THE ALKALOIDS OF Mahonia aquifolia

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UDC 547.92

From the roots of Mahonia aquifolia (introduced into the botanical garden of VILR [All-Union Scientific-Research Institute for Medicinal and Aromatic Plants], Moscow oblast) collected in October, 1968 at the end of the vegetation period, we have isolated the alkaloids berbamine and berberine [1] found previously in this species growing in Western Europe [2-5]. The quaternary-alkaloid fraction contained, according to our results, not less than four previously unknown alkaloids. Their reduction with zinc dust in acid gave a phenolic (I) and two nonphenolic (II and III) bases.

Base I has the composition $C_{20}H_{23}O_4N$, mp 211-212°C (ethanol), $[\alpha]_D^{17}$ 0° (c 0.09; chloroform), R_f 0.73 [butan-1-ol–glacial acetic acid–water (10 : 1 : 3) system, Leningrad B paper]. The alkaloid contains three OCH_3 and one OH group. The composition of the base was confirmed by the preparation of the O-acetyl derivative $C_{22}H_{25}O_5N \cdot 0.5H_2O$, mp 134-135°C (ether), R_f 0.85. In the UV spectrum of I (in ethanol) there is a maximum at 283 nm (log ε 3.76). In 0.1 N NaOH (ethanolic), the maximum shifts to 298 nm (log ε 3.7) which confirms the phenolic nature of the hydroxyl. In the IR spectrum (mull in paraffin oil) there is a hydroxyl absorption band at 2700 cm^{-1}. The NMR spectrum ($CDCl_3$, O–TMS, δ, ppm) has the following signals: 3.87 (6H, $2CH_3O-Ar$), 3.90 (3H, CH_3O-Ar), 4.25 (1H, doublet, J = 16 Hz), 6.68 (1H, singlet, H–Ar), 6.72 (1H singlet, H–Ar) two ortho aromatic protons, 6.87 (1H, doublet, J = 9 Hz) and 6.79 (1H, doublet, J = 9 Hz). The remaining seven protons give a complex pattern in the 2.40-3.66 ppm region. In the mass spectrum there are peaks with m/e 341 (M^1, 42%), 176 (31%), 164 (100%), 149 (77%). The O-methyl derivative of I was identified by its melting point and IR spectrum as d,*l*-tetrahydropalmatine. A comparison of the characteristics given with those found in the literature [6, 7] permits I to be identified as tetrahydrojatrorrhine (d,*l*-corypalmine).

Base II had the composition $C_{20}H_{21}O_4N$, mp 168-169°C (ethanol), $[\alpha]_D^{17}$ 0° (c 1.61); chloroform), R_f 0.83. The UV spectrum of II has a maximum at 286 nm (log ε 3.80). The IR spectrum lacks the absorption band of a hydroxyl. The NMR spectrum (CCl_4, O – TMS, δ, ppm) contains signals at 3.80 (6H, $2CH_3O-Ar$), 4.07 (1H, doublet, J = 16 Hz), 5.85 (2H, $O-CH_2-O$), 6.47 (1H, singlet, H–Ar), 6.63 (1H, singlet, H–Ar), and 6.66 (2H, ortho aromatic protons). The remaining protons give a complex pattern in the 2.40-3.70 ppm region. The mass spectrum has peaks with m/e 329 (M^+, 22%), 174 (13%), 164 (100%), 149 (49%). What has been said above permits base II to be identified as d,*l*-canadine (tetrahydroberberine).

The base III, with mp 130-132°C (ethanol), $[\alpha]_D^{17}$ 0° (c 0.12; chloroform), R_f 0.71 was isolated in very small amount. Its structure is being studied.

LITERATURE CITED

1. L. P. Naidovich, B. K. Rostotskii, and P. N. Kibal'chich, Farmatsiya, No. 5, 1970.
2. C. Rudel, Arch. Pharm., 229, 631, 1891.
3. H. Pommerehne, Arch. Pharm., 233, 127, 1895.
4. H. M. Jordin, Arch. Pharm., 240, 146, 1902.
5. T. A. Henry, The Plant Alkaloids [Russian translation], Moscow, 1956, p. 340.
6. V. Preininger, A. D. Cross, J. W. Wurphy, F. Santavy, and T. Toube, Coll., 34, 875, 1969.
7. C. Y. Chen and D. B. MacLean, Can. J. Chem., 46, 2501, 1968.

All-Union Scientific-Research Institute for Medicinal Plants. Translated from Khimiya Prirodnykh Soedinenii, No. 6, p. 775, November-December, 1970. Original article submitted August 25, 1970.