3. G. P. Sidyakin, Author's abstract of doctoral dissertation [in Russian], Tashkent (1966).
4. A. Kholmuradov, Author's abstract of Candidate's dissertation [in Russian], Tashkent (1971).
5. D. Kurbanov and S. Yu. Yunusov, Khim. Prir. Soedin., 289 (1967).
6. T. P. Toube, J. W. Murphy, and A. D. Cross, Tetrahedron, 23, 2067 (1967).
7. R. Storer and D. W. Young, Tetrahedron, 29, 1721 (1973).
8. D. M. Razakova, I. A. Bessonova, Kh. A. Abdullaeva, and S. Yu. Yunusov, Khim. Prir. Soedin., 395 (1983).
9. G. P. Sidyakin, M. Eskairov, and S. Yu. Yunusov, Dokl. Akad. Nauk UzSSR, No. 8, 27 (1958).

NMR INVESTIGATION OF ALKALOIDS.

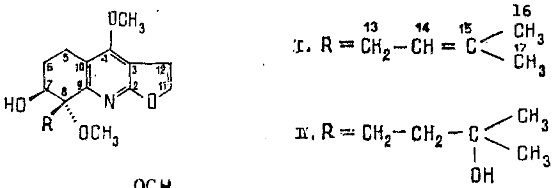
X. ^{13}C NMR SPECTRA AND STRUCTURE OF ALKALOIDS OF THE 5,6,7,8-TETRAHYDROFURANOQUINOLINE TYPE

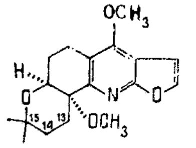
M. P. Yagudaev and I. A. Bessonova

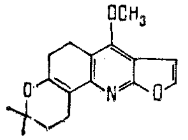
UDC 547.944.1.92

On the basis of a study of the spin-spin coupling constants J_{CH} and the ^{13}C chemical shifts of haplophyllidine an assignment has been made of the signals of the carbon atoms of the 5,6,7,8-tetrahydrofuranoquinoline alkaloids haplophyllidine, perforine, anhydroperforine, their derivative (IV), and the furanoquinoline base γ-fagarine.

Haplophyllidine (I), perforine (II), and anhydroperforine (III) are the first derivatives of the new 5,6,7,8-tetrahydrofuroquinoline series of alkaloids. Their structures, established by chemical transformations, interconversions, and the method of spectral analysis [1-3] have been confirmed by the X-structural investigation of anhydroperforine [4].

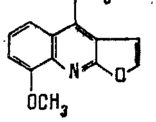






III

IV



V

There is information in the literature on a study of the ^{13}C NMR spectra of a number of furanoquinoline alkaloids [5, 7] and also of modified derivatives – perfamine and

---

Institute of the Chemistry of Plant Substances, Uzbek SSR Academy of Sciences, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 25-30, January-February, 1989. Original article submitted March 5, 1988.

0009-3130/89/2501-0020 $12.50

TABLE 1. Chemical Shifts of the Carbon Atoms of Haplophyllidine (I), Perforine (II), Anhydroperforine (III), Compound (IV), and γ-Fagarine (V) (δ, ppm; 0 – TMS)

C-atom	Multiplicity	I ($CDCl_3$)	II (DMSO-d_6)	III ($CDCl_3$)	IV ($CDCl_3$)	V ($CDCl_3$)
C-2	s	161,87	161,54	161,90	163,60	162,72
C-3	s	116,79	116,54	118,01	110,72	119,12
C-4	s	157,87	157,94	153,30	156,00	156,33
C-5	t	18,37	18,02	18,24	18,05	107,32 (d)
C-6	t	23,93	23,87*	22,26*	19,85*	122,90 (d)
C-7	d	69,35	67,21	70,76	156,04 (s)	113,70 (d)
C-8	s	78,81	78,01	73,00	105,66 (s)	154,11
C-9	s	150,09	151,15	149,22	152 78	137,07
C-10	s	104,66	104,90	104,92	103,37	163,32
C-11	d	142,04	142,69	142,00	140,60	143,28
C-12	d	104,23	104,56	104 53	104,93	104,07
C-13	t	29,71	35,88	34,03	33,23	
C-14	d	119,49	23,18* (t)	25,65* (t)	26,94* (t)	
C-15	s	133 15	69 23	71,02	74,99	
C-16	q	25,77	29,36	30,75	25,66	
C-17	q	17,79	29,36	21,77	26,65	
4-OCH_3	q	58,03	58,55	58,15	58,47	58,45
8-OCH_3	q	50,28	49,55	50,00		55,43

---

*The assignments may be interchanged.

TABLE 2. Experimental Values of the Constants J_{CH} for Haplophyllidine (I), Hz

^1J (one-bond)		^3J (geminal)		^3J (vicinal)	
designation	value	designation	value	designation	value
C-11—H-11	224,1	C-11—H-12	—9,1	C-2—H-11	8,6
C-12—H-12	179,3	C-12—H-11	—12,5	C-2—H-12	8,6
C- 5—H-5	127,0	C-5—H-6	—5,3	C-3—H-11	6,5
C- 6—H-6	127,4	C-6—H-5	—3,7 —4,0		
C- 7—H-7	145,0	C-8—H-7	≈—1,5		
C-13—H-13	127,1	C-10—H-5	—4,7		
C-14—H-14	145,9	C-13—H-14	≈—2,0		
C-16—H-16	125,2	C-14—H-13	—6,5		
C-17—H-17	125.0	C-15—H-14	- 5.5		
4-OCH_3	143,0	C-15—H-16	—5 5		
8-OCH_3	143 0	C-15—H-17	—5,5		

dihydroperfamine [8]. It must be mentioned that in the latter the assignment of the signals of the C-5 and C-6 methylene carbon atoms should be reversed because of the considerable α-contribution of the carbonyl group in position 7 (Δδ ≈ +12 ppm) [9], i.e., the weak-field signal at 38.74 ppm relates to the C-6 atom and the strong-field signal at 19.92 ppm to the C-5 atom.

In the present paper we consider the results of a study of the ^{13}C NMR spectra of haplophyllidine, perforine, anhydroperforine, their derivative (IV), and γ-fagarine (V) with the aim of establishing a correlation between the CSs of the ^{13}C atoms and structure (Table 1). The assignment of the signals of the carbon atoms was made on the basis of the spectra obtained with complete and incomplete suppression of C—H interactions, and also by analyzing the ^{13}C—H SSCCs in the high-resolution spectrum (without the suppression of C—H interactions) of haplophyllidine (I) (Table 2, Fig. 1). In addition, in the assignment of certain signals of carbon atoms the spatial effects of substituents on the ^{13}C CSs [10] were taken into account and a comparison was made with ^{13}C NMR spectra of furoquinoline alkaloids close in structure known in the literature [5-7].

As can be seen from Table 1, in the ^{13}C NMR spectra of haplophyllidine, perforine, and anhydroperforine the signals of all 18 carbon atoms are clearly shown, the values of the chemical shifts of the carbon atoms of the furanopyridine fragment of their molecules being close to those in γ-fagarine (see Table 1) and other furanoquinoline alkaloids [5-7].

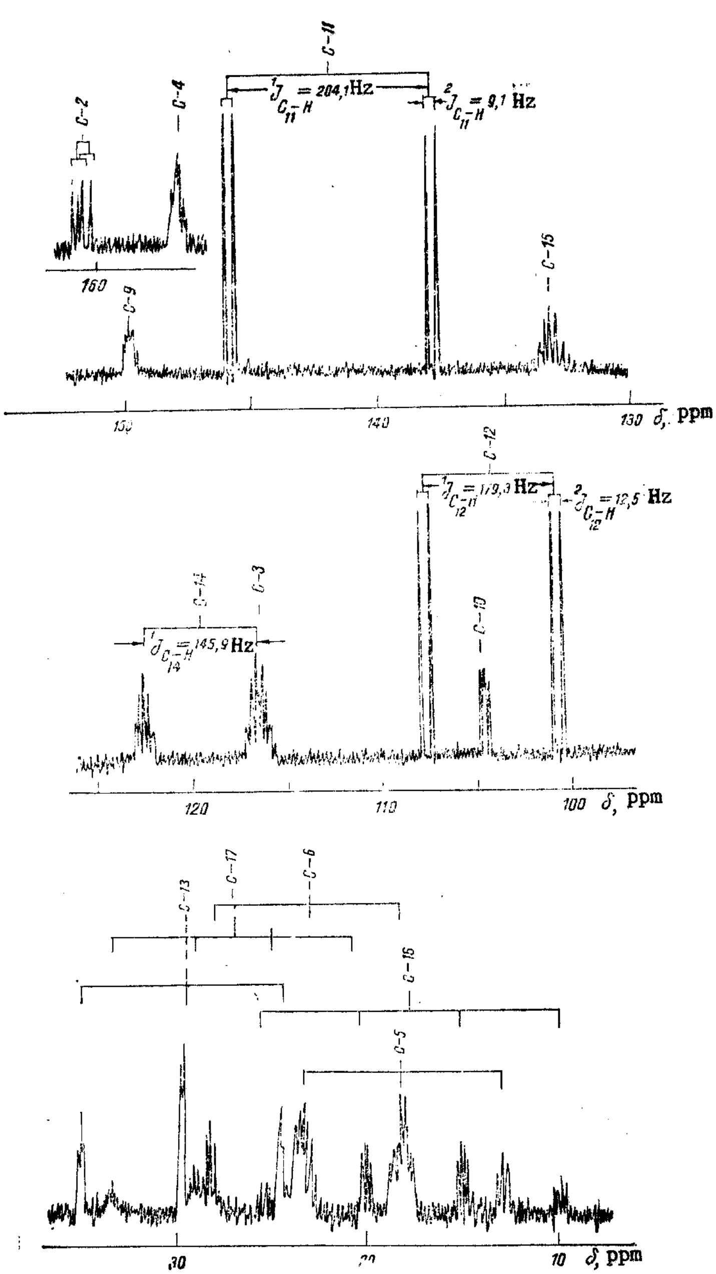


Fig. 1. High-resolution ^{13}C NMR spectrum of haplophyllidine.

The results of the analysis of the one-bond ($^1J_{CH}$), geminal ($^2J_{CH}$), and vicinal ($^3J_{CH}$) SSCCs in the high-resolution ^{13}C NMR spectrum of haplophyllidine (I) permit an unambiguous assignment to be made of the signals of the majority of the carbon atoms (Table 2 and Fig. 1).

The values of the one-bond (204.1 and 179.3 Hz) and geminal (−9.1 and −12.5 Hz) J_{CH} constants of the signals of the C-11 and C-12 atoms of the furan ring of (I) observed in the form of doublets of doublets (see Fig. 1) are similar to the $^1J_{CH}$ and $^2J_{CH}$ values of the signals in the spectra of furan and benzofuran [11, 12]. The signal of the C-2 quaternary atom consists of a doublet of doublets due to the existence of two approximately equal vicinal SSCCs ($^3J_{C-2-H-11}$ and $^3J_{C-2-H-12} \approx 8.6$ Hz), while the signal of the C-4 atom appears in the form of a multiplet through vicinal interaction with the H-12 and H-5 protons and those of the 4-OCH_3 group. These values of ^1J and ^2J give grounds for assigning the signal at 161.87 ppm to the C-2 atom and that at 157.87 ppm to the C-4 atom (see Table 1).

In the strong-field region of the high-resolution ^{13}C NMR spectrum at 18.37 ppm there is a signal in the form of a triplet of triplets with values $^1J = 127.0$ Hz and $^2J = -5.3$ Hz (see Table 2 and Fig. 1). The triplet nature of the components of this signal indicates that they can be assigned only to the C-5 carbon atom, since the methylene group at C-6 is adjacent to it.

An alternative assignment of the signals of the methylene carbon atoms C-6 and C-13 was made on the basis of the following considerations. The signal at 23.93 ppm is a triplet of multiplets with $^1J = 127.4$ and $^2J = -3.7$ and -4.0 Hz, while the signal at 29.71 ppm appears in the form of a triplet of quartets with $^1J = 127.1$ and $^2J = -2.0$ Hz. The multiplet nature of the component of the signal of the carbon atom at 23.93 ppm unambiguously shows that this carbon atom interacts with more than two vicinal protons, i.e., the signal at 23.93 ppm belongs to the C-6 methylene atom, since the latter can interact with the three protons at C-5 and C-7. The quartet nature of the components of the triplet at 29.71 ppm, and also the value of its vicinal constant ($J \approx -2$ Hz, which is twice as great as $^2J_{CH}$ for the C-5 and C-6 signals probably because of the influence of the sp^2-hybridized C-14 atom [13]), given grounds for assigning this signal to the C-13 atom.

It can be seen from Table 2 that the values of the one-bond constants for C-7, 4-OCH_3, and 9-OCH_3 are considerably higher than $^1J_{CH}$ of the signals of the C-5 and C-6 carbon atoms. This is obviously due to the influence of groups containing electronegative oxygen atoms [13, 14]. The $^1J_{CH}$ value of the signal of the C-14 olefinic carbon atom is close to that of trimethylethylene [15].

The signal of the C-15 quaternary olefinic atom consists of a multiplet due to the vicinal interactions with the protons of the gem-dimethyl group and the olefinic proton.

A comparison of the CSs of the C-16 and C-17 atoms of the methyl groups of haplophyllidine shows that they differ ($\Delta\delta = 7.98$ ppm). Such a difference of their CSs agree with figures given in the literature [5, 10].

In perforine (II), the molecule of which lacks the double bond in the side chain, the carbon atoms of the gem-dimethyl group become equivalent and resonate at 29.36 ppm (see Table 1). In the case of anhydroperforine (III), the carbon atoms under consideration, C-16 and C-17, are nonequivalent ($\Delta\delta = 8.98$ ppm) because of the chair conformation of the tetrahydropyran ring [4]. The introduction of a double bond into the 7,8 position of anhydroperforine [compound (IV)] leads to a flattening of the conformation of the dihydropyran ring, as a result of which the CSs of the carbon atoms of the gem-dimethyl group become equivalent. Furthermore, in compound (IV) the C-7—C-8 double bond is conjugated with the furanopyridine fragment, which, naturally, has an effect on the CSs of the sp^2-hybridized carbon atoms in its ^{13}C NMR spectrum; a powerful effect on C-3 and a slight one on C-9, C-10, and C-11 (see Table 1).

EXPERIMENTAL

The ^{13}C NMR spectra of (I-IV) were obtained on Varian CFT-20 and XL-100-16 ($\nu_C = 25.16$ MHz) and Bruker WM-250 ($\nu_C = 62.9$ MHz) spectrometers in $CDCl_3$ (I, III, IV, V) and DMSO-d_6 (II). The chemical shifts of the carbon atoms are given in the δ scale relative to TMS ($\delta_{TMS} = \delta_{CDCl_3} + 76.91$ ppm, and $\delta_{TMS} = \delta_{DMSO\text{-}d_6} + 39.6$ ppm).

SUMMARY

On the basis of the results of a study of the spin-spin coupling constants J_{CH} and the ^{13}C chemical shifts of haplophyllidine an assignment has been made of the signals of the carbon atoms of the 5,6,7,8-tetrahydrofuranoquinoline alkaloids haplophyllidine (I), perforine (II), and hydroperforine (III), their derivative (IV), and 4,8-dimethoxyfuranoquinoline (γ-fagarine) (V).

LITERATURE CITED

1. Z. Sh. Faizutdinova, I. A. Bessonova, and Yu. S. Yunusov, Khim. Prir. Soedin., 360 (1968).
2. I. A. Bessonova, Kh. A. Abdullaev, and Yu. S. Yunusov, Khim. Prir. Soedin., 682 (1974).
3. I. A. Bessonova, M. R. Yagudaev, and Yu. S. Yunusov, Khim. Prir. Soedin., 597 (1978).
4. Z. Karimov, I. A. Bessonova, M. R. Yagudaev, and Yu. S. Yunusov, Khim. Prir. Soedin., 805 (1979).

5. N. M. D. Brown, M. F. Grundon, D. M. Harrison, and S. A. Surgenor, Tetrahedron, 36, 3579 (1980).
6. A. Ahond, F. Picot, P. Potier, Ch. Poupart, and T. Sevenet, Phytochemistry, 17, 166 (1978).
7. Kh. A. Rasulova, I. A. Bessonova, M. R. Yagudaev, and Yu. S. Yunusov, Khim. Prir. Soedin., 876 (1987).
8. Zs. Rozsa, M. Rabik, K. Szendrei, A. Kalman, Gz. Argav, I. Pelczer, M. Aynechi, I. Mester, and J. Reisch, Phytochemistry, 25, 2005 (1986).
9. Gorudata and J. B. Stothers, Can. J. Chem., 47, 3601 (1969).
10. P. A. Coperus, A. D. H. Clague, and J. P. C. M. Dongen, Org. Mag. Reson., 8, 426 (1976).
11. F. J. Weigert and J. D. Roberts, J. Am. Chem. Soc., 90, 3543 (1968).
12. N. Platzer, J.-J. Basselier, and P. Demerseman, Bull. Soc. Chim. Fr., Nos. 5-6, 905 (1974).
13. N. M. Sergeev, NMR Spectroscopy [in Russian], Izd. MGU (1981), p. 97.
14. G. C. Levy and G. L. Nelson, Carbon-13 Nuclear Magnetic Resonance for Chemists, Wiley, New York [Russian translation, Mir, Moscow (1975), p. 82].
15. E. Breitmaier and W. Voelter, ^{13}C NMR Spectroscopy, Verlag Chemie, New York (1978), pp. 97 and 162.

STRUCTURE OF THE ALKALOID SCHOBERINE

B. Tashkhodzhaev, A. A. Ibragimov,
B. T. Ibragimov, and S. Yu. Yunusov

UDC 547.944/945+548.737

The structure of an alkaloid of a new type, schoberine, isolated from plants of the genus Nitraria has been established by the x-ray structural method as perhydro-1,10-propano-4a,8a-diazaphenanthrene. Its chemical and spectral properties have been studied.

Schoberine (I) was first isolated from the plant Nitraria schoberi L. [1, 2] and then from Nitraria sibirica Pall. (family Zygophyllaceae) [3]. Structure (Ia) [1] (Fig. 1) of the type of the Ormosia alkaloids (see, for example, [4]) was suggested for it. However, a detailed analysis of the spectral characteristics (IR, PMR) and of some chemical properties of (I) (see below) showed that its molecule contains an aminal grouping and both nitrogen atoms are tertiary. With the aim of a reliable determination of the structure of schoberine, we have made an x-ray structural investigation of the base, the results of which have led to structure (I).

In agreement with the space group $P2_1/n$ in which schoberine crystallizes, the elementary cell contains molecules of both optical antipodes. The spatial structure of the molecule of (I) is shown in Fig. 2 in a projection on the bc plane. The molecule of (I) consists of four linked six-membered rings A, B, C, and D having chair conformations. The linkages of rings A/B and B/C are trans, and of B/D and C/D cis. The lengths of the valence bonds and the angles in the molecule of (I) are given in Fig. 2. The mean values of the C_{sp^3}–C_{sp^3} and N–C_{sp^3} bonds (1.520 and 1.471 Å, respectively) are close to the corresponding standard values [5] and correlate well with the values given for six-membered azacycles [6]. The errors in the determination of the lengths of the valence bonds and angles are not greater than 0.006 Å and 0.3°, respectively.

As has been mentioned above, schoberine exhibits the properties of tertiary bases and, in particular, it does not undergo methylation or acetylation under the usual conditions.

Institute of the Chemistry of Plant Substances, Uzbek SSR Academy of Sciences, Tashkent. Translated from Khimiya Prirondnykh Soedinenii, No. 1, pp. 30-34, January-February, 1989. Original article submitted March 28, 1988.

0009-3130/89/2501-0024 $12.50