Berberis ALKALOIDS.

2'-N-METHYLISOTETRANDRINE FROM Berberis oblonga

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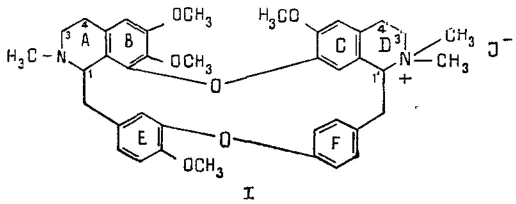
We have investigated the alkaloid composition of young shoots of Berberis oblonga (Regl.) Schneid. (family Berberidaceae), collected in June, 1983, at Shakhimardan (Fergana province). Extraction gave 0.9% of combined quaternary alkaloids in the form of iodides and 0.4% of combined tertiary alkaloids. When the combined quaternary alkaloids were separated according to solubility, by obtaining salts 0.22% of berberine, 0.4% of magnoflorine and 0.05% of columbanine were obtained in the form of the iodides. They were identified with authentic samples by means of mixed melting points and by thin-layer chromatography on silica gel plates. When the combined tertiary alcohols were separated by the procedure described in [1], oxyacanthine, berbamine, and base (I) were isolated. Base (I) was characterized in the form of the iodide, which crystallized from tetrahydrofuran with mp 221-222°C. $[\alpha]_D$ +29.5° (c, 0.1; $CHCl_3$). Thin-layer chromatography on plates with Al_2O_3 in the chloroform–methanol (9:1) and (95:5) and benzene–methanol (4:1) systems gave a single spot. The Beilstein test showed a positive reaction for halogen. UV spectrum: $\lambda_{max}^{C_2H_5}$ 284 nm (log ε 3.91). Mass spectrum: m/z 636 (M – HI), 622 (M – CH_3I), 607, 431, 395, 381, 198, 175, 142, 127, 58 (100%). The PMR spectrum (in $CDCl_3$, 0 is HMDS, JNM 4 H-100/100 MHz, δ scale, ppm) showed the signals of an $N\text{-}CH_3$ group (2.15; 3 H, s), of $\overset{+}{N}(CH_3)_2$ groups (3.06; 3 H, s; 3.55; 3 H, s) and of ten aromatic protons in the 6.20-6.90 ppm region.

According to its spectral characteristics, (I) belonged to the dimeric monoquaternary bisbenzylisoquinoline alkaloids [2]. The presence in the mass spectrum of an ion with m/z 485, formed by the ejection of ring E, indicated that (I) was a representative of the alkaloids of the berbamine group having a methoxy group in the diphenyl oxide moiety of the molecule [3]. According to the facts given, (I) was N-methyltetrandrine or N-methylisotetrandrine. The physicochemical constants and spectral properties of (I) differed sharply from those of the N-methyl derivatives of tetrandrine. Consequently, (I) may be one of the two N-methyl derivatives of isotetrandrine. When (I) was compared with the O-methyl ether of 2'-N-methylberbamine [1] their identity was shown by IR spectroscopy, TLC, and the absence of a depression of the melting point of a mixture.

Thus, compound (I) was 2'-N-methylisotetrandrine.

We have obtained 2'-N-methylisotetrandrine previously in determining the structure of 2'-N-methylberberine [1].



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STRUCTURE OF GLAUFININE

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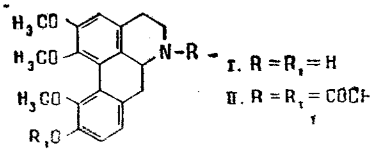
Continuing a study of the alkaloid composition of Glaucium fimbrilligerum [1, 2], from the epigeal part of the plant collected at Talas (Kirghiz SSR) in the flowering period we have isolated a new amorphous base with the composition $C_{19}H_{21}NO_4$ having $[\alpha]_D$ +165° (c, 0.4; methanol), which we have called glaufinine (I). The UV spectrum of (I) has three absorption maxima, at 222, 270, and 309 nm (log ε 4.35, 3.82, 3.43). The mass spectrum of (I) showed the peaks of ions with m/z 327 (M^+), 326, 312, 310, 298, 296, and 163.5 (M^{2+}). In the PMR spectrum ($CDCl_3$, δ scale) there were the signals of three methoxy groups at (ppm) 3.62 (OCH_3) and 3.80 (2 OCH_3) and of three aromatic protons in the form of a one-proton singlet at 6.63 and a two-proton singlet at 6.75. At 2.30-3.70 there was a multiplet corresponding to methylene and methine protons. The presence in the mass spectrum of the base of the peak of the $(M - 29)^{+\cdot}$ ion, and also the absence of the signal of the protons of a N-methyl group from the PMR spectrum showed the secondary nature of the nitrogen atom [3]. On the basis of the facts given above, glaufinine was assigned to the noraporphine alkaloids of the type of corydine [3] with three methoxy and one hydroxy groups.

When (I) was acetylated with acetic anhydride in pyridine, the N,O-diacetyl derivative (II) was obtained. The PMR spectrum of (II) showed the signals of two acetoxy groups, at 2.10 and 2.17 ppm, of three methoxy groups at 3.34, 3.76, and 3.78 ppm, and of three aromatic protons in the form of one siglet at 6.61 ppm and two doublets with J = 8 Hz at 6.80 and 7.06 ppm. The methylene and methine protons gave signals in the form of multiplets in the 2.00 – 3.70 ppm region.

The hydroxy group in glaufinine must be located at C_{10}, since in the PMR spectrum of (II) the signal of the aromatic proton at C_9 is shifted downfield (7.06 ppm) and the signal of one methoxy group is shifted upfield ($C_{11}-OCH_3$, 3.34 ppm) as compared with those for (I), while the chemical shifts of the other aromatic protons and of the methoxy groups have changed only slightly.

Consequently, glaufinine has the structure (I):



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