

observed at 4.0 ppm ( $J = 5.0, 12.5$  Hz). The H-1 signal in the 3.1 ppm region is masked by a complex multiplet. The configuration of H-1 can be judged from the SSCs ( $J = 12, 12, 12$  Hz) in the H-2 quartet resonating at 2.70 ppm. Thus, the H-1 and H-3 protons are axial and the relative stereochemistry of ring A corresponds to (I).

The second base, with the composition  $C_{33}H_{45}NO_{10}$ ,  $M^+$  615, mp 179–181°C (methanol) had a PMR spectrum similar to that of (I). A difference consisted in the absence of the signal of a proton geminal to a hydroxyl at C-3 in the 3.0–4.0 region. On this basis, the alkaloid was identified as hydraconitine (II). According to the literature [4], mp 185–187°C (ethyl acetate). In the  $^{13}C$  spectrum the majority of signals coincided with the chemical shifts of 3-deoxyaconitine [2]. Only the C-5, C-19, and  $OCH_3$ -18 signals differed (48.4, 56.1, and 62.3, respectively) which can be explained by the dissimilar conditions of recording the spectrum and by the conformational mobility of ring A.

The PMR spectra were taken on a Bruker WP-200 SY instrument at 200.13 MHz and the  $^{13}C$  NMR spectra on a JEOL FX-90 Q radiospectrometer, 22.49 MHz, in  $CDCl_3$  at 25°C. In the interpretation of the signals we used the method of double resonance, paramagnetic additives, and INEPT.

The chemical composition of this plant is being studied for the first time.

#### LITERATURE CITED

1. S. Yu. Yunusov, Alkaloids [in Russian], Tashkent (1981), p. 92.
2. S. W. Pelletier and Z. Djarmati, J. Am. Chem. Soc., **98**, 2626 (1976).
3. S. W. Pelletier, N. V. Mody, and R. S. Sawhney, Can. J. Chem., **57**, 1652 (1979).
4. C. Konno, M. Shirasaka, and H. Hikino, J. Nat. Prod., **45**, 128 (1982).

#### CYCLOVIROBUXINE-F — A NEW ALKALOID FROM

*Buxus sempervirens*

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Continuing the separation of the total alkaloids of *Buxus sempervirens* L. cultivated in the environs of Kobuleti, Adzhar ASSR [1], we have isolated a new alkaloid which has been named cyclovirobuxine-F and has the composition  $C_{26}H_{46}N_2O$  (I), mp 224–226°C (ethanol),  $[\alpha]_D + 52.71^\circ$  (c 0.702; chloroform).

The IR spectrum of (I) showed absorption bands at ( $cm^{-1}$ ) 3310, 3050, 1460 (OH, methylene of a cyclopropane ring); 1642, 1592 ( $-NH_2$  group) [2]. The NMR spectrum of (I) exhibited resonance signals in the form of singlets at (ppm) 0.71, 0.76, 0.88, 0.94 (12 H,  $CH_3$ ), and 2.23 [6H,  $N(CH_3)_2$ ]; and in the form of doublets at 0.89 (3H,  $CH_3$ ,  $J = 2$  H) and 4.06 (m, 1 H,  $-CH-OH$ ). The mass spectrum of alkaloid (I) had the main peaks of ions with  $m/z$  71, 72 (100%), 84, 386, 371, and 402 ( $M^+$ ).

The peak of the ion with  $m/z$  72, the maximum in the mass spectrum, arises as the result of the cleavage of the bond between  $C_{17}$  and  $C_{20}$  and confirms the presence of a dimethylamino group in the  $C_{20}$  position of the pregnane nucleus [3, 4].

The acetylation of (I) with acetic anhydride in pyridine formed N,O-diacetylcyclovirobuxine-F, with the composition  $C_{30}H_{50}N_2O_3$  (II), mp 229–231°C (acetone-petroleum ether (1:3)),  $[\alpha]_D -39.61^\circ$  (c 0.807; chloroform).

In the IR spectrum of (II), the absorption bands of the hydroxy and primary amino group had disappeared but absorption bands had appeared at ( $cm^{-1}$ ) 1742 (O-acetyl) and 1636 (N-acetyl).

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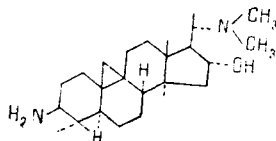
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The NMR spectrum of (II) showed signals at (ppm) 0.80, 0.81 (s, 6 H, CH<sub>3</sub>), 0.83 (s, 6 H, CH<sub>3</sub>), 0.94 (d, 3 H, CH<sub>3</sub>), 2.05 (s, 3 H, N-acetyl), 2.28 [s, 6 H, N(CH<sub>3</sub>)<sub>2</sub>], and 4.94 (m, 1 H, -HC-O-acetyl). In the mass spectrum of (II) the main peaks were those of ions with m/z 70, 71, 72, (100%), 84, 100, 314, 386, 451, and 486 (M<sup>+</sup>).

The Hess methylation of (I) led to a N-dimethyl derivative with the composition C<sub>28</sub>H<sub>50</sub>N<sub>2</sub>O (III), mp 224-246°C (ethanol), [α]<sub>D</sub> + 42.5° (c 0.901; chloroform) M<sup>+</sup> 430.

The N-dimethyl derivative (III) was identified by means of a mixed melting point and also from its IR, NMR, and mass spectra as N,N'-dimethylcyclovirobuxine-D [5-10].

Consequently, cyclovirobuxine-F (I) has the structure and configuration of 3β-amino-20-α-dimethylamino-16α-hydroxy-4,4',14α-trimethyl-9β,19-cyclo-5α-pregnane.



#### LITERATURE CITED

1. B. U. Khodzhaev, I. M. Primukhamedov, N. Yu. Nakaidze, and S. Yu. Yunusov, *Khim. Prir. Soedin.*, 802 (1984).
2. I. O. Kurakina, N. F. Proskurina, A. U. Stepanyants, and D. M. Mondeshka, *Khim. Prir. Soedin.*, 231 (1970).
3. Z. Voticky and I. Tomko, *Collect. Czech. Chem. Commun.*, **30**, 2869 (1965).
4. W. Vetter, P. Longevialle, F. Khuong-Huu-Laine, Khuong-Hun-Quy, and R. Goutarel, *Bull. Soc. Chim. Fr.*, 1324 (1963).
5. S. M. Kupchan and K. S. Brown, *J. Am. Chem. Soc.*, **86**, No. 20, 4430 (1964).
6. T. Nakano and S. Terao, *J. Chem. Soc.*, 4512 (1965).
7. W. B. Dopke and B. Muller, *Pharmazie*, **21**, 769 (1966).
8. F. Khuong-Huu-Laine, P. Renne, R. Roger, C. Andre, and R. Goutarel, *C. R. Acad. Sci.*, **C273**, 558 (1971).
9. K. S. Brown and S. M. Kupchan, *Tetrahedron Lett.*, **39**, 2895 (1964).
10. Z. Voticky and I. Tomko, *Abh. Dtsch. Acad. Wiss., Berlin, K. 1*, *Chem. Geol. Biol.*, **3**, 93 (1966).