NMR INVESTIGATION OF ALKALOIDS.

XI. ^{13}C NMR SPECTRA AND STRUCTURE OF CODONOPSINE AND CODONOPSININE

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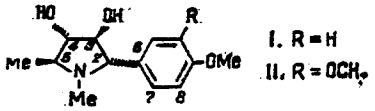
An assignment of the signals in the ^{13}C NMR spectra of the alkaloids codonopsinine and codonopsine has been made on the basis of selective double heteronuclear resonance experiments.

We have previously reported the determination of the structures of the alkaloids codonopsinine (I) and codonopsine (II) [1, 2]. Attempts have been made to establish the relative configurations of the C-2, C-3, C-4, and C-5 centers of these substances [3]. Having carried out a stereodirected synthesis of (I), with the aid of NOE experiments and x-ray structural analysis Japanese workers have established the absolute configuration of codonopsinine as 2R,3R,4R,5R [4-6].

In the present paper we give the results of correlation of the chemical shifts of the ^{13}C carbon atoms with the structure and stereochemistry of codonopsinine (I) and codonopsine (II) (Table 1).



In view of the fact that in the off-resonance spectra the four signals of the C-2, C-3, C-4, and C-5 atoms produce doublets, unique assignment close to the CS values of the oxygen-containing C-3 and C-4 atoms was difficult. To a degree, increments of α-, β-, and γ-substituents were also difficultly assigned to the signals of the C-2 and C-5 atoms. Therefore, the assignments of the signals of the C-2, C-3, C-4, and C-5 atoms in the ^{13}C NMR spectra of the substituted pyrrolidine rings of (I) and (II) were carried out by means of ^{13}C (^{1}H) selective double heteronuclear resonance and comparison with literature data on the ^{13}C CSs of the $N-CH_3$ and $C-CH_3$ groups. Signals of the carbon atoms of the methoxy-substituted aromatic ring were assigned based on data of the α-, ortho-, meta-, and para-contributions of the OCH_3 group to the CSs of the corresponding aromatic carbon atoms of the benzene ring [7, 8].

As was to be expected, the values of the chemical shifts of the C-2, C-3, C-4, and C-5 atoms of the substituted pyrrolidine rings of codonopsinine and codonopsine practically coincided within the limits $\Delta\delta = \pm 0.07$ ppm, i.e., the introduction of the additional methoxy group into the aromatic ring of codonopsine does not affect the chemical shifts of the carbon atoms of the neighboring ring. It can be seen from Table 1 that the chemical shifts of the C-2 atoms were shifted downfield by more than 9 ppm in comparison with those of the C-5 atoms. This difference in the chemical shifts of these carbon atoms is obviously due to a difference in their environments. The C-2 atom experiences the α-influence of the substituted benzene ring, while the C-5 atom experiences that of a methyl group. The hydroxy groups at C-3 and C-4 will apparently make approximately the same β- and γ-contributions to the chemical shifts of the C-2 and C-5 atoms in view of the identical mutual orientations of the latter relative to the OH groups. Consequently, the α-contribution of the methoxy-substituted benzene ring to the CS of the carbon atom to which it is attached is approximately 9 ppm greater than the α-contribution of a methyl group.

EXPERIMENTAL

The ^{13}C NMR spectra of codonopsinine and codonopsine were obtained on Tesla BS-567 A, Varian XL-206, and Bruker WM-250 spectrometers under conditions of complete, incomplete, and selective decoupling of C—H interactions in Py-d_5 solution; 0 – TMS.

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TABLE 1. Chemical Shifts of the Carbon Atoms in the ^{13}C NMR Spectra of Codonopsinine (I) and Codonopsine (II), δ, ppm, Py-d_5, 0 – TMS

Compound	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	C-11	C–CH_3	N–CH_3	OCH_2
I	74,15 d	86,98 d	84,86 d	64,8 d	135,00 s	129,65 d	113,94 d	159,06 s	113,94 d	129,65 d	13,76 q	34,56 q	55,00 q
II	74,49 d	86,94 d	84,86 d	64,93 d	135,48 s	121,10 d	112 08 d	150,07 s	149,00 s	112,08 d	13,65 q	34,60 q	55,08 55,84 q

SUMMARY

An assignment of the signals in the ^{13}C NMR spectra of the alkaloids codonopsinine and codonopsine has been made on the basis of results of selective heteronuclear resonance experiments.

LITERATURE CITED

1. S. F. Matkhalikova, V. M. Malikov, and S. Yu. Yunusov, Khim. Prir. Soedin., 606 (1969).
2. S. F. Matkhalikova, V. M. Malikov, M. R. Yagudaev, and S. Yu. Yunusov, Khim. Prir. Soedin., 210 (1971).
3. M. R. Yagudaev, S. F. Matkhalikova, V. M. Malikov, and S. Yu. Yunusov, Khim. Prir. Soedin., 495 (1972).
4. H. Iida, N. Jamazaki, and C. Kibayashi, Tetrahedron Lett., 3255 (1985).
5. H. Iida, N. Jamazaki, and C. Kibayashi, Tetrahedron Lett., 5393 (1986).
6. H. Iida, N. Jamazaki, and C. Kibayashi J. Org. Chem., 52, 1956 (1987).
7. F. W. Wehrli and T. Wirthlin, Interpretation of Carbon-13 NMR Spectra, Heyden, London (1976).
8. E. Breitmaier and W. Voelter, ^{13}C NMR Spectroscopy, Verlag Chemie, Weinheim (1978).

GC-MS ANALYSIS OF TOTAL DITERPENE ALKALOIDS FROM ROOTS OF Aconitum septentrionale

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For the first time, using a MS 25RF chromato-mass spectrometer with a Carlo Erba 5160 chromatograph and a packed column, the possibility of the partial separation of the mixture of diterpene alkaloids of various types from the roots of Aconitum septentrionale has been shown. From their chromatographic parameters and mass-spectral characteristics 18 bases have been detected, including a new one with M^+ 407 which was probably deoxydelcorine, while 6-O-methyldelcorine and 6-O-methyleldelidine have been found in plants for the first time.

We have described a procedure for the qualitative and quantitative analysis of the mixtures of diterpene bases from two species of plants of the genus Aconitum [1]. It appeared of interest to confirm the presence of the predicted bases in the same mixture by chromato-mass spectrometry. There is no information on the gas-chromatographic behavior of the diterpene bases.

We set ourselves a dual aim: together with the solution of the concrete problem of the analysis of plant material, to determine the possibility of using the GC-MS method for the identification of diterpene alkaloids of various types. Having prepared equimolar solutions of standard samples of songorine (I), talatisine (II), lappaconine (III), 10-hydroxylappaconine

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