

We have studied the combined alkaloids for the roots of Convolvulus subhirsutum Regel. collected in the phase of incipient budding in the environs of the village of Dzhigla, Chimkent province. From 2.8 kg of the roots we obtained 26.75 g of ether-extracted and 23.0 g of chloroform-extracted alkaloids, which amounts to 1.78% on the weight of the roots. By treating this semicrystalline ether-extracted material with acetone we made a partial separation of convolvine containing convolamine as impurity. The mother liquor was deposited on a column of alumina and elution was carried out with petroleum ether and then with diethyl ether. The diethyl ether fractions yielded crystals (I) with mp 189-190°C, R_f 0.55 (system 1: cyclohexane-chloroform-diethylamine (5:4:1) readily soluble in acetone and chloroform and sparingly soluble in ethanol and ether.

The IR spectrum of (I) contained absorption bands of a conjugated ester carbonyl group (1715 cm^{-1}) and of a 1,2,4-trisubstituted benzene ring ($830, 880, 1605\text{ cm}^{-1}$).

The mass spectrum of (I) contained the peaks of the molecular ion with m/z 608 and peaks with m/z 304, 182, 165, 123, and 83, which are characteristic for alkaloids of the tropane series. The peak of the molecular ion with m/z 608 indicates a dimeric nature of the alkaloid, and the presence in the spectrum of an ion with m/z 304 showed that the molecule of (I) consists of two symmetrical convolvine molecules linked with one another, probably by a $\text{CH}_2\text{-CH}_2$ group.

The PMR spectrum of the alkaloid contained a singlet at 3.82 ppm from aromatic methoxy groups, a multiplet of 5.15 ppm from $\text{C}_{3\alpha}\text{H}$, a multiplet at 3.41 ppm from $\text{C}_{1,\text{SH}}$, and a doublet at 6.77 ppm and a multiplet at 7.41 ppm from aromatic protons.

A singlet at 2.50 ppm was due to the signal of the equivalent protons of a $\text{CH}_2\text{-CH}_2$ group.

All the spectral characteristics, the melting point, and the R_f value indicated that we were dealing with the alkaloid convolvidine isolated by A. P. Orekhov and R. A. Konovalova from Convolvulus pseudocanthabrica [1]. These authors showed [1] that convolvidine was an artifact, i.e., the product of the condensation of convolvine with dichloroethane formed in the extraction of the alkaloids from the plant with dichloroethane, and also in the separation of the combined alkaloids into the individual bases, which was carried out with the aid of dichloroethane. In our case, dichloroethane was completely excluded from the extraction of the combined alkaloids and the separation of the mixture of bases. We used chloroform and methanol as the solvents, and this enables us to state that the alkaloid convolvidine is a native compound.

Convolvidine is actually formed when convolvine is heated with moist dichloroethane [2]. The condensation takes place through the active hydrogen at the secondary nitrogen atom in convolvine and one of the two chlorine atoms in dichloroethane [2]. This forms three reaction products: convolvine hydrochloride, which precipitates directly, and in the mother liquor, a base with mp 189-190°C (convolvidine) and a base (II) (M^+ 353). Substance (II) is the product of the addition of one molecule of convolvine to dichloroethane. The NMR spectrum of this substance showed the signals of the protons characteristic for convolvine; 3.84 (s, 3 H-2 OCH_3 and 5.13, 1 H, $s\text{-C}_{3\alpha}\text{H}$), and also the signals of the protons of a CH_2 group attached to nitrogen (with its center at 2.63, t, 2 H) and of a CH_2 group linked to halogen (with its center at 3.48, 2 H, t).

In [2], no alcoholic extraction was performed, which made it possible to draw an unambiguous conclusion. We extracted the combined alkaloids with methanol, and after careful separation succeeded in isolating convolvidine, which convinced us of its native nature.

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The second condensation product was not detected, although, a priori, one would have expected the isolation of this product.

The results of the extractions that we have performed without the use of dichloroethane permit the statement that convolvidine is a product of the vital activity of the plant organism itself.

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ALKALOIDS OF Aconitum zeravschanicum

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We have previously reported the isolation from epigeal parts of Aconitum zeravschanicum Steinb. collected at two growth sites of the alkaloids heteratisine ["heteratizine"], reticuline, and a number of unidentified bases [1]. In the present communication we give results on the identification of bases (II), (III), and (VI).

The composition of (II) [1] and its spectral characteristics corresponded to those of the alkaloid nominine [2]. A direct comparison of (II) with an authentic sample of nominine kindly sent by Prof. S. Sakai (Japan) showed their identity.

From the results of a comparison of the spectral characteristics and some chemical properties with those given in the literature, bases (III) and (IV), having the same composition $C_{22}H_{23}NO_2$, were identified as the alkaloids isoatisine and atisine [3], respectively. Thus, on being boiled with methanol, (VI) was readily converted into (III) [4]. On reduction with sodium tetrahydroborate, both (III) and (IV) gave a dihydroderivative [5] the oxidation of which with potassium ferricyanide [3] led back to (III) and (VI). Furthermore, on being heated with a 10% solution of hydrochloric acid (III) isomerized into a keto derivative [7] the IR spectrum of which had at 1713 cm^{-1} the strong absorption band of a carbonyl group in a six-membered ring.

The identity of (III) and (VI) as the alkaloids isoatisine and atisine, respectively, was also confirmed by the results of a preliminary stage of x-ray structural analysis, according to which the parameters of the elementary cell of a single crystal of (III) coincided with those of isoatisine [3] to within an accuracy of 0.01 Å.

Atisine has also been isolated in the form of the chloride from the epigeal part of A. zeravschanicum [7].

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