^{13}C NMR SPECTRUM OF LAGOCHILIN AND ITS DERIVATIVES

Z. I. Mavlyankulova, U. N. Zainutdinov,
S. I. Mukhamedkhanova, V. B. Leont'ev,
and Kh. A. Aslanov

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The commonest diterpenoids have the labdane skeleton, and these include lagochilin, which has been isolated from Central Asian plants of the genus Lagochilus [1-4].

Discussions of the structure of lagochilin [5-8] have led to the suggested stereochemical configuration (I).

In order to investigate in more detail features of the spatial and electronic structure of the lagochilin molecule, we have studied the ^{13}C NMR spectra of lagochilin and of its derivatives. The ^{13}C spectra were taken on a Varian XL-100 spectrometer in pyridine solution.

The ^{13}C spectrum of lagochilin (Fig. 1) has four signals at 93.13, 86.37, 45.15, and 42.53 ppm due, respectively, to C_9, C_{13}, C_{10}, and C_4, as is confirmed by a spectrum with incomplete decoupling from protons (off-resonance). The C_9 atom resonates in the strongest field since the chemical shift of this carbon atom must have three β contributions and two α contributions, one of them being from an oxygen atom (~ +40 ppm). It is obvious that the presence of the oxygen contribution permits the line at 86.37 ppm to be assigned to the C_{13} carbon atom, while the signals at 43.15 and 42.53 ppm are due to the C_{10} and C_4 carbon atoms which have no oxygen atoms in the α position [9]. Attention must be directed to the fact that in diterpenes with the labdane structure the chemical shift of C_4 varies from 45 to 32 ppm and that of C_{10} from 42 to 33 ppm. The chemical shifts of these atoms are sensitive to a distortion of the conformation of rings A/B due to the introduction of double bonds and of $C=O$ and hydroxy groups [10-12].

This phenomenon is apparently connected with the existence of 1-3-diaxial interaction between the C_{17} and C_{19} methyl groups which considerably distorts the geometry of ring A [6]. This interaction labilizes the chair conformation of ring A, thanks to which it becomes more sensitive to the steric influence of the substituents, and this is reflected in the chemical shifts of the C_1, C_2, C_3, and C_4 carbon atoms (see Table 1).

In the spectrum it is possible to isolate the signals of three tertiary carbon atoms from off-resonance results at 74.23, 41.07, and 36.90 ppm. It is obvious that the signal at 74.23 ppm belongs to C_3(α-OH). The lines at 41.07 and 36.90 ppm belong to C_5 and C_8, respectively.

The spectrum shows ten triplets (off-resonance), the lines at 69.10, 66.70, and 59.35 ppm obviously relating to C_{18}, C_{15}, and C_{16}. A consideration of the individual secondary carbon atoms in the rings shows that in the best degree they must correspond to an additive scheme of contributions to the chemical shifts of the C_6, C_7, C_1, and C_2 signals. To calculate their chemical shifts it is sufficient to take into account the βa or βe and γa contributions. Consequently, C_1 which has an axial methyl group in the β position is responsible for the signal at 41.07 ppm and C_7 for that at 35.90 ppm. It is obvious that the lines at 22.16, 27.82, and 29.73 ppm belong to the C_6, C_2, and C_{14} carbon atoms, respectively, while C_{11} and C_{13} are represented by lines at 32.00 and 31.93 ppm, respectively.

The arrangement of the signals of the methyl groups of lagochilin is unusual, since lagochilin is characterized by the A/B-trans conformation with axial methyl groups at C_{10} and C_4 and an equatorial methyl group at C_8 [8]. Consequently, the signals at 18.50 and 18.30 ppm must be assigned to the equivalent methyl groups at C_{10} and C_4, and a line in the high field at 12.70 ppm to the methyl group at C_8.

Even in fairly complex compounds, the signals of equatorial methyl groups are usually found in fields weaker by 6-8 ppm than those of axial methyl groups. Consequently, to explain this assignment of the signals it must be borne in mind that there are considerable γ contributions to the chemical shift of the methyl group at C_8 through interaction with the C-H bonds of the five-membered ring at C_{10} and C_{11}.

The most probable conformation for 3,18-O-isopropylidenelagochilin has D/A-trans and A/B-trans linkages (II).

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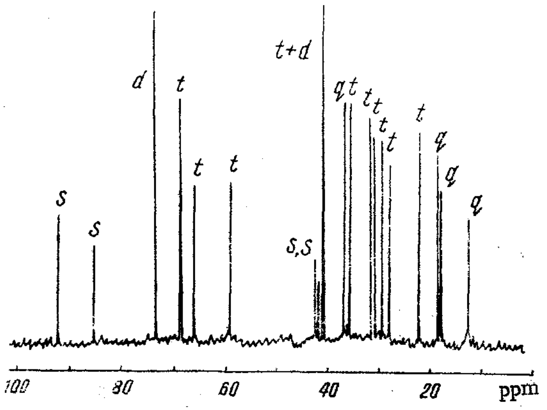

Fig. 1. ^{13}C NMR spectra of lagochilin and its derivatives.

TABLE 1. Table of ^{13}C Chemical Shifts (Relative to HMDS)*

Carbon atoms	Lago-chilin	3,18-O-Isopropylidene lago-chilin	15,16-Di-O-acetyl-lagochilin
C_1	40,07	40,47	35,90
C_2	27,82	23,45	26.64
C_3	74,23	76,43	72,94
C_4	42,53	36,17	41,97
C_5	41,07	42,07	39,67
C_6	22,16	20.20	20,87
C_7	35,90	34.60	34,80
C_8	36,90	35,70	39,67
C_9	93,13	91,93	92,54
C_{10}	43,15	41.65	41,28
C_{11}	32,00	30.54	30,60
C_{12}	31,93	30,54	30,00
C_{13}	86,37	85,44	81,90
C_{14}	29.73	28.33	28,33
C_{15}	59.35	58.14	60,40
C_{16}	65,70	65,80	66.30
C_{17}	18,50	17,50	17,20
C_{18}	69,10	71.47	67,77
C_{19}	18,30	29,33	17.20
C_{20}	12,70	11,73	11.43
C_{21}		97,60	169.33
C_{22}		18,10	34.80
C_{23}		18,60	169,33
C_{24}			34,80

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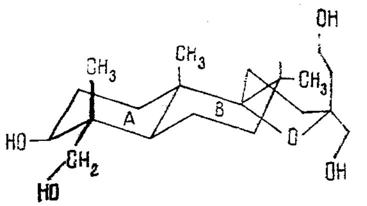
* The accuracy of measuring the chemical shifts was 0.04 ppm.



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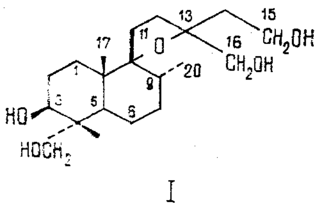

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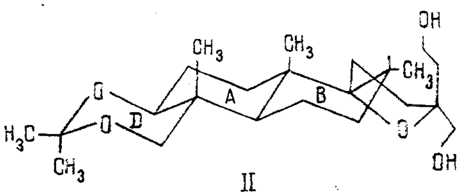

II

It can be seen from a comparison of the carbon spectra of lagochilin and its acetyl and isopropylidene derivatives (Table 1) that the chemical shifts of the signals of the C_3 carbon have not changed appreciably (74.23 ppm in lagochilin, 76.43 ppm in 3,18-O-isopropylidenelagochilin, and 72.23 ppm in 15,16-di-O-acetyllagochilin). It follows from this that 3,18-O-isopropylidenelagochilin has the D/A- trans,A/ B-trans conformation.

Thus, the ^{13}C NMR spectra confirm the A/B-trans chair conformation of lagochilin, and the methyl groups at C_{10} and C_4 have the axial and the methyl group at C_8 the equatorial and α orientation (I).

The study of the ^{13}C NMR spectra of lagochilin and its derivatives has shown a dependence of the change in the configurational state of the individual centers with a variation of the structure of the substituents at C_3, C_{18}, C_{15}, and C_{16}.

SUMMARY

The ^{13}C NMR spectra of lagochilin and its derivatives have been studied. A complete assignment has been made of the lines of the spectrum and the values of the chemical shifts of the carbon atoms have been discussed in connection with the spatial structure of the molecules of these compounds.

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