

M 299, containing a carbonyl group in a six-membered ring (1700 cm<sup>-1</sup>). The results of acidcatalytic isomerization, showing the presence of a C15- $\beta$ OH group in (II) [9], permitted the assumption that (II) was atisine azomethine, which had been obtained previously from atisine [8]. To confirm this, we performed the passage from atisine to atisine azomethine by the procedure of [8]. A direct comparison showed the identity of (II) and atisine azomethine.

This is the first time that atisine azomethine has been isolated from plants.

## LITERATURE CITED

- 1. Z. M. Vaisov, B. T. Salimov, and M. S. Yunusov, Khim. Prir. Soedin., 800 (1984).
- Z. M. Vaisov, B. Y. Salimov, B. Tashkhodzhaev, and M. S. Yunusov, Khim. Prir. Soedin., 658 (1986).
- 3. B. T. Salimov, B. Tashkhodzhaev, I. M. Yusopova, S. V. Lindeman, and Yu. T. Struchkov, Khim. Prir. Soedin., 375 (1992).
- 4. S. W. Pelletier, J. Am. Chem. Soc., <u>87</u>, 799 (1965).
- 5. S. W. Pelletier and T. N. Oeltmann, Tetrahedron, 24, 2019 (1986).
- 6. N. V. Mody and S. W. Pelletier, Tetrahedron, 34, 2421 (1978).
- 7. S. W. Pelletier, Chem. Ind. (London), 1016 (1956).
- 8. D. Dvornik and O. E. Edwards, Can. J. Chem., <u>35</u>, 860 (1957).
- 9. S. W. Pelletier and N. V. Mody, J. Nat. Prod., <u>43</u>, 41 (1980).

ALKALOIDS OF Aconitum firmum AND A. tokii

Z. M. Vaisov, I. A. Bessonova, and V. A. Tel'nov UDC 547.944/945

Continuing a systematic investigation of alkaloids from plants of the genus <u>Aconitum</u> L. collected in various growth sites [1], we have studied the epigeal part and roots of <u>Aconitum</u> <u>firmum</u> Reichb., gathered in the Transcarpathian province (Tyachev region, left bank of the R. Luzhanki). Aconitine has been isolated from this plant previously [2].

The air-dry comminuted epigeal part (1000 g) and roots (350 g) were first treated with sodium carbonate solution and then the alkaloids were isolated by extraction with chloroform and subsequent treatment of the concentrated chloroform extracts with sulfuric acid. After being made alkaline, the acid solutions yielded ether (3.1 g, A) and chloroform (0.67 g, B) fractions of alkaloids from the epigeal part and hexane (1.47 g, C), ether (3.14 g, D), and chloroform (0.76 g, E) fractions from the roots (the total amounts of alkaloids being 0.38% of the weight of the air-dry epigeal part and 1.53% of the weight of the roots).

When fraction A was treated with acetone a crystalline mixture (0.55 g) separated out the chromatography of which on alumina gave hypaconitine with mp 190-191°C, mesaconitine with mp 207-208°C, 3-deoxyaconitine with mp 174-176°C, and songorine with mp 201-202°C. From the mother solution (2.50 g) after the separation of the crystalline mixture of alkaloids we isolated similarly not only the alkaloids mentioned above but also taurenine with mp 100-102°C. All these subtances were identified by direct comparison with authentic samples of the alkaloids [1, 3, 4].

By chromatographing the chloroform fraction B of the alkaloids on silica gel we obtained an amorphous base with the composition  $C_{23}H_{37}NO_6$  (M<sup>+</sup> 423). A comparative analysis of the

Institute of Chemistry of Plant Substances, Uzbekistan Republic Academy of Sciences, Tashkent. Translated from Khimiya Prirodnykh SOedeninii, No. 1, pp. 86-87, January-February, 1993. Original article submitted March 30, 1992.

spectral characteristic of this alkaloid with those of sebusine A [5] and a direct comparison with an authentic sample [1] showed their identity.

Treatment with methanol of the hexane and ether fractions of the bases from the roots of this plant (fractions C and D) gave a mixture of crystals which was separated by the method described above into hypaconitine and mesaconitine. Chromatography of the methanolic mother solution (3.5 g) on alumina gave the amorphous base tadzhaconine and neoline with mp 159-160°C, which were identified by direct comparison with authentic samples [6, 7] (TLC, PMR and mass spectra), and also an alkaloid with mp 174-176°C, composition  $C_{24}H_{33}NO_4$  (M<sup>+</sup> 399), the spectral properties of which showed its identity with 15-acetylsongorine [8]. This was confirmed by the formation of songorine on its saponification and by the presence of a broadened singlet at 5.55 ppm in the PMR spectrum of the base isolated.

Aconitum tokii Nakai is found in the south of Maritime Territory [9] and in northeastern China (Manchuria) [10]. It has not previously been studied at all. We have investigated the epigeal part gathered in the flowering phase in the environs of the village of Razdolnoe, Maritime Territory. The total alkaloids amounted to 0.1% on the weight of the air-dry raw material. From them, by chromatography, we isolated mesaconitine (0.2 g), glaucine (0.05 g), and isoboldine (0.01 g). The remaining mixture of alkaloids was separated into phenolic and nonphenoloic fractions. The latter (0.8 g) yielded N-methyllaurotetanine by chromatography on silica gel. The glaucine, isoboldine, and N-methyllaurotetanine were identified by direct comparison with authentic samples of these alkaloids (TLC and mass and PMR spectra) [11].

A base that was called anthroroidine, the structure of which was not studied, has been isolated previously from the epigeal part of <u>Aconitum anthoroideum</u> [12]. By means of its IR spectrum, TLC and a mixed melting point, the alkaloid was identified as tadzhaconine [6], and therefore the name anthroroidine for the alkaloid is abandoned.

## LITERATURE CITED

- 1. Z. M. Vaisov, V. A. Tel'nov, I. A. Bessonova, and A. P. Gorelova, Khim. Prir. Soedin., 82 (1993).
- S. W. Pelletier, N. V. Mody, B. S. Joshi, and L. C. Schram, in: Alkaloids. Chemical and Biological Perspectives, S. W. Pelletier (ed.), Wiley, New York, Vol. 2 (1984), p. 216.
  M. N. Sultankhodzhaev, M. S. Yunusov, and S. Yu. Yunusov, Khim. Prir. Soedin., 127
- (1973).
- 4. V. A. Tel'nov, Z. M. Vaisov, M. S. Yunusov, and A. P. Gorelova, Khim. Prir. Soedin., 108 (1992).
- 5. C. Konno, M. Shirasaka, and H. Hikino, J. Nat. Prod., <u>45</u>, 128 (1982).
- 6. I. M. Yusupova, B. T. Salimov, and B. Tashkhodzhaev, Khim. Prir. Soedin., 382 (1992).
- 7. N. M. Golubov, V. A. Tel'nov, M. S. Yunusov, N. K. Fruentov, and S. Yu. Yunusov, Questions of Pharmacy in the Far East [in Russian], No. 2, Kharabovsk (1977), p. 10.
- 8. A. D. Kuzovkov and T. F. Platonova, Zh. Obshch. Khim., <u>31</u>, 1389 (1961).
- 9. V. V. Voroshilov, Far-Eastern Species of the Genus <u>Aconitum</u> [in Russian], No. 52, Byul. Glavn. Bot. Sada SSSR (1964), p. 46.
- 10. T. Nakai, Rep. First Sci. Exped. Manch, Sec. 4 (1935), Chap. 2, p. 160.
- 11. S. Yu. Yunusov, Alkaloids [in Russian], Fan, Tashkent (1981), pp. 157, 165, 109.
- 12. V. A. Tel'nov, M. S. Yunusov, and S. Yu. Yunusov, Khim. Prir. Soedin., 383 (1971).