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COMPLETE ASSIGNMENTS IN ^{1}H AND ^{13}C NMR SPECTRA OF URAPHINE AND 6-OXOCORUMDEPHINE USING 2D NMR SPECTROSCOPY

T. M. Gabbasov,* E. M. Tsyrlina, L. V. Spirikhin, and M. S. Yunusov

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We reported earlier on the isolation from the aerial part of *Delphinium uralense* Nevski of the unreported norditerpene alkaloids uraphine (**1**) and 6-oxocorumdephine (**2**) [1, 2]. The structures of these alkaloids were determined based on PMR, ^{13}C NMR, and IR spectroscopy and mass spectrometry in addition to a comparison with the corresponding literature data on closely related compounds.

We performed a series of DEPT, 2D COSY, 2D HSQC, 2D HMBC, and 2D NOESY experiments in order to assign more reliably resonances in the PMR and ^{13}C NMR spectra.

The starting point for solving 2D spectra of **1** were resonances of methylenedioxy protons (δ_H 5.12, 5.09 ppm), which had cross peaks in the 2D HMBC spectrum with resonances of quaternary C atoms C-7/C-8. Of these C atoms, only one had a cross peak with proton H-14. This fact enabled the resonances of C-7 and C-8 to be differentiated.

The characteristic triplet for the C-14 proton had two cross peaks in the 2D COSY spectrum for coupling with resonances of H-9 and H-13. Of these, only one had a cross peak with C-8 in the HMBC spectrum. These data as a whole enabled the resonances of H-9 and H-13 to be differentiated. Cross peaks in the 2D COSY spectrum were noted for coupling of H-13 with one of the H-12 protons and the H-16 proton. The cross peak for coupling of H-9 was used to find the resonance of H-10, which in turn had a cross peak with one of the H-12 protons. The presence of cross peaks between the resonances for C-14, C-16, and protons of the corresponding methoxyls in the 2D HMBC spectrum helped to differentiate these groups. Relying on the basic correlations in the 2D COSY (Fig. 1) and 2D HMBC spectra tuned to through-space ^{1}H–^{13}C SSCC and DEPT and 2D HSQC spectra, we made further assignments of resonances in the PMR and ^{13}C NMR spectra of **1**, including resonance lines of C atoms without H atoms (Table 1). The series of 2D spectral experiments were used to switch the chemical shifts for C-2 and C-3, and for C-9 and C-10 compared with those proposed earlier [1].

Additional proof of the structure was obtained from an analysis of 2D NOESY spectra. The presence of a NOE between H-10 and H-1, and between H-10 and H-14, and additional effects between H-1 and H-5 confirmed that these protons were closely spaced and had identical β-orientations. For α-oriented proton H-14, NOE should be observed between H-14 and one of H-15, H-14, and H-16; for β-H-6, coupling with H-9 and H-10, which were absent in the 2D NOESY spectrum.

2D spectra for **2** were solved using the fragment with characteristic NMR parameters, namely the C-6=O group, as the starting point. The resonance of this C atom in the ^{13}C NMR spectrum was observed at weak field at δ_C 217.1 ppm. Cross peaks between C-6 and protons of two CH groups were noted in the 2D HMBC spectrum tuned to through-space ^{1}H–^{13}C SSCC. These could be assigned only to H-5 and H-17. One of these protons also had cross peaks with the resonance of one of the two quaternary C atoms bound to the methylenedioxy (C-7/C-8) and the C atom of the CH_2(Et) group. This enabled it to be identified as H-17 and differentiated H-5 and H-17. Their C resonances were determined using the 2D HSQC spectrum.

Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences, Russian Federation, 450054, Ufa, Prosp. Oktyabrya, 71, fax: (347) 235 60 66, e-mail: ivanov_sp@anrb.ru. Translated from *Khimiya Prirodnykh Soedinenii*, No. 4, July–August, 2012, pp. 640–641. Original article submitted February 21, 2012.

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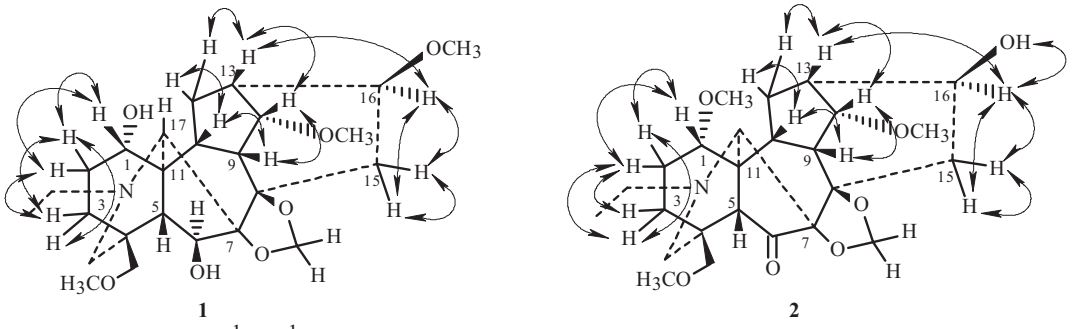
TABLE 1. Chemical Shifts in PMR and ^{13}C NMR Spectra of Uraphine (**1**) and 6-Oxocorumdephine (**2**) (δ, ppm)

C atom	1		2		C atom	1		2	
	δ_C	δ_H	δ_C	δ_H		δ_C	δ_H	δ_C	δ_H
1	71.9	3.78	83.2	3.22	14	83.5	3.72	82.8	3.74
2	29.2	1.63; 1.51	26.0	2.50; 2.03	15	33.7	2.50; 1.92	35.4	2.54; 1.75
3	27.0	1.94; 1.66	32.3	1.77; 1.59	16	82.2	3.29	71.3	3.77; 4.35 (OH)
4	37.1	–	38.8	–	17	65.5	3.01	63.6	3.75
5	47.6	1.59	56.1	2.05	18	78.5	3.28; 3.20	76.6	3.24; 3.06
6	78.9	4.37	217.1	–	19	58.1	2.58; 2.35	53.4	2.67; 2.07
7	92.0	–	91.8	–	CH_2O_2	93.3	5.12; 5.09	95.3	5.55; 5.12
8	85.2	–	81.4	–	21	50.0	2.84; 2.69	50.3	2.79; 2.62
9	40.0	3.59	41.3	2.37	22	13.4	1.11	13.8	1.06
10	45.1	2.17	47.7	1.92	1-O$\underline{CH_3}$	–	–	56.0	3.31
11	51.2	–	45.9	–	14-O$\underline{CH_3}$	57.7	3.43	58.3	3.40
12	30.3	2.13; 1.73	26.6	1.95; 1.88	16-O$\underline{CH_3}$	56.3	3.37	–	–
13	36.8	2.48	39.6	2.45	18-O$\underline{CH_3}$	59.5	3.36	59.2	3.34



1 **2**

Fig. 1. Principal ^1H—^1H COSY Correlations for uraphine (**1**) and 6-oxocorumdephine (**2**).

The presence of a cross peak for H-5 with the resonance of only one quaternary C atom bound to the methylenedioxy enabled the resonances of C-7 and C-8 to be differentiated. The presence in the 2D HMBC spectrum of a cross peak between C-14 and protons of the corresponding methoxyl helped to differentiate this group. Relying on the principal correlations in the 2D COSY (Fig. 1) and 2D HMBC spectra tuned to through-space ^1H–^{13}C SSCC and on DEPT and 2D HSQC spectra, we made further assignments of resonances in the PMR and ^{13}C NMR spectra for **2**, including resonances of C atoms without H atoms (Table 1). The series of 2D spectral experiments were used to switch the chemical shifts for C-9 and C-10 of **2** compared with those proposed earlier [2].

Data from the 2D NOESY experiment were also invoked in order to solve the question of the relative configuration of the C-1 and C-14 substituents. The presence of NOE between H-10 and H-1, H-10 and H-14, and H-1 and H-5 confirmed that these protons were closely spaced and had the β-orientation; between one of the H-15 protons and H-17, and H-16, the α-orientation. For α-oriented H-1 and H-14, a NOE between H-14 and H-16, and between H-1 and H-17 should be observed. These were missing in the 2D NOESY spectrum.

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