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THE STRUCTURE OF DUBINIDINE AND DUBININE

I. A. Bessonova and S. Yu. Yunusov

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In the NMR spectra of O-acetyldubinidine (II), O,O-diacetyldubinidine (III), and the product of the oxidation of dubinidine with periodic acid (IV) [1, 2], the C-methyl group appears in the form of a singlet (table). Consequently, this is attached to a tertiary carbon atom. The chemical shift of the protons from a $C-CH_3$ group in substance (II) shows the presence of a descreening hydroxy group in the α-position to it. This is confirmed by the fact that in diacetyldubinidine (III) there is a paramagnetic shift of the protons from the methyl group ($\Delta\tau = 0.33$ ppm).

Chemical Shifts (τ scale)

Compound	Aromatic 5-, 6-, 7-, and 8-protons	$CH-CH_2-$	$CH-CH_2-$	$CH_2-O-\overset{O}{\overset{\|}{C}}-$	$-OCH_3$	$-OCOCH_3$	$C-CH_3$
(II)	2.57–3.20 m	5.18 m	6.15–6.70 m	5.55 s	6.05 s	7.95 s	8.78 s
(III)	1.97–2.85 m	4.92 t	6.48 d	5.51 s	5.90 s	8.07 s (6H)	8.45 s
(IV)	2.00–3.10 m	5.05 t	6.35 d	—	5.95 s	—	7.70 s

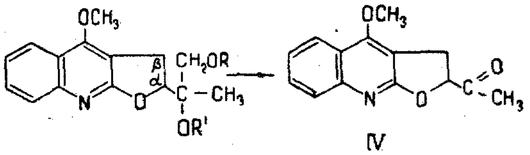
Note. m–multiplet, t–triplet, d–doublet, s–singlet.

These data contradict the formulas proposed earlier for dubinidine and dubinine (II) [1, 2] in which the C-methyl group is present on a tertiary carbon atom and in the γ-position to a descreening hydroxy group.

The NMR spectra of (II) and (III) confirm the presence in dubinidine of one methoxy and two alcoholic hydroxy groups and an unsubstituted aromatic ring in positions 5, 6, 7, and 8. The spectrum of (III) has a one-proton triplet at 4.92 ppm (J = 8 Hz) and a two-proton doublet at 6.48 ppm (J = 8 Hz). The values of the chemical shifts and the spin-spin coupling constants of these protons are typical for the α-methine and β-methylene protons of a dihydrofuran ring [3, 4].

Thus, dubinidine lacks a substituting group in the β-position of the dihydrofuran ring. The production on the oxidation of dubinidine with periodic acid of formaldehyde and the ketone (IV), and the presence of a two-proton singlet in the spectra of (II) and (III) (at 5.55 and 5.51 τ) shows that the hydroxymethylene group must be located on a tertiary carbon atom. Consequently, only structure (I) is possible for dubinidine. Correspondingly, the structure of the product of the oxidation of dubinidine with periodic acid will be (IV), which agrees well with its NMR spectrum, in which there are five signals with an intensity ratio of 4 :1 :3 :2 :3 due to the presence in the substance of aromatic, methine, methoxy, methylene, and methyl protons. The chemical shift of 7.70 ppm is typical for a methyl group attached to a carbonyl group [5]. The absence from the NMR spectrum of (IV) of a signal from the proton of an aldehyde group, and also the paramagnetic shift of the signal from the protons of the methyl group ($\Delta\tau = 1.08$) shows that the oxidation of dubinidine with periodic acid forms not an aldehyde [1] but a ketone. The ketone (IV) gives the silver mirror reaction because of the presence of an oxygen atom in the α-position with respect to the carbonyl group (dihydrofuran ring), and it condenses with dimedone on boiling [1, 6].

I. $R = R' = H$
II $R = -COCH_3$; $R' = H$;
III $R = R' = -COCH_3$;



IV

It is interesting to note that dubinidine differs from platydesmine [4, 7] only by the presence of a hydroxymethyl group in place of a methyl group, while in the dihydrofuranoquinoline series from the plant only the acetyl derivatives of these alkaloids were isolated.

The NMR spectra were taken by M. R. Yagudaev on a JNM-4H-100/100 MHz instrument in deuterochloroform with HMDS as internal standard.

Conclusions

The structures of dubinidine and dubinine have been corrected; they are α-substituted derivatives of 4-methoxy-α, β-dihydrofuranoquinoline [formulas (I) and (II)].

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Institute of the Chemistry of Plant Substances, AS USSR