OBLONGINE – A NEW QUATERNARY ALKALOID FROM Berberis oblonga

A. Karimov, N. D. Abdullaev,
M. V. Telezhenetskaya, K. Lutfullin,
and S. Yu. Yunusov

UDC 547.944/945

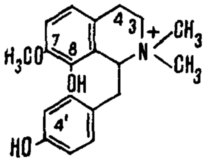
Continuing the separation of the phenolic fraction of the combined a alkaloids of the roots of *B. oblonga* [1], we have isolated a new base in the form of the iodide which we have called oblongine (I), mp 158–1589°C (chloroform–methanol), $[\alpha]_D$ + 8.5° (c 1.2; methanol); UV spectrum: $\lambda_{max}^{ethanol}$ 224 nm (shoulder), 284 nm (log ε 4.47, 3.78). The IR spectrum of (I) had absorption bands in the region of ortho- and para-substituted rings at 765 and 810 cm^{-1} and of active hydrogen at 3260 cm^{-1} [2]. The mass spectrum had ions with m/e 313, 206, 192 (100%), 142, 127, 107, and 58.

The facts given show that oblongine is a benzyl-N-methyltetrahydroisoquinoline or phenethyl-N-methyltetrahydroisoquinoline derivative [3], in the isoquinoline moiety of which there are a hydroxy and a methoxy group and in the phenyl moiety a hydroxy group, since the ion with m/e 313 could arise as the result of the splitting out of HI or CH_3I from a quaternary iodide [4]. In the mass spectrum of the des-base of (I) there were strong peaks of ions with m/e 313, 107, and 53 (100%). Consequently, (I) is the methiodide of a hydroxy(1-hydroxybenzyl)methoxy-N-methyltetrahydroisoquinoline.

In the PMR spectrum of (I) (deuteropyridine, 0 – HMDS, JNM 4H-100/100 MHz, δ scale) three-proton singlets at 3.31 and 3.46 ppm, like those of other quaternary benzylisoquinolines [4, 5], are due to the protons of an $= N^+(CH_3)_2$ group, and a three-proton singlet at 3.64 ppm can be assigned to an OCH_3 group. Also in the spectrum can be seen two two-proton multiplets with centers at 4.09 and 2.92 ppm. The PMR spectra taken under conditions of proton–proton double resonance show that the multiplets mentioned are connected by spin–spin coupling (SSC) only with one another. Thus, they can be assigned to the methylene protons at C_3 and C_4, respectively. From the value of its chemical shift, a one-proton quartet with broadened components at 5.38 ppm was assigned to C_1H. Saturation of the resonance transitions of this nucleus led to a simplification of the multiplicity of part of the spectrum (3.1-3.9 ppm) and to the appearance of two doublets at 3.3 and 3.7 ppm partially overlapping with the signals from the methyl group. On the simultaneous saturation of C_1H and the nuclei responsible for one of the doublets, the second was converted into a singlet. Hence, it may be concluded that the hydroxybenzyl substituent is located at C_1 of the oblongine molecule.

The two-proton doublets 6.98 and 7.35 ppm connected with one another by SSC (^3J = 8.5 Hz) are assigned to the two pairs of ortho protons of the p-hydroxybenzyl substituent. Two one-protons doublets at 6.55 and 6.85 ppm, also coupled with one another with ^3J = 8.4 Hz, show that there are two ortho protons in the tetrahydroisoquinoline moiety of the molecule. Consequently, the substituents can be located in positions 5,6; 7,8; or 5,8. The choice between them was made on the basis of the results of a measurement of the intramolecular nuclear Overhauser effect. When the protons at C_4 (2.92 ppm) were irradiated with a strong radio frequency field, the intensity of the doublet at 6.55 ppm rose by 28%. This means that the latter belongs to C_5H and the 5,6 positions are unsubstituted. Irradiation of the protons of the methoxy group caused an increase in the intensity of the doublet at 6.85 ppm relating to C_6H by 23%. On the basis of the results given, it may be concluded unambiguously that the methoxy and hydroxy groups occupy the C_7 and C_8 positions, respectively. Thus, oblongine has the structure (I):

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. M. I. Kalinin Andizhan State Medical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 117-118, January-February, 1976. Original article submitted July 1, 1975.



I

LITERATURE CITED

1. A. Karimov, M. B. Telezhenetskaya, K. L. Lutfullin, and S. Yu. Yunusov, Khim. Prirodn. Soedin., 433 (1975).
2. K. Nakanishi, Infrared Absorption Spectroscopy. Practical, Holden-Day, San Francisco (1962); M. Shamma, The Isoquinoline Alkaloids, Academic Press, New York (1972), p. 80.
3. A. B. Battersby, R. Ramage, A. F. Cameron, C. Hannawy, and F. Santavy, J. Chem. Soc., C, 3514 (1971).
4. G. Grethe, M. Uskokovic, and A. Brossi, Tetrahedron Lett., 1599 (1966); J. Slavic, L. Dolejs, and P. Sadmera, Coll. Czech. Chem. Commun., 35, No. 9, 2597 (1970).
5. E. Sanchez and J. Comin, Tetrahedron, 23, 1139 (1967); M. Albonica, A. M. Kuck, and V. Deulojen, Ann. Chem., 685, 200 (1965).