THE STRUCTURE OF ANHYDRODEMETHANOLLAPPACONINE

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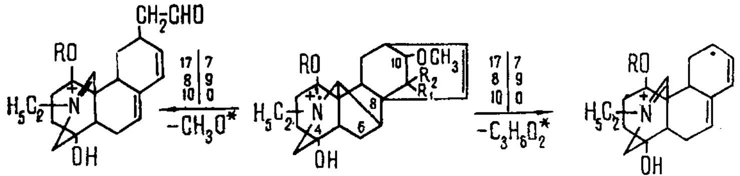
In order to obtain additional confirmation of the structures proposed previously for anhydrodemethanollappaconine (I) and anhydrodemethanollappaconidine (II) [1, 2], we have performed the hydrogenolysis of the methoxy group of (II), which is in the α position to a carbonyl group, in acetic acid in the presence of zinc dust. However, instead of the expected hydrogenolysis of the methoxy group, the monoacetate of (II) was formed in quantiative yield; in its NMR spectrum were found the signals of one acetyl group at 1.93 ppm (singlet) and of a proton geminal to the acetyl group in the form of a poorly resolved quartet at 4.93 ppm (J_1 12 Hz; J_2 6 Hz), i.e., acetylation of the hydroxy group at C-1 had taken place. Under the conditions of mass spectrometry, the acetyl group at C-1, in contrast to the situation in relation to the spectra considered previously of the corresponding derivatives of songorine [3], does not affect the main fragmentation pathway, since in the mass spectrum of the monoacetate of (II), as in the mass spectrum of (II) the maximum peak is that of the ion M−43 (M−28−15) and the peak next in intensity is that of M−28 (31%). To confirm the possibility of the acetylation of the secondary hydroxy groups by this method, we acetylated talatisamine [4]. Under the same reaction conditions, a quantitative yield of monoacetyltalatisamine was obtained (the hydroxy group at C-10 was acetylated).

We have previously [2] described the fragmentation of the products of the reduction of anhydrodemethanollappaconine (IIIa) and (IVa) under the conditions of mass spectrometry and assumed that the peak of the ion M−31 arose by the splitting off of the substituent from C-1. However, the above-described fragmentation of the monoacetate of (II) induced us to check this assumption.



I. R = CH_3; $R_1 + R_2 = O$

II. R = H; $R_1 + R_2 = O$

344 (41) IIIa, R = CH_3; R_1 = OH; R_2 = H; M^+ 375 (34) 301 (100)

330 (56) IIIb, R = H; R_1 = OH; R_2 = H; M^+ 361 (33) 287 (100)

The reduction of (II) with sodium tetrahydroborate in methanol led to a crystalline product $C_{21}H_{31}NO_4$ (IIIb) with mp 225-227°C in the mass spectrum of which the maximum peak was that of an ion with m/e 287 and the second most intense peak was that of an ion with m/e 330. Consequently, the loss of 31 mass units is connected with the ejection of the methoxyl from C-10, and not from C-1 as was assumed previously for (IIIa).

The Adams hydrogenation of (II) gave a crystalline tetrahydro derivative with mp 195-197°C, $C_{21}H_{33}NO_4$ (IVb). In the mass spectrum of (IVb), the maximum peak was that of the ion M−31. The fragmentation of (IVa) was analogous.

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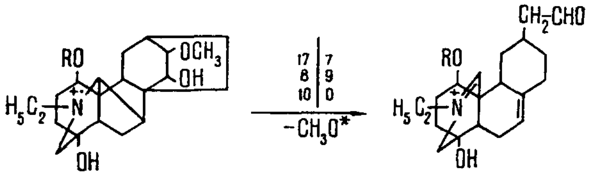

IVa, $R = CH_3$; M^+ 377(20) 346 (100)
IVb, $R = H$; M^+ 363 (31) 332 (100)

Thus, the peak of the ion with M−31 is formed through the C-10 methoxyl.

LITERATURE CITED

1. V. A. Tel'nov, M. S. Yunusov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 583 (1970).
2. V. A. Tel'nov, M. S. Yunusov, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 622 (1971).
3. M. S. Yunusov, Ya. V. Rashkes, S. Yu. Yunusov, and A. S. Samatov, Khim. Prirodn. Soedin., 101 (1970).
4. M. S. Yunusov and S. Yu. Yunusov, Khim. Prirodn. Soedin., 90 (1970).