

of 55% [1]. The addition of an excess of (II) (1.0 mmole per 0.5 mmole of (I)) to the reaction mixture gave a 67.9% yield of the monoglucoside (IV) and a 14.7% yield of the 12,25-diglucoside (III). The maximum yield of (III) (50%) was obtained with a threefold excess of (II) and 0.72 mmole of mercury bromide per mmole of the alcohol [3]. The formation of (IV) (21%) took place simultaneously. When the amount of catalyst was halved and the threefold excess of (II) was retained, a mixture of the 12-mono- and 12,25-diglucosides of BFTO (37 and 43%, respectively) was formed. The cholesterol present in (II) was recovered from the reaction mixture with an unchanged structure in a yield of the order of 80%.

In no case was the formation of the 3-monoglucoside of BFTO observed, which confirms the influence of the intraHB on the regiochemistry of glycosylation.

The structures of the compounds obtained were determined on the basis of the identification characteristics of ^{13}C NMR spectroscopy and the absence of a depression of the melting point of mixtures with authentic samples.

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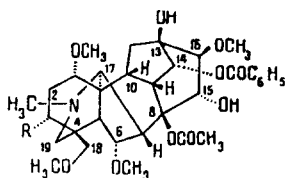
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MESACONITINE AND HYPACONITINE FROM *Aconitum czekanovskiyi*

Ts. Zhapova, L. D. Modonova, and A. A. Semenov

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The epigeal part of *Aconitum czekanovskiyi* Steinb., collected in the flowering phase in the Irkutsk province containing 0.23% of combined alkaloids. Two cases were isolated by column chromatography on alumina in hexane-acetone and with the aid of repeated recrystallization.



i. R = OH

ii. R = H

The first was identified as mesaconitine (I): its mp of 195.5–196°C (methanol), $[\alpha]_D^{20} + 32.75$ (c 3.74; CHCl_3), elementary composition $\text{C}_{33}\text{H}_{45}\text{NO}_{11}$, and molecular weight M^+ 631, coincided with those given in the literature [1] for (I). The majority of the signals in the ^{13}C spectrum of the alkaloid were identical with those reported in [2]. However, for some carbon atoms of ring A deviations in the chemical shifts of up to 1 ppm were observed. We ascribe these deviations to the conformational mobility of this ring. In order to refute another possible reason — epimerization at positions 1 and 3 — we analyzed the PMR spectrum of the alkaloid. PMR spectrum, CDCl_3 , 25°C, δ , ppm (J, Hz): 4.86, d (5.0), H-14; 4.45, dd (5.5, 2.5), H-15; 4.35, d (2.5), OH-15; 4.03, d (6.5), H-6; 3.94 s, OH-13; 3.72, dd (10.0, 5.0), H-3; 3.73, s, OCH_3 -16; 3.59, dd (9.0), 2 H-18; 3.32, d (5.3), H-16; 3.29, s, OCH_3 -18; 3.27, s, OCH_3 -6; 3.15, s, OCH_3 -1; 2.87, br.s, H-17; 2.33, s, N- CH_3 ; 1.36, s, COCH_3 . In deuteroypyridine at 80°C ring A is stabilized in the chair form [3], the H-3 resonance being

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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.

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CYCLOVIROBUXINE-F — A NEW ALKALOID FROM

Buxus sempervirens

B. U. Khodzhaev, I. M. Primukhamedov,
and S. Yu. Yunusov

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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).

Tashkent Pharmaceutical Institute. Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnikh Soedinenii, No. 5, pp. 718–719, September–October, 1985. Original article submitted April 4, 1985.