ALKALOIDS OF Stephania delavayi

II. 16-OXODELAVAYINE

T. N. Il'inskaya, M. E. Perel'son,
I. I. Fadeeva, D. A. Fesenko,
and O. N. Tolkachev

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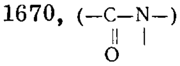
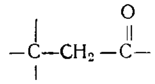
From the herb Stephania delavayi Diels (Menispermaceae) grown in Transcaucasia, by chromatography on alumina we have isolated a new base (I) with the composition $C_{20}H_{21}O_6N$, mp 221-222°C (from methanol, Kofler), $[\alpha]_D$ −180° (c 1.55; chloroform) for which the structure of 16-oxodelavayine is proposed.

The UV spectrum of (I)($\lambda_{max}^{ethanol}$ 242 and 268 nm; log ε 3.79 and 4.05, λ_{min} 228, 246 nm; log ε 3.70 and 3.78) is extremely similar to that of delavayine [1] ($\lambda_{max}^{ethanol}$ 240 and 270 nm; log ε 3.73 and 4.00; λ_{min} 228 and 246 nm; log ε 3.67 and 3.71).

The IR spectrum of the new base (Fig. 1) has bands at (cm^{-1}) 1686 (C=O, α,β-unsaturated ketone), 1670,  $(-\underset{\underset{O}{\|}}{C}-\underset{|}{N}-)$, 1605, 1510, and 1490 (C=C).

The base gives a positive reaction for a methylenedioxy group.

The NMR spectrum of (I) is also very similar to the spectrum of delavayine. Below we give the characteristics of the NMR spectrum of 16-oxodelavayine (HA-100D, $CHCl_3$; O − TMS), showing its structural similarity to delavayine [1].

Chemical shift, δ, ppm (multiplicity,* J=Hz)	Assignment
6,64 (s)	C_4-H
6,46 (s)	C_1-H
5,88 (s)	$-O-CH_2-O-$
4,10 (s)	$CH_3O-C=C-C=O$
3,66 (s)	 $CH_3O-\underset{\underset{C}{\|}}{C}-C=O$
2,96 (s)	$CH_3-N<$
2,90 (d; 16,0)	 $-\overset{|}{\underset{|}{C}}-CH_2-\overset{\overset{O}{\|}}{C}-$
2,66 (d; 16,0)	
2,5–2,8 (m)	$H-C_{10}-H$
2,5–2,8 (m)	$H-C_{15}-H$
2,1–2,35 (m)	$H-C_9-H$

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*s − singlet; d − doublet; m − multiplet.

It can be seen from the facts given that the differences in the spectra are due exclusively to the presence of an amide carbonyl in (I); as was to be expected, the signal of the $N-CH_3$ group is shifted downfield to 2.96 ppm, the multiplet from the methylene group at C_{16} is absent, and the multiplet of the C_{15} methylene protons has been shifted downfield to 2.5-2.8 ppm. As in the case of delavayine, long-range spin−spin coup-

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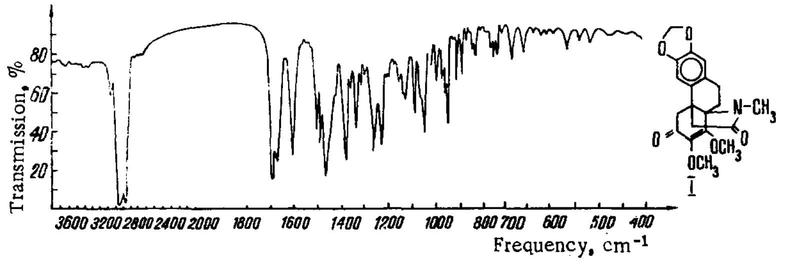

Fig. 1. IR spectrum of 16-oxodelavayine (mull in paraffin oil).

ling is observed between the protons at C_{10} and C_1-H, which was shown by means of double resonance. (When the multiplet in the 2.5-2.8 ppm region was irradiated, the broadening of the signal at 6.46 ppm decreased.)

What has been said above permits us to put forward structure (I) as the most probable for the base isolated.

LITERATURE CITED

1. I. I. Fadeeva, T. N. Il'inskaya, M. E. Perel'son, and A. D. Kuzovkov, Khim. Prirodn. Soedin., 7, 784 (1971).