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Buxus ALKALOIDS. N-BENZOYLCYCLOPROTOBUXIN C FROM *Buxus sempervirens*

B. U. Khodzhaev and R. Shakirov

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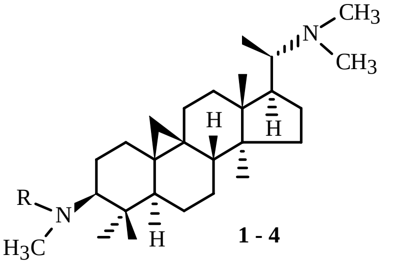
In continuation of studies of alkaloids from *Buxus sempervirens* cultivated near Tashkent [1, 2], we isolated by extraction with $CHCl_3$ from leaves and thin branches ethereal (20.15 g) and chloroformic (4.15 g) fractions of the total alkaloids.

The ethereal fraction was dissolved in benzene and separated according to basicity by citrate—phosphate buffer at pH 8.0-2.0 (pH intervals of 0.5). Fractions of the total alkaloids with pH 8.0, 7.5, 7.0, 6.5, and 6.0 were chromatographed over an aluminum oxide column with elution by ether:ethanol mixtures of increasing ethanol concentration of 5, 10, 15, 20, 25, and 30% to isolate cyclobuxine-D, cyclovirobuxine-D, cycloprotobuxine-A, cycloprotobuxine-D, buxamine-E, and isodihydrocyclomicrophyllin-A, respectively [1-4]. Compounds were identified by comparison with authentic samples.

The mother liquor (6.5 g) after separation of buxamine-E and isodihydrocyclomicrophyllin-A was treated with acetone. The fraction soluble in acetone was chromatographed over a silica gel coulmn (1:100) with elution by $CHCl_3:C_6H_{14}:C_2H_5OH:NH_4OH$ (5:7:3:0.5). The volume of each eluate was 10 mL. A total of 105 fractions was collected. Combined fractions 85-105 were treated with ethanol to afford base **1**, 0.34 g, mp 231-233°C (benzene), $C_{34}H_{52}N_2O$.



1 - 4

1: R = C_6H_5-CO; **2:** R = H;
3: R = CO-CH_3; **4:** R = CH_3

The IR spectrum of **1** (KBr, ν, cm^{-1}) contains absorption bands at 3042 and 1455 (methylenecyclopropane ring) [5], 2960-2830 (CH_3–, CH_2–), and 1642 (N-benzoyl carbonyl).

The PMR spectrum (100 MHz, $CDCl_3$, δ, ppm, J/Hz) exhibits signals at 0.81, 0.88, 0.93, and 1.02 (s, each 3H, tertiary methyls), 0.78 (3H, d, J = 7.5, CH_3), 2.36 [9H, s, $N(CH_3)_2$, NCH_3], 7.36-7.64 (5H, m, H-Ar).

The mass spectrum has principal peaks for ions with *m/z* 504 $[M]^+$, 490, 462, 446, 424, 400, 384, 344, 104, 98, 84, 72 (100%), 71, 70, 58, 57, 56, 44.

Base hydrolysis of alkaloid **1** produced a base of formula $C_{27}H_{48}N_2$ (**2**), $[M]^+ = 400$, mp 206-208°C (ethanol). The IR spectrum of **2** lacks an absorption band at 1642 cm^{-1} that is characteristic of an N-benzoyl carbonyl. The signal of aromatic protons also disappears in the PMR spectrum.

Acetylation of **2** by acetic anhydride in pyridine forms the N-acetyl derivative with mp 232-234°C (**3**), $[M]^+ = 442$.

Methylation of **2** according to Hess produced the N,N′-dimethyl derivative with mp 209-211°C (ethanol) that was identical with cycloprotobuxine-A (**4**) (IR and mass spectra and R_f).

Benzoylation of **2** synthesized a compound that was identical with **1**. Therefore, **1** is the N-benzoyl derivative of **2**.

The mass spectrometric decomposition of base **2** is analogous to that of cycloprotobuxine-C [6, 7]. The base peak with

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S. Yu. Yunusov Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax (99871) 120 64 75, e-mail: cnc@icps.org.uz. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 45-46, January-February, 2003. Original article submitted January 27, 2003.

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m/*z* 72 confirms the presence of a dimethyl group on C-20; that with *m*/*z* 44, (NH–CH_3) on C-3 of the pregnane core [8, 9].

The fact that methylated base **2** is identical with cycloprotobuxine-A [1] proves that alkaloid **2** is cycloprotobuxine-C [10].

Thus, the data lead to the conclusion that base **1** isolated by us is N-benzoylcycloprotobuxine-C [10], which is observed for the first time in plants.

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