ALKALOIDS OF Buxus hyrcana

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UDC 547.944/945

Continuing a study of the steroid alkaloids of the box [1, 2], we have investigated the chemical composition of the epigeal part of the previously unstudied species Buxus hyrcana Pojark., collected in the environs of the village of Vasyurinskaya, Krasnodar territory.

The combined alkaloids were isolated by the usual dichloroethane method and were thenfractionated according to basicity [1]. The chromatography of the pH 6.5 and pH 7.5 fractions on columns of alumina (activity grade II) gave three individual bases.

Base (I), $C_{25}H_{39}NO_2$, mp 178-180°C (from acetone), M^+ 399 (yield 0.02%), on the basis of its IR spectrum [3400 cm^{-1} (OH), 1700 cm^{-1} (C=O), 3040 and 1463 cm^{-1} (methylene of a cyclopropane ring)] and its UV spectrum [λ_{max}^{EtOH} 203 nm (log ε 4.88)] was assigned to derivatives of 9β,19-cyclo-5α-pregnane. NMR spectrum of base (I) [Varian H-100D, $CDCl_3$, 0 – HMDS, 20°C, δ, ppm]: 2.08, s, 3 H (CH_3); 2.26, s, 6 H, $N(CH_3)_2$; 2.97, d, 1 H, J = 6.5 Hz $(-\underline{CH}-\underset{OH}{CH}-CH_2-)$; 4.83, m, 1 H $(-CH_2-\underset{OH}{\underline{CH}}-CH-)$; 4.58 and 4.89 u.s.,* 2 H ($C=CH_2$). The IR, UV, NMR, and mass spectra of base (I) were identical with the corresponding spectra of cyclomicrobuxine, isolated previously from Buxus microphylla [3].

Base (II), $C_{25}H_{42}N_2O$, mp 233-235°C (from ethanol), M^+ 386 (yield 0.015%). The characteristics of the IR spectrum [3310, 3150 cm^{-1} (OH, NH), 3040, 1460 cm^{-1} (methylene of a cyclopropane ring), and 1650, 910 cm^{-1} ($C=CH_2$)] and of the NMR spectrum [4.75, 4.52 ppm, d, 2 H, J = 1 Hz ($C=CH_2$); 4.08, m, 1 H $(-CH_2-\underset{OH}{\underline{CH}}-CH-)$; 2.42, 2.38 ppm, s, 6 H (2 $N-CH_3$); 1.09, 0.90 ppm, s, 6 H (2CH_3); 1.05 ppm, d, 3 H, J = 7 Hz ($CH-CH_3$)] permitted it to be identified as the alkaloid cyclobuxine-D [4-7].

Base (III), $C_{27}H_{50}N_2$, mp 196-197°C (from acetone), M^+ 402 (yield 0.01%). The IR spectrum of this substance showed absorption bands at 3042 and 1463 cm^{-1} (methylene of a cyclopropane ring). Its NMR spectrum (δ, ppm) had signals at 2.38, s, 3 H ($N-CH_3$), 2.10, s, 6 H [$N(CH_3)_2$]; 0.68, 0.83, 0.85, 0.85, s, 12 H (4CH_3); and 0.78 ppm, d, 3 H ($CH-CH_3$), J = 6 Hz. Compound (III) was identified as the alkaloid cycloprotobuxine-C [8, 9].

From the fraction obtained at pH 9 we isolated a base (IV), $C_{33}H_{48}N_2O_4$, mp 273-275°C (from acetone), M^+ 436 (yield 0.018%). The IR spectrum of (IV) showed absorption bands at (cm^{-1}) 3290 (OH), 1630, 1540 (H–CO–), 1670 (C=O), 3050, 1460 (methylene of a cyclopropane ring). The UV spectrum of (IV) showed absorption maxima at λ_{max}^{EtOH} 225 nm (log ε 4.15), 230 nm (log ε 4.15), and 245 nm (log ε 3.84) due to two chromophores: ($C_6H_5-CO-NH-$) and a cyclopropane ring (C=O) [sic]. In the NMR spectrum of the base (IV) there are signals at 0.58, 0.77, 0.77 ppm, s, 9 H (3CH_3); 0.80 d, 3 H, J = 7 Hz ($CH-CH_3$), 2.17, s, 6 H [$N(CH_3)_2$]; 3.07, 3.40, 2 d, 2 H, J = 12.5 Hz ($-CH_2OH$); 4.05, m, 1 H $(-CH_2-\underset{OH}{\underline{CH}}-CH-)$; 6.1, d, 1 H, J = 9 Hz ($-CO-NH-$); 7.34 and 7.80, m, 5 H (C_6H_5-).

The IR, UV, NMR, and mass spectra, and also the melting point, of base (IV) are identical with the corresponding characteristics of N-3-benzoylcycloxobuxidine-F, isolated previously from Buxus balearica Willd. [10].

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*Signal with weak resolution appearing in the form of a singlet.

All-Union Scientific-Research Institute of Medicinal Plants. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 814-815, November-December, 1974. Original article submitted June 25, 1974.

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