UDC 547.944/945:541, 6:543.42

NMR SPECTRA AND STRUCTURE OF UNGMINORINE

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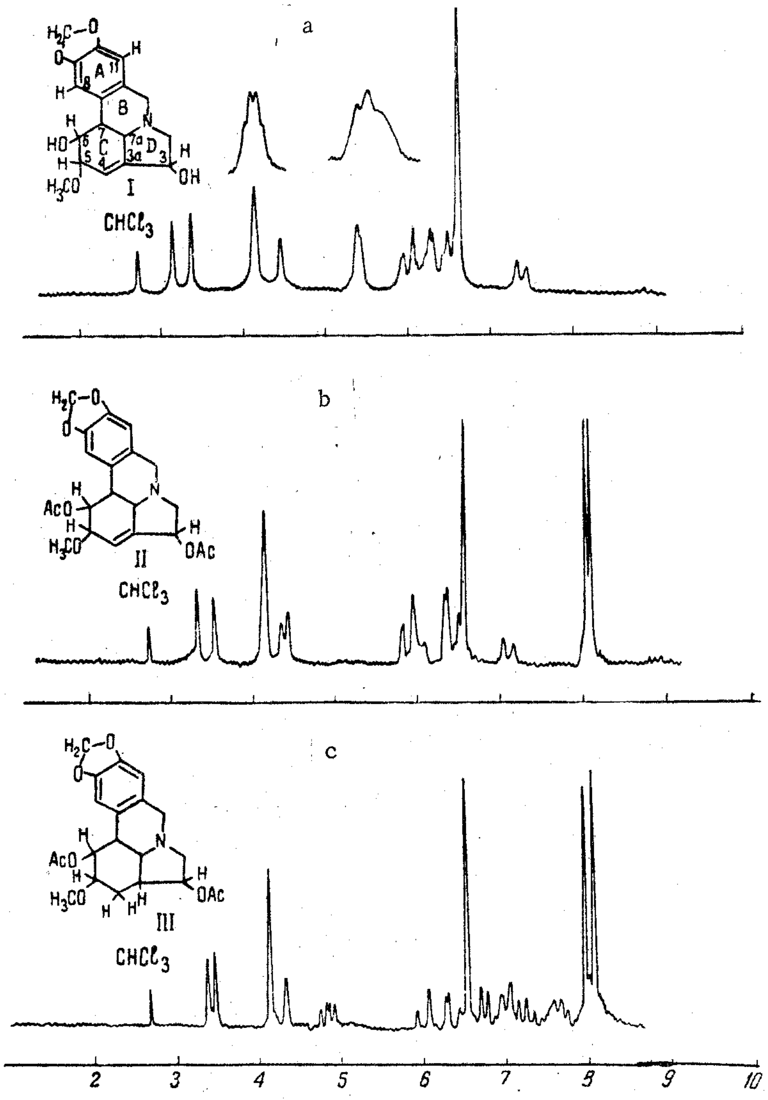
Khimiya Prirodnykh Soedinenii, Vol. 5, No. 2, pp. 99–102, 1969

Structure I has been proposed previously for ungminorine [1]. However, the NMR spectrum of this substance had not been studied. In the present paper we give an analysis of the NMR spectra of ungminorine (I), ungminorine diacetate (II), and dihydroungminorine diacetate (III) (figure, a, b, and c).



NMR spectra of ungminorine (a), ungminorine diacetate (b), and dihydroungminorine diacetate (c).

In the NMR spectrum of ungminorine (figure, a), in the weak-field region there are two one-proton singlets at 3.20 ppm and 3.43 ppm corresponding to aromatic protons 8 and 11, respectively. This unambiguously confirms the correctness of the location of the methylenedioxy group in the aromatic nucleus in structure I. In addition to the aromatic protons, the spectrum of I has well-defined signals from the protons of the OCH_2O group at 4.20 ppm. Because of their nonequivalence, the two protons of the methylene group form a system of the AB type, and therefore they give a quartet with a geminal coupling constant J_{AB} = 1.5 Hz. Likewise, the signals of the olefinic proton 4 at 4.45 ppm and the protons of the nonaromatic methoxyl at 6.65 ppm are clearly defined.

Integration of the whole spectrum of ungminorine has shown that the total intensity of the signals at 4.20 ppm (OCH_2O) and 4.45 ppm corresponds to five proton units, i.e., in this region, apart from the signals of the two protons of OCH_2O and the one olefinic proton 4, there are also the signals of two other protons. It was natural to assume that the

the signals of the protons of the two OH groups would fall in this region. In actual fact, in the spectrum of ungminorine heated to 50° C an additional two-proton signal appeared at 4.65 ppm and the intensities of the signals at 4.20 and 4.45 ppm amounted to two and one proton units, respectively. The signal at 4.65 ppm is due to the two OH groups of I. At 5.49 ppm the spectrum of I (see figure, a) has a two-proton signal, which we have ascribed to protons 3 and 5 at HCOH. The correctness of this assignment is confirmed by the fact that in the NMR spectrum of ungminorine diacetate is confirmed by the fact that in the NMR spectrum of ungminorine diacetate (II) (see figure, b) this signal undergoes a paramagnetic shift in the weak-field direction, while the signal of one of the protons at HCOH shifts to a greater extent and is superposed on the signal of the OCH_2O group at 4.20 ppm, as was confirmed by integration.

The total intensity of the signals in the 6–7 ppm region in the spectrum of I was nine proton units. Consequently, in addition to the three protons of the OCH_3 group in this region there are six others. It is likely that the four protons of the CH_2-N-CH_2 group and the two methine protons at 5 and 7a fall in this region. The one-proton doublet of the strong field at 7.48 ppm in the spectrum of I (see figure, a) apparently relates to the benzyl proton 7. From the vicinal spin-spin coupling constant of protons 6, 7, and 7a ($J_{7,6}$ = 10.0 Hz and $J_{7,5}$ = 1.8 Hz), it may be concluded that proton 7 is in the axial orientation with respect to one of protons 6 and 7a and in the equatorial orientation with respect to the other.

It is obvious that the signal at 4.32 ppm in the spectrum of ungminorine diacetate (II) (see figure, 6) can be ascribed to proton 6, its half width being $\Delta f_{1/2}$ = 8.0 Hz, i.e., protons 7 and 7a have the axial orientation while the hydroxy group at 7 is in the equatorial orientation in ring C [2].

It can be seen from the NMR spectra of II and III (see figure, b and c) that the signals of the benzyl proton 7 and the protons of the OCH_3 group undergo a weak paramagnetic shift. This can be explained by a change in the screening of protons 7 and the OCH_3 protons when the hydroxyl at position 6 is acetylated. At the same time, acetylation and hydrogenation of the 3a–4 double bond leads to a diamagnetic shift of the aromatic protons 8 and 11, the signals of which are displaced in the direction of strong fields by 0.09–0.23 ppm in the spectra of II and III (see figure, a, b, and c). In the NMR spectra of II and III, the signals of CH_3 in the $OCOCH_3$ group are clearly shown at 7.97 and 8.02 ppm and at 7.99 and 8.10 ppm, respectively (see figure, b, c). On considering the NMR spectrum of dihydroungminorine diacetate (III) (see figure, c), the two one-proton signals at 4.40 ppm (singlet) and at 4.88 ppm (quartet) can be clearly detected. These, of course, relate to the signals of the protons at $HCOCOCH_3$ in positions 3 and 6, respectively. The quartet at 4.88 ppm (proton in position 6) can give useful information on the orientation of the substituents at carbon atoms 5 and 6 of the hydrogenated ring C. In fact, the vicinal coupling constants of protons 6, 5, and 7 are large ($J_{6,7}$ = 10.0 Hz and $J_{6,5}$ = 7.5 Hz), which shows their diaxial interaction.

Consequently, the $-OCOCH_3$ and $-OCH_3$ groups are present in the equatorial orientation on carbon atoms 5 and 6 of the hydrogenated ring C.

The NMR spectra of all the compounds were recorded on a JNM-4H-100/100 MHz instrument. The signal of hexamethyldisiloxane, taken as 10 (τ scale) in deuterochloroform solution, was used as an internal standard.

Conclusions

On the basis of an analysis of the NMR spectra of ungminorine, ungminorine diacetate, and dihydroungminorine diacetate the correctness of the structures proposed previously has been shown and the orientation of the substituents in ring C has been determined.

REFERENCES

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28 December 1967

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