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ALKALOIDS OF THE FLORA OF MONGOLIA

V. TURPELLINE — A NEW ALKALOID FROM *Aconitum turczaninowii*

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In the course of a further study of the alkaloids of the epigeal part of Aconitum turczaninowii *a new alkaloid has been isolated, which has been named turpelline. A structure for turpelline has been proposed on the basis of a study of its IR, mass, PMR, ^{13}C NMR, and 2D COSY spectra.*

Continuing a study of the alkaloid composition of the epigeal part of *Aconitum turczaninowii* [1, 2], we have isolated a new base, which has been called turpelline. Turpelline (I) has the composition $C_{22}H_{23}NO_4$ (M^+ 375.24095), mp 268-271°C. Its IR spectrum contained the absorption bands of hydroxy groups (3445-3300 cm^{-1}). The PMR spectrum showed the signals of a N-ethyl group, a tertiary C-methyl group, and a terminal methylene group, and also the signals of four protons geminal to hydroxy groups (Table 1).

The mass-spectral fragmentation of turpelline was close to that of napelline (II). The maximum peak in it was that of the molecular ion, M^+ 375, and the peaks of $M^+ - 15$ (20%), $M^+ - 17$ (40%), $M^+ - 18$ (21%) and $M^+ - 59$ (26%) ions were also observed. Thus, the peak of the molecular ion of (I) is 16 a.u. greater than that of napelline, which showed the possible presence of an additional hydroxy group in the former. The presence of the peak of a $M^+ - 17$ ion permits the assumption that this hydroxy group is located at C-1 [3]. What has been said above gives grounds for assuming that turpelline is an alkaloid of the napelline type.

The main information required for establishing the structure of (I) was obtained from PMR spectra taken at a working frequency of the spectrometer of 500 MHz, with the inclusion of the results of a 2D COSY experiment (Fig. 1).

Thus, the spectrum of (I) included the signal of a proton geminal to th C-1 hydroxy group at 4.58 ppm in the form of a doublet of doublets, showing its α-orientation [4]. On the basis of this signal, in the 2D COSY we identified the signals of protons at C-2 and C-3. Then, using the H-7 signal (2.25 ppm, doublet) for orientation, we traced the link with the protons at C-6, C-5, and C-20.

The H-13 signal is informative and characteristic for alkaloids of the napelline type. In the PMR spectrum of turpelline, H-13 appeared in the form of a doublet with the SSCC $J_{13,14\beta}$ = 4.4 Hz. Consequently, the two other possible constants, $J_{13,14\alpha}$ and $J_{13,12\beta}$ are equal to zero. Assuming the presence of a dihedral angle of 90°C, zero constants are possible when the hydroxy group at C-12 has the α-orientation, as follows from (III) and the literature [5, 6]. Moreover, as can be seen from (III), such an oriention of the OH group explains the long-range $H_{12}-H_{14\beta}$ SSCC in view of the presence of a W system [7].

The signal of the H-11 proton consists of a doublet of doublets with the SSCCs 7.8 Hz and 10.3 Hz. The dihedral angles calculated for the observed constants show that all three interacting protons (H-11, H-12, and H-9) occupy axial positions. Consequently, the hydroxy group at C-11 has the β-orientation. In the PMR spectrum of (I) the H-15 signal appears at 4.45 ppm in the form of a triplet with J = 2.4 Hz. According to the 2D COSY spectrum, it is linked by an allyl interaction with the protons of the terminal methylene group at C-17. Thus, in an analysis of the cross-peaks in the 2D COSY spectrum of turpelline we made the assignments of the proton signals that is given in Table 1.

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TABLE 1. Details of the Analysis of the 2D COSY Spectrum of Turpelline

H	м. д., J	H	м д., J
1	4.58; dd, 7.1; 12.2 Hz	14.B	2.09; d, 12.1 Hz
2.A	2.01; m	15	4.45; t, 2.4 Hz
2.B	2.9; m	17.A	5.32; br.s
3.A	1.16; m	17.B	5.16; d, 2.0 Hz
3.B	1.36; m	18	0.62; s
5	1.56; br.d 7.9 Hz	19.A	2.45; br.d, 13.5 Hz
6.A	1.34; d.d 4.5and13.5 Hz	19.B	2.9; m
6.B	3.23; d.d 8.3and13.5 Hz	20	3.98; br.s
7	2.23; d, 5.0 Hz	$N-CH_2$	2.86; m
		CH_3	1.37; m, 7.4 Hz
9	2.31; d 10.3 Hz		
11	4.82; dd, 7.8 и 10.3 Hz		
12	3.90; br.d, 7.5 Hz		
13	2.81; br.d, 4.4 Hz		
14.A	1.05; dd, 12.1 and 4.4 Hz		

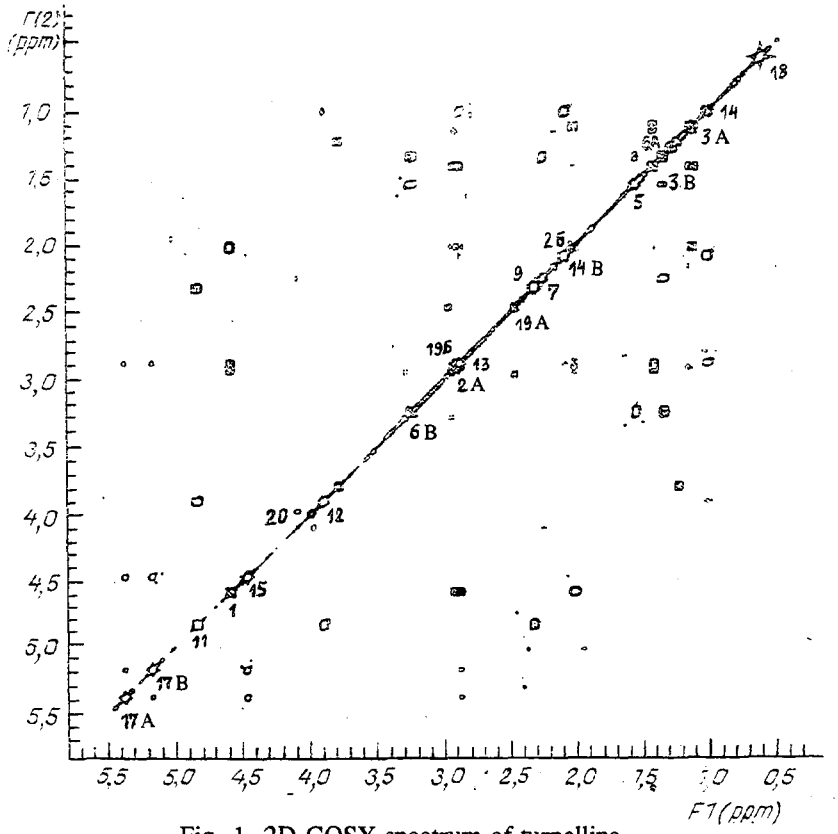

Fig. 1. 2D COSY spectrum of turpelline.

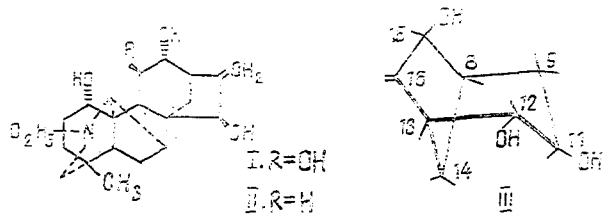

Fig. 2.

TABLE 2. Chemical Shifts of the Carbon Nuclei of Turpelline (II) and Napelline (II)

Carbon	I	II	Carbon	I	II
1	68.9	70.5	16	158.6	160.8
2	30.22	31.9	17	109.8	107.4
3	31.2	32.4	18	25.6	26.4
4	36.8	34.7	19	59.2	57.7
5	48.4	49.4	20	66.8	66.2
6	23.6	23.5	$N-\overset{CH_2}{\underset{CH_3}{}}$	51.5	51.6
7	45.8	45.0		10.7	13.3
8	55.2	50.3			
9	46.8	38.2			
10	55.5	53.5			
11	73.5	29.4			
12	82.7	76.2			
13	46.8	49.9			
14	37.2	38.4			
15	77.4	77.8			

The proposed structure was confirmed by a study of the ^{13}C NMR spectrum of turpelline. The multiplicities of the signals were established with the aid of the J-modulation spectrum. The assignment of the signals was made by comparison with the spectrum of napelline (Table 2). The close values of the chemical shifts of the C-15 carbons in turpelline and in napelline permit us to consider that the hydroxy groups at these carbon atoms have the same orientation. The facts given above permit the conclusion that turpelline is 11β-hydroxynapelline.

EXPERIMENTAL

Type KSK silica gel and alumina (activity grade I) were used for chromatography.

Mass spectra were taken on a MKh-1310 instrument with a system for direct insertion into the ion source, and IR spectra on a UR-20 spectrometer (KBr). PMR and ^{13}C NMR spectra were recorded on a Varian UNITY-500 MHz spectrometer in deuteromethanol and deuteropyridine.

Two-dimensional NMR Spectroscopy. 2D NMR spectra were recorded on Varian VXR-500 spectrometer fitted with a SUN 3/50 computer, using the stanard VNMR software. The following procedure was used to obtain the two-dimensional $^1H-^1H$ spectrum.

COSY — the standard relay program. Dimensions of the matrix 1K × 0.5K. Width of the spectrum 2802 Hz. Relaxation delay 1.4 s. Before Fourier transformation, the free induction decay signal was multiplied by a bell-shaped function with zero shift.

The extraction and separation of the total alkaloids has been described in [2]. On treatment with acetone of a chloroform–methanol (93:3) eluate, 0.06 g of turpelline precipitated.

Turpelline (I). IR spectrum (ν_{max}^{KBr}, cm^{-1}): 3440, 3300, 1080, 1040. Mass spectrum, m/z (%): M^+ 375 (100), 360 (20), 358 (40), 357 (21), 340 (13), 316 (26), 246 (13), 228 (10), 200 (20). Details of the PMR spectrum are given in Table 1, and those of the ^{13}C NMR spectrum in Table 2.

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