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^{13}C NMR SPECTROSCOPY OF THE RING-CHAIN TAUTOMERISM OF THE PRODUCT OF REDUCTION OF DUBINIDINONE

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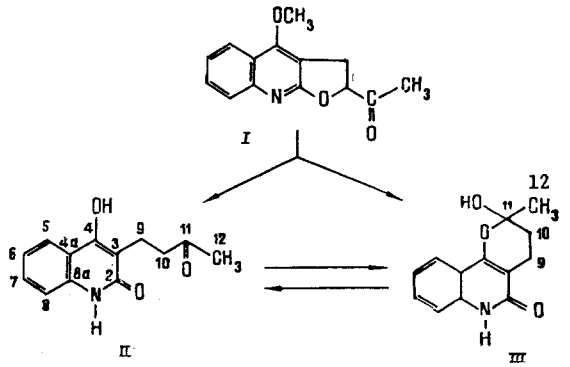
The existence of ring-chain tautomerism between a cyclic semiketal form and an open-chain δ-ketol form of the product of the reduction of dubinidinone has been shown unambiguously by ^{13}C NMR spectroscopy, and this has been confirmed by the results of PMR spectroscopy. It has been shown that in the solution in deuteropyridine and deuterodimethyl sulfoxide the tautomeric equilibrium is shifted in the direction of the formation of the cyclic semiketal, while in trifluoroacetic acid it is shifted in the direction of the open-chain δ-ketol. Analysis of the IR spectrum has shown that the product of the reduction of dubinidinone exists predominantly in the cyclic semiketal form in the crystalline state.

Earlier [1], for a compound obtained on the Clemensen reduction of dubinidinone (I), structure (II) was proposed [2] on the basis of the change in the absorption curve of the UV spectrum in an alkaline medium, the results of a study of the mass spectrum of (II), and its d_7-deutero analog obtained by the method of [3], and an analysis of the IR, PMR, and mass spectra of the O-acetyl derivative of product (II).



It is known, however, that when the molecule of a substance contains two groups capable of intramolecular interaction (in particular, CO and OH), the formation of a cyclic tautomer is possible, and if, in this process, a six-membered ring is produced, the cyclic tautomer is fairly stable [4]. In compound (II), the phenolic hydroxyl is present in the δ-position to the carbonyl group and, therefore, this substance may exist in tautomeric equilibrium with the six-membered semiketal (III).

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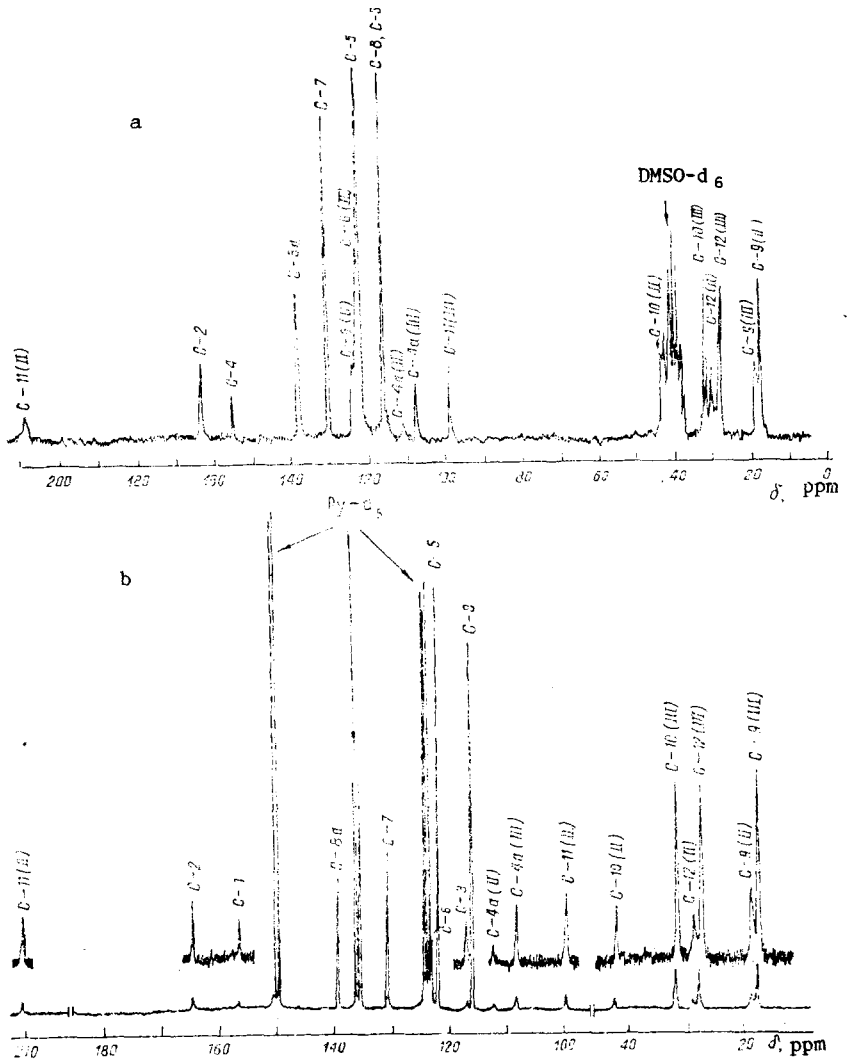

Fig. 1. ^{13}C NMR spectra of the product of the reduction of dubinidinone: a) in DMSO-d_6; b) in Py-d_5.

TABLE 1. Chemical Shifts of the Carbon Atoms of the ^{13}C NMR Spectra of the Tautomers (II) and (III) (δ, ppm)

C-atom	Multiplicity	II	III	II	III
		in DMSO-d6		in C_5D_5N	
C-2	s	162,92	162,92	165,00	167,70
C-3	s	115,04*	115,04*	116,50*	116,50*
C-4	s	154,90	154,90	156,60	156,60
C-4a	s	110,48*	106,41*	111,90*	107,70*
C-5	d	121,17	121,17	121,60	121,60
C-6	d	123,00	122,66	122,70	122,70
C-7	d	129,91	129,91	128,98	128,98
C-8	d	115,04	115,04	115,58	115,58
C-8a	s	137,53	137,53	138,78	138,78
C-9	t	18,01	16,74	19,00	18,00
C-10	t	42,07	31,31	42,90	32,50
C-11	s	209,12	98,01	210,50	99,00
C-12	q	29,32	27,28	29,35	28,05

*The assignments may be mutually reversed.

The aim of the present work was to determine the existence of the ring-chain tautomerism (II) ⇄ (III) by the method of ^{13}C NMR spectroscopy. The NMR spectroscopic method is the most effective, unambiguous, and reliable for distinguishing the structures of chain and ring tautomers [5, 6].

The assignment of the signals of the carbon atoms in the ^{13}C NMR spectrum of the product of the reduction of dubinidinone was made by a comparative study of the spectra obtained from experiments with complete and incomplete suppression of C–H interactions, a comparison with literature figures of the values of the CSs of the carbon atoms in compounds close in structure to the 2-quinolone alkaloids [7], and a consideration of the α-, β-, and γ- contributions of various groups [8].

In the ^{13}C NMR spectrum of the product of the reduction of dubinidinone in DMSO-d_6 in the strong field region at 43-16 ppm (Table 1 and Fig. 1a) there are sign signals (excluding the signals of the DMSO-d_6) from the C-9, C-10, and C-12 carbon atoms of the tautomers (II) and (III) in the form of two pairs of triplets (16.74, 18.01; and 31.31, 42.07) and one pair of quartets (27.28; 29.52) with a ratio of the intensities of approximately 3:1. This pattern of the spectrum indicates the existence of tautomers in DMSO-d_6 solution.

The signals of the carbon atoms of the C-12 methyl and C-10 methylene groups in the spectrum of the open-chain tautomer (II) should be observed in a weaker field than in the spectrum of the cyclic tautomer (III), since the value of the α-contribution of the C=O group to the chemical shifts of these carbon atoms is considerably greater than that of a semiketal group. The ring-chain tautomerism is shown particularly clearly by the presence in the spectrum of singlet signals from the C-11 atoms of the two tautomers: at 98.01 ppm from the sp^3-hybridized carbon atom of the cyclic tautomer (III), and at 209.12 ppm from the sp^2-hybridized carbon atom of the open-chain tautomer (II). A difference in the values of the CSs of the carbon atom of the 2-quinolone nucleus in (III) and (II) is observed for C-4a (or C-3).

We obtained completely similar results with the same ratio of intensities of the signals from C-9, C-10, and C-12 of cyclic (III) and open-chain (II) tautomers in a study of the ^{13}C NMR spectrum of the product of the reduction of dubinidinone in deuteropyridine (Table 1 and Fig. 1b).

What has been said above unambiguously shows the existence of the ring-chain tautomerism (II) $\rightleftarrows$ (III), the equilibrium being shifted to the right in deuterodimethyl sulfoxide and deuteropyridine.

The results of an analysis of the ^{13}C NMR spectra were completely confirmed by PMR and IR spectroscopy. In the PMR spectrum of the product of the reduction of dubinidinone in deuteropyridine, there was a broadened singlet at 1.73 ppm in the strong-field region the CS value of which showed that it belonged to the protons of the methyl group of the cyclic tautomer (III), while the $COCH_3$ signal of the δ-ketol (II) appeared at 1.93 ppm, the ratio of their intensities being approximately 3:1, i.e., similar to what was observed in the ^{13}C NMR spectrum. A similar pattern of the change in the CSs and intensities of the signals of the protons of the methyl group was observed in the PMR spectrum recorded in deuterodimethyl sulfoxide. However, in the PMR spectrum of the product of the reduction of dubinidinone taken in trifluoroacetic acid (TFA) the pattern was the opposite: the intensity of the weak-field signal of the methyl group at 1.93 ppm was approximately three times greater than that of the strong-field signal at 1.63 ppm. Consequently, in an acid medium the tautomeric equilibrium is shifted in the direction of the open form, which is in harmony with literature information [9].

The question of which structure, (II) or (III), the reduction product has in the crystalline state was solved on the basis of the IR spectrum, in which only a strong band at 1650 cm^{-1}, relating to the carbonyl of the 2-quinolone fragment was observed in the region of carbonyl absorption. The expected band of the carbonyl group of the δ-ketol (II) was practically absent.

Thus, the results of spectral analysis have shown that in the crystalline state the product of the reduction of dubinidinone has predominantly the cyclic structure (III), while in solution it exists in the form of a mixture of the tautomers (II) and (III), this equilibrium being shifted to the right in DMSO-d_6 and C_5D_5N [approximately two thirds being the semiketal (III) and one third the chain δ-ketol (II)]. In TFA, the equilibrium is shifted to the left with a ratio of the tautomers of 1:3 in favor of the δ-ketol.

EXPERIMENTAL

PMR spectra were obtained on JNM-C-60HL and JNM-4M-100 spectrometers (JEOL) with working frequencies of 60 and 100 MHz; 0 – HMDS, in DMSO-d_6, C_5D_5N, and TFA solutions, and ^{13}C

NMR spectra on BS-567A (Tesla) and WM-250 (Bruker) instruments with ν_0 = 25.142 and 65.2 MHz in DMSO-d_6 and C_5D_5N, the ^{13}C chemical shifts being given relative to TMS; $\delta_{TMS} = \delta_{DMSO\text{-}d_6} + 39.6$ ppm, and $\delta_{TMS} = \delta_{C_5D_5N} + 123.6$ ppm. The IR spectrum was obtained on a UR-20 instrument in KBr.

The product of the reduction of dubinidinone – crystals mp 189°C (from ethanol) – was obtained by the method described in [1].

CONCLUSIONS

The existence of ring-chain tautomerism (III) of the product of the reduction of dubinidinone has been established unambiguously by ^{13}C NMR spectroscopy, (III) being the cyclic semiketal form and (II) the open-chain δ-ketol form. It has been shown that in deuteropyridine and deuterodimethyl sulfoxide solutions the tautomeric equilibrium is shifted in the direction of a predominance of the cyclic tautomer (III), while in trifluoroacetic acid the open-chain tautomer (II) predominates.

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STRUCTURE OF OXOSECODELTERINE

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Periodic acid does not oxidize delterine, an alkaloid from Delphinium ternatum. However, the further oxidation of 19-oxodelterine, obtained on oxidation by Marion's method, led to oxosecodelterine, which is a semiacetal formed through the C-7 carbonyl group and the C-10 hydroxy group. The treatment of this compound with sulfuric acid led to oxosecodemethanoldelterine.

The isolation from Delphinium ternatum of a new alkaloid, delterine, for which the structure (I) was established, has been reported previously [1]. In the present paper we give the results of the attempted periodate oxidation of delterine and that of its 19-oxo derivative, and also of an experiment on the isolation of delterine from plant raw material and its synthesis from eldelidine [1].

The attempted periodate oxidation of (I) was unsuccessful. On oxidation with potassium permanganate [2], an oxodelterine $C_{25}H_{39}NO_8$ (II) having a lactam carbonyl group in a

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