

ALKALOIDS OF *Aconitum coreanum*

IX. TANGUTISINE AND 2,11,13-TRIACETYL-14-HYDROXYHETISINE

I. A. Bessonova

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The isolation from the epigeal part of *Aconitum coreanum* (Levl.) Rapaics, gathered in Primorskii krai, of C₂₀-diterpenoid alkaloids of the hetisine [1] and atisine [2] types and also of coryphine [3] and coryphidine [4], containing a hexahydro-N-methylindole fragment unusual for this group of bases, has been reported previously. On continuing the chromatographic separation of the mixture of alkaloids from this plant [1], we obtained from chloroform—methanol (1:1) eluates fractions that have now been rechromatographed on silica gel. Elution with ethanol containing hydrochloric acid gave crystals of the hydrochloride of base (1) (153 mg), which, after recrystallization from methanol and ethanol, had mp 320—321°C (decomp.). Composition of (1): C₂₀H₂₇NO₄ (HRMS 345.1932). Calculated for C₂₀H₂₇NO₄, 345.1940.

In its IR spectrum there were a broad maximum in the 3600—3200 cm⁻¹ region (OH) and a band at 1650 cm⁻¹ (=CH₂). The main peaks in its mass spectrum, *m/z* (%): 345 (M⁺, 87), 330 (70), 328 (100), 317 (49), 316 (40), 300 (71), and 289 (41). In the PMR spectrum of the hydrochloride of the base (100 MHz, CD₃OD+D₂O, 0 — HMDS) there were signals at 1.10 (3H, s, 18-CH₃), 2.44 (1H, d, J=3.5 Hz, H-12), 2.86 and 3.83 (each 1H, d, J=11.5 Hz, H-19β and H-19α), 3.95 (2H, br.s, H-6, H-13β), 4.08 (1H, br.s, H-2β), 4.21 (1H, d, J=8.5 Hz, H-11β), 4.55 (1H, s, H-20), 4.82 and 4.87 (each 1H, br. S, H-17). When (1) was acetylated with acetic anhydride in the presence of *para*-toluenesulfonic acid a tetraacetyl derivative was obtained in the form of an amorphous powder (M⁺ 513). The facts presented correspond to the structure of 14-hydroxyhetisine — i.e., that of tangutisine, isolated from *A. tanguticum* [5]. This is the first time that tangutisine has been obtained from *A. coreanum*.

By the chromatographic separation on silica gel of the hexane-ether fraction after the elimination of acorine and guan-fu-bases Z and F [1] we obtained the crystalline alkaloid (2) with mp 176°C (hexane—acetone) having the developed formula C₂₀H₂₃N(OCOCH₃)₃OH (HRMS 471.5560. Calculated for C₂₆H₃₃NO₇ (471.5554).

In the mass spectrum of (2) we observed the peaks of the ions, *m/z* (%): 471 (M⁺, 21), 454 (M⁺ - OH, 7), 429 (M⁺ - COCH₂, 20), 428 (M⁺ - Ac, 22), 412 (M⁺ - OAc, 23), 385 (428 - Ac, 10), 370 (23), 369 (428 - OAc, 100) 352 (9), 342 (40), and 43 (24). In the PMR spectrum of (2) (100 MHz, deuteropyridine) the protons of acetoxy groups appeared at 1.93, 1.90, and 1.87 ppm in the form of three-proton singlets, and the signals of three geminal and exomethylene protons were observed in the 5.00—5.60 ppm region. The saponification of (2) yielded an aminoalcohol in the form of an amorphous powder identical with tangutisine according to TLC, mass spectrum, and PMR spectrum.

Consequently, base (2) was the 2,11,13-triacetyl derivative of 14-hydroxyhetisine (guan-fu-base G), which has previously been isolated from the plant *A. coreanum* growing in China [6, 7].

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Institute of the Chemistry of Plant Substances, Academy of Sciences of the Republic of Uzbekistan, Tashkent, fax (371) 120 64 75. Translated from *Khimiya Prirodnikh Soedinenii*, No. 1, pp. 123—124, January-February, 1999. Original article submitted April 4, 1998.

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