A comparison of the ^{13}C NMR spectra of (I) and the frondoside A (II) described previously [2], showed that (I) differed from (II) only by the presence of an additional double bond in the side chain of the aglycon. In actual fact, the ^{13}C NMR spectra of (I) showed signals at 145.9 and 110.9 ppm, and in the ^{1}H NMR spectra there were signals at 4.77 ppm (2 H-26) and 1.68 ppm (CH_3-27), which is characteristic for a terminal 25(26) double bond.

The catalytic hydrogenation of (I) (Adams catalyst, 20°C, 24 h) led to the dihydro derivative (II) (mp 234-236°C, $[\alpha]_{578}$ −31° (c 0.1; pyridine), coinciding completely in all its physicochemical characteristics and spectra with frondoside A.

Thus, cucumarioside A_0-2 is 16β-acetoxy-3β-O-{O-(3-O-methyl-β-D-glucopyranosyl)-(1→3)-O-β-D-xylopyranosyl-(1→4)-[O-β-D-xylopyranosyl-(1→2)]-O-β-D-quinovopyranosyl-(1→2)-(4-O-(sodiumsulfato)-β-D-xylopyranosyl)}holosta-7,25-diene.

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ALKALOIDS OF THE MONGOLIAN FLORA

II. ALKALOIDS OF Aconitum turczaninowii

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We have investigated the alkaloids of the epigeal part of Aconitum turczaninowii gathered in the budding period near Mungun-Mor't sumon of the Central aimak of Mongolia. Simple chloroform extraction yielded 1.5% of total alkaloids on the weight of the dry plant.

Five bases were isolated by chromatographing the total alkaloids on a column of alumina with elution by hexane containing gradually increasing amounts of chloroform, then with choroform, and then with chloroform to which methanol was gradually added. Four of them were identified, on the basis of a study of their spectral characteristics and comparison with authentic specimens, as aconitine [1], delsonine [2], delcosine [3], and lepenine [4].

Alkaloid (I) was new, and we named it tursoline. It had the composition $C_{25}H_{41}NO_8$ (HRMS, M^+ 483.28366), mp 249-251°C (acetone). The IR spectrum of the base contained absorption bands of hydroxy groups at 3460 cm^{-1} and of ether bonds at 1110 cm^{-1}. In the PMR spectrum (500 MHz, $CDCl_3$, δ scale), we observed the signals of an N-ethyl group (1.08 ppm, 3 H, t), of four methoxy groups (3.32, 3.33, 3.37, 3.43, 3 H each, s), and of a C-14-β proton (4.08 ppm, t, J = 5 Hz). The mass spectrum of the alkaloid was close to that of delsonine and showed that it differed from the latter by the presence of an additional hydroxy group. The mass spectrum was characterized by the following ion peaks (m/z, %): M^+ 483(16), 468(100), 466(58), 452(7), 450(41), 434(6), 432(10), 427(2), 412(6), 396(5), 336(4), 332(16). The maximum intensity of the peak of the ($M^+ - 17$ and $M^+ - 33$ ions showed the presence in the alkaloid of a hydroxy group at C-1 and a methoxy group at C-6 and also of a 7,8-diol system [5].

On the acetylation of (I) with acetic anhydride in the presence of pyridine, an amorphous 1-acetyl derivative (II) was obtained. Mass spectrum: M^+ 525, $M^+ - 59$ (100%). IR spectrum: 1710 cm^{-1} (ester carbonyl). PMR spectrum (100 MHz, $CDCl_3$, δ scale, ppm) 1.02 (3H, t, N−CH_2−CH_3), 1.95 (3H, s, $OCOCH_3$), 3.20; 3.25, 3.35; 3.35 (each 3H, 6, 4 × OCH_3), 4.01 (1H, t, J = 5 Hz, C-14-β-H), 5.21 (1H, q, J_1 = 10 Hz, J_2 = 7 Hz, C-1-β-H). The downfield shift and the multiplicity of the signal of the C-1-β proton in the PMR spectrum of (II) confirmed the presence of a hydroxy group in the alkaloid at C-1 and showed its α-

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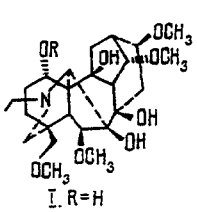
TABLE 1. Chemical Shifts of the Carbon Atoms of Tursoline 1-Monoacetate (II), Delcarpoline (III), and Delsonine (IV) ($CDCl_3$, 100 MHz)

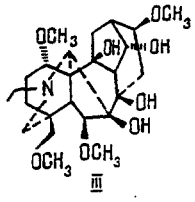
Carbon	II	III	IV	Carbon	II	III	IV
1	71,5	79,4	72,6	17	64,3	65,1	66,0
2	27,4	25,5	27,2	18	77,7	77,2	77,3
3	32,0	32,2	29,3	19	53,2	52,5	57,2
4	37,8	38,1	37,4	N–CH_2	50,5	51,3	50,3
5	45,7	45,1	43,9	N–CH_3	14,0	14,3	13,5
6	90,6	90,8	90,4	6′	57,9	57,7	57,2
7	87,9	88,0	87,8	16′	56,2	56,3	56,3
8	76,6	75,1	78,5	18′	59,0	59,1	59,1
9	52,7	54,0	44,9	14′	57,6	—	57,9
10	80,6	79,9	37,7	C=O	170,5	—	—
11	53,2	53,8	49,3	CH_3	22,0	—	—
12	40,0	37,6	30,5				
13	38,1	37,0	43,3				
14	82,0	73,6	84,5				
15	34,3	33,9	33,5				
16	82,4	81,3	82,9				

orientation. According to its empirical formula and functional composition, (I) belonged to the C_{19} diterpene alkaloids. In the light of the fact that acetylation with acetic anhydride in the presence of pyridine led to a monoacetyl derivative, it was possible to draw the conclusion that the substituents at C-18, C-14, and C-16 were methoxy groups. In the PMR spectrum of (I) the signal of the C-14-β proton was detected in the weak field (4.08 ppm), which is obviously explained by the descreening influence of a C-10 hydroxy group [6].

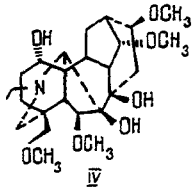
What has been said above and also its combined isolation with delsonite permitted the conclusion that alkaloid (I) was N-ethyl-1α,7β,8β,10β-tetrahydroxy-6β-14α,16β-trimethoxy-4β-methoxymethylaconitane. This conclusion was confirmed by a study of the ^{13}C NMR spectrum of the tursoline C-1 monoacetate (II). The multiplicities of the signals were established with the aid of the "off resonance" spectrum. The assignment of the signals was made by a comparison with the spectra of delcarpoline (III) and delsonine (IV) [7, 8] (Table 1).



I. R=H
II. R=Ac



III



IV

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