (the C(1), C(3), C(4), and C(11) atoms lie in one plane with an accuracy of 0.07 Å), and ring D (the C(8)C(9)C(13)C(14)C(15)C(16) atoms) also has the boat shape but with a slight flattening on the side of the C(16) atom. The seven-membered ring B (the C(5)C(6)C(7)C(8)C(9)C(10)C(11) atoms) has the boat conformation (with an accuracy of 0.05 Å); the departure of the C(5), C(6), and C(9) atoms from the plane of the other four amounts to 1.25, 1.45, and 0.50 Å, respectively (see Table 1). The five-membered ring C (the C(9)C(10)C(12)C(13)C(14) atoms) and F (the C(5)C(6)C(7)C(11)C(17) atoms) have the envelope conformation, but in ring F this form is somewhat distorted. The heterocycle E (the C(4)C(5)C(11)C(17)N(18)C(19) atoms) has the chair conformation. Ring linkages are as follows: A/B — trans; A/E — cis; B/C — cis; B/D — cis; B/F — cis. The conformations of the rings and also their linkages agree completely with those observed in hydroxymethyllycoctine hydriodide [2]. The hydroxy group in ring A is present in position 1 and is α-oriented, which confirms

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