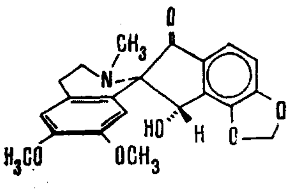
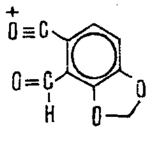
2.25 ppm. The signal of a methine proton geminal to a hydroxy group, ArC(OH)H, which is located at 5.08 ppm, shows a configuration similar to that of corpaine [3-5].

The mass spectrum of the compound, in addition to the molecular peaks $M^+$383 (100%) and $M^{++}$ (191.5), shows the peaks of the ions M − 15 (368), M − 45 (338), and 206 (6,7-dimethoxy-2-methyl-3,4-dihydroisoquinoline) (a), 206 − $CH_4$ (190), and M − 206 (177) of fragment (b). Thus, it may be concluded that the substance is 1-O-methylcorpaine (I):



I



b

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# A NEW ALKALOID FROM Spirea japonica

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UDC 547.944/945

From the combined alkaloids of Spirea japonica (Japanese spirea) by chromatography on alumina we have isolated an alkaloid with composition $C_{20}H_{25}O_2N$ (I), mp 280-282°C, m/e 311 ($M^+$) the IR spectrum of which contains bands at 1710 $cm^{-1}$ (C = O group), 3100 $cm^{-1}$ (OH group), and 1655 $cm^{-1}$ (double bond). The NMR spectrum of the alkaloid shows the presence of a quaternary methyl group (3H, singlet at 1.33 ppm) and of an exocyclic methylene group [singlets at 4.73 ppm (1H) and 4.87 ppm (1H)]. The presence of the latter was confirmed by the catalytic hydrogenation of the alkaloid in ethanol, which led to a dihydro derivative $C_{20}H_{27}O_2N$ (II), mp 290-292°C, m/e 313 ($M^+$), in the NMR spectrum of which the signal of a secondary methyl group appeared (doublet at 0.93 ppm, J = 5 Hz) in place of the signals of the exocyclic methylene group. On treatment with methyl iodide in methanol, the alkaloid gave a crystalline product $C_{20}H_{25}O_2N \cdot CH_3I$ the space group of which, $P2_12_12_1$, and the parameters of the elementary cell of which, $a$ = 14.04 Å, b = 15.88 Å, c = 8.55 Å, were determined from an x-ray diagram obtained on a Weissenberg equi-inclination x-ray goniometer.

These facts make it possible to identify the alkaloid isolated as spiradine A [1].

In addition to spiradine A we isolated a new alkaloid $C_{22}H_{27}O_3N$ (III), mp 163°C, m/e 353 ($M^+$), which we have called spiredine. Its IR spectrum has bands at 1720 $cm^{-1}$ (C = O group in an unstrained ring) and 1690 $cm^{-1}$ (C = O group in a transannular position with respect to nitrogen). By means of the NMR spectra of the

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new alkaloid in neutral ($CDCl_3$) and protonated ($CF_3COOH$) forms we established the presence of the following groupings in its structure:

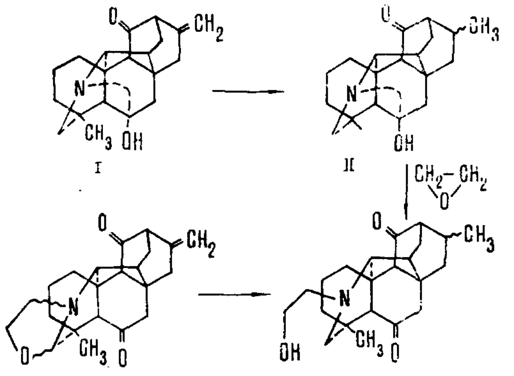
1. A methyl group on a quaternary carbon atom – singlets at 1.43 and 1.47 ppm with a total intensity of three proton units, corresponding to different conformers [2]; in the protonated form a singlet at 1.47 ppm (3H).

2. An exocyclic methylene group $C{=}CH_2$, singlets at 4.73 ppm (1H) and 4.91 ppm (1H).

3. An oxazolidine ring, singlet at 4.1 ppm (in the protonated form, 5.04 ppm) corresponding to a proton on a carbon atom attached to oxygen and nitrogen, multiplet between 3.0 and 3.5 ppm (in the protonated form, between 4.0 and 4.6 ppm), with an intensity of two proton units, corresponding to an $N{=}CH_2$ grouping, and a multiplet between 3.5 and 4.0 ppm (2H), corresponding to an $-O-CH_2$ group.

The catalytic hydrogenation of spiredine in a mixture of ethanol and acetic acid in the presence of $PtO_2$ led to product (IV), mp 274-275°C, which was identified by its IR, mass, and NMR spectra and a mixed melting point as a compound obtained by the addition of ethylene oxide to dihydrospiradine A.

According to the facts given, spiredine has the structure illustrated by formula (III) (of the hetisine type).



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