The fifth cardenolide, having $[\alpha]_D^{20}$ −43 ± 5° (c 0.4; methanol) was, apparently, a new cardiac glycoside. Its structure is being established.

Erycordin was also detected chromatographically.

A feature of rockery erysimum is that neither erysimoside nor erysimin is the main glycoside, as in the majority of Erysimum species. In rockery erysimum, bipindogulomethyloside predominates, and in this respect it is closer to the genus Cheiranthus than to Erysimum. The synomym of rockery erysimum, Cheiranthus pulchellus Willd, is apparently not fortuitous.

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DIHYDROSONGORINE FROM THE EPIGEAL PART OF Aconitum karacolicum

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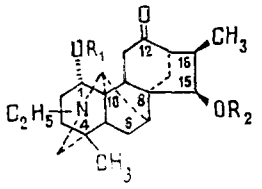
UDC 547.944/945

Continuing the separation of the total alkaloids of the epigeal part of Aconitum karacolicum Rapaics., collected in the valley of the R. Irisu (KirgSSR) [1], we have isolated a base with the composition $C_{22}H_{33}NO_3$ (I), mp 202-204°C (ethanol). The IR spectrum of the alkaloid had the absorption bands of hydroxy groups at 3400-3500 cm^{-1} and of a carbonyl group in a six-membered ring at 1700 cm^{-1}. The PMR spectrum ($CDCl_3$, δ scale), showed signals from a N-ethyl group (1.00 ppm, 3 H, triplet, J = 7 Hz), from a tertiary C-methyl group (0.68 ppm, singlet), and from a secondary methyl group (0.74 ppm, 3H, doublets J = 7 Hz). The mass spectrum of the alkaloid was close to those of bases of the songorine group [2]. When the alkaloid was acetylated with acetic anhydride in the presence of pyridine, a diacetyl derivative (II) was obtained with mp 128-130°C (petroleum ether), the PMR spectrum of which showed the signals of a secondary methyl group (0.63 ppm, 3H, d, J = 7 Hz), a tertiary C-methyl group (0.68 ppm, 3H, s), a N-ethyl group (1.00 ppm, 3H, t, J = 7 Hz), and two acetoxy groups (1.97 and 2.02 ppm, 3H each, singlets), and also a one-proton quartet at 4.97 ppm (H-1α) [3] and a one-proton doublet at 5.12 ppm (J = 8 Hz). Consequently, the developed formula of the base is: $C_{15}H_{19}$ (> $N—C_2H_5$) (> C—CH_3) (> HC—CH_3) (> C=O) $(OH)_2$. A comparison of the developed formulas of (I) and of songorine showed that in (I) there was a secondary methyl group in place of the terminal methylene group in songorine. These facts indicated that the alkaloid (I) was dihydrosongorine, which has been obtained previously by the catalytic hydrogenation of songorine [2, 4]. In actual fact, a comparison of the constants and also of mass and IR spectra showed their identity. It must be mentioned that the configuration of the secondary methyl group at C-16 in dihydrosongorine had remained unelucidated. Analysis of the PMR spectrum of dihydrosongorine diacetate permitted the conclusion that this methyl group is β-oriented. As already mentioned, in the PMR spectrum of (II), in addition to the H-1α signal, there is a one-proton doublet at 5.12 ppm with a splitting constant of 8 Hz which is obviously due to the H-15α atom at an acetoxy group. A study of a model of dihydrosongorine showed that the dihedral angle between the α-proton at C-15 and the β-proton at C-16 is 110-120° (J_{calc} = 2.5 Hz), and that with the α-proton at C-16 is 10-20° (J_{calc} = 8.5 Hz). The observed splitting constant agrees well with the β-configuration of the methyl group at C-16, and, consequently, the structure of dihydrosongorine can be represented by formula (I).



I. $R_1 = R_2 = H$

II. $R_1 = R_2 = Ac$

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CHROMATOPHOTOCOLORIMETRIC DETERMINATION OF INDOLE ALKALOIDS IN A CULTURE OF Rauwolfia serpentina TISSUE

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The known chromatophotocolorimetric method of determining ajmaline (I) in the biomass of a Rauwolfia tissue culture [1] includes a lengthy and laborious process of separating the alkaloids on previously impregnated paper. The disadvantages of the method are eliminated by replacing paper chromatography by thin layer chromatography (Silufol UV-254). The clear separation of derivatives of ajmaline (I) and of 17-O-acetylajmaline (II) makes it possible to determine them when they are present simultaneously. Standard samples of (I) (batch 10183, KhPKhFO "Zdorov'e") and of (II) obtained by acylating (I) [2] (followed by the separation of the mixture of di- and monoacyl derivatives by preparative chromatography) was used as control. In view of the retention in the (II) molecule of the indoline chromophore that is responsible for the bright red coloration on interaction with concentrated nitric acid, its photocolorimetric determination was carried out by the use of the graph plotted for (I) [3]. The mixture of alkaloids from the biomass isolated from 5 g of raw material [4] was dissolved in 5 ml of 95% ethanol. A 0.02-ml sample of this solution and 0.06 ml each of 0.5% ethanolic solutions of (I) and (II) (control) were deposited as bands on the starting line of a chromatogram. Chromatography was carried out by the ascending method in the chloroform–methanol–ammonia (90:10:0.2) solvent system. After the chromatogram had been examined in UV light, λ 254 nm, the sections containing the alkaloids being analyzed (R_f (I) 0.26; R_f (II) 0.50) were cut out and each was eluted with 10 ml of 95% ethanol by steeping with constant shaking for 2 h (which ensures the 95-97% elution of the (I) and (II)). The filtered eluate (6 ml in each case) was subjected to photocolorimetric analysis [3] (FÉK [photoelectric colorimeter] 56 M). The amounts of (I) and (II) in percentages of the absolutely dry raw material were calculated from the formula

$$X = \frac{a \cdot 0.5 \cdot 0.06 \cdot 100}{a_0 \cdot 0.02 \cdot 10^3 \cdot (100 - B)},$$

where a is the amount of (I) or (II) in 1 ml of colored solution (experiment) determined from the calibration curve, μg; a_0 is the amount of (I) or (II) in 1 ml of colored solution (control) determined from the calibration curve, μg; and B is the loss in weight in drying (%).

The metrological characteristics of the method show that it is not inferior in accuracy to the known method [1].

Batch No. of the raw material	I			II		
	$\bar{X}$	$S_{\bar{X}}$	$\varepsilon_{0,95\%}$	$\bar{X}$	$S_{\bar{X}}$	$\varepsilon_{0,95\%}$
1	0,83	0.01	3.61	0,105	0.03	7.54
2	0.77	0.02	6.49	0,082	0.002	4.88
3	1.06	0.02	4.72	0,048	0.002	8.33

The time of analysis is considerably shortened.

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