

The combined alkaloids were separated through their solubility in acetone; heliotrine [1] was isolated. Paper chromatography showed that the mother liquor contained three other alkaloids besides heliotropine, with  $R_f$  0.32, 0.67 and 0.73, which could not be isolated in the crystalline state. The solvent system was butanol–acetic acid–water (20:1:20) and the revealing agent iodine vapor.

Solenanthus coronatus Rgl. We studied four species of plants of the genus *Solenanthus* [2, 3] and from them we isolated rinderine, turkestanine, and carategine. From the epigeal part of *S. coronatus* prepared in Sary-Dasht, Tadzhik SSR in the budding stage (12 June 1964) we obtained 0.82% of a mixture of alkaloids on the total weight of the plant.

The combined alkaloids were separated according to their solubility in acetone. Echinatine [3] was isolated (53% of the total). Paper chromatography showed the presence in the mother liquor of two noncharacterized alkaloids with  $R_f$  0.42 and 0.51.

Lindelofia stylosa (K. et K.) Brand. We have studied various organs (except the seeds) of this plant collected from various sites in the Kirgiz SSR previously [4], isolating three alkaloids. To study this plant we used seed of the 1964 crop (Alai valley, KirgSSR).

The alkaloids were extracted from the defatted seeds with chloroform and then with methanol. This gave 1.34% (from the chloroform extract) and 1.19% (from the methanolic extract) of combined alkaloids referred to the weight of the seeds (a total of 2.53%).

The combined alkaloids isolated by chloroform extraction were separated according to the solubility of the alkaloids in acetone, and viridiflorine [5] and echinatine [3] were obtained. The combined alkaloids obtained by methanolic extraction were chromatographed on alumina. The methanol–chloroform fractions (5:95) and (10:90), respectively, yielded echinatine N-oxide [6] and viridiflorine N-oxide [4].

By paper chromatography, the mother liquor was found to contain a mixture of these four bases.

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#### CONDENSATION PRODUCT OF LUPININIC ACID WITH PIPERIDINE

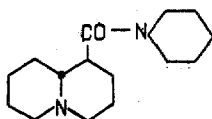
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The condensation product of piperidine with lupininic acid, obtained from the alkaloid lupinine, a crystalline substance with mp 240–241° C and  $[\alpha]_D^{25} +17.7^\circ$ , has been described previously [1].

A further study of the reaction products has shown that the product of the condensation of lupininic acid with piperidine is a liquid with bp 228–230° C (5 mm),  $[\alpha]_D^{25} +54.2^\circ$  (c 2.13; ethanol),  $R_f$  0.78, composition  $C_{15}H_{26}N_2O$ , melting point of the perchlorate 199–200° C (from water) and of the hydrochloride 114–115° C (from acetone).

The crystalline substance that we had isolated previously [1] proved to be a mixture of the hydrochlorides of the condensation product and piperidine.



The IR spectrum of the base  $C_{15}H_{26}N_2O$  contains bands at  $1623\text{ cm}^{-1}$  ( $>N-CO$  group) and  $2800-2700\text{ cm}^{-1}$  (trans-quinolizidine system). Its saponification with 20% sulfuric acid gave lupinic acid and piperidine. Consequently, the substance  $C_{15}H_{26}N_2O$  is lupinoylpiperidine. In order definitively to establish which of the epimers this substance was, we reduced it with lithium aluminum hydride. An oxygen-free base  $C_{15}H_{28}N_2$  corresponding in composition to piperidinolupinane was obtained.

For a direct comparison of piperidinolupinanes, we synthesized them by published methods [2-4]. The results of a direct comparison of the substances showed that the oxygen-free base  $C_{15}H_{28}N_2$  is piperidino-d-epilupinane. Thus, the compound  $C_{15}H_{26}N_2O$  has the structure d-epilupinoylpiperidine.

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#### STRUCTURE AND CONFIGURATION OF PEIMISINE

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Peimisine has the composition  $C_{27}H_{41}O_3N$ ,  $[\alpha]_D -44.62^\circ$  (c 0.98; ethanol) [1],  $R_f 0.25$  on alumina [ethyl acetate-ligroin-methanol (50:90:8)]. IR spectrum of peimisine:  $\nu_{\max}$   $3520\text{ cm}^{-1}$  (OH),  $1665$  ( $\frac{f}{\text{cm}}$ ),  $1700$  ( $C=O$ ),  $2930$ ,  $1470$  ( $C-CH_3$ ) and  $3260\text{ cm}^{-1}$  ( $>N-H$ ), and of O, N-diacetylpeimisine:  $\nu_{\max}$   $1735$ ,  $1245\text{ cm}^{-1}$  ( $-OCOCH_3$ ),  $1670$  ( $>N-CO-CH_3$ ),  $1718\text{ cm}^{-1}$  ( $C=O$ ). One oxygen atom in peimisine is inert. UV spectrum of peimisine:  $\lambda_{\max}$   $290\text{ m}\mu$  ( $\log \epsilon 1.74$ ). The reduction of the alkaloid ( $C_2H_5OH$ ,  $H_2$ , Pt) gave an amino alcohol with mp  $199-201^\circ\text{C}$  (from methanol), the IR spectrum of which lacked the absorption band of a carbonyl group. The mass spectra of peimisine and jervine are very similar [2].

Substance	Chemical shifts, $\tau$						
	C-19CH <sub>3</sub>	C-18CH <sub>3</sub>	C-21CH <sub>3</sub>	C-26CH <sub>3</sub>	O-CO-CH <sub>3</sub>	N-CO-CH <sub>3</sub>	C-3 $\alpha$ H
(I)	9.38	8.44	9.15	9.10	—	—	—
(II)	9.12	8.44	9.15	9.15	—	—	—
(III)	9.36	8.35	9.21	9.03	8.04	7.96	5.36

Thus, peimisine is based on the heterocyclic skeleton of jervine. The results of the NMR spectra of peimisine (I), the amino alcohol (II), and O, N-diacetylpeimisine (III) are given in Table 1.

The presence in the spectra of singlets at  $8.44\tau$  and  $9.36\tau$  and of peaks with  $m/e$  110, 124, and 125 show that the double bond in peimisine is between C-12 and C-13, as in jervine [3]. According to the NMR spectrum, the substance investigated has a C-3 $\beta$  OH and a carbonyl group in position 6 [4]. In addition, the signal from the C-19 methyl group in deoxypeimisine must be observed in a strong field and correspond to the  $5\alpha\text{-H}$ ,  $19\beta\text{-CH}_3$  configuration. Consequently, in peimisine the tertiary hydrogen atoms and the methyl groups on the carbon atoms of rings A, B, C, and D are in the same positions as in 11-deoxy-5 $\alpha$ , 6-dihydrojervine [4].

The mass spectra of jervine and peimisine differ not only in the mass numbers of the molecular ions but also in the intensities of the peaks with  $m/e$  110 and 125. In the spectrum of peimisine, the peak with  $m/e$  125 is more intense (100%) than the 110 peak (46%), and in jervine the 110 peak is more intense (100%) than the 125 peak (50%). This shows that in jervine the hydrogen atom at C-20 is oriented in the  $\beta$ -position and in peimisine in the  $\alpha$ -position.