5. G. G. Zapesochnaya, V. A. Kurkin, and L. N. Pervykh, Khim. Prir. Soedin., 694 (1990).
6. A. Mallabaev, D. A. Rakhimov, and Yu. M. Murdakhaev, Khim. Prir. Soedin., 425 (1989).
7. R. Hardman and S. M. A. Mahar, Planta Med., 33, No. 3, 278 (1978).

AGLYCONS FROM GLYCOSIDES OF THE STARFISH Lethasterias nanimensis chelifera

A. A. Kicha, A. I. Kalinovskii,
and V. A. Stonik

UDC 547.925:593.93

Continuing investigations of steroid metabolites of the Far Eastern starfish Lethasterias nanimensis chelifera, we have isolated the total glycoside fraction from an ethanolic extract of the animals by a known method [1]. Acid hydrolysis of the total glycosides (6.0 g) was performed with 2 N HCl at 100°C for 0.5 h. The aglycons were extracted with chloroform, the extract was evaporated, and the residue was chromatographed twice on a column of silica gel in chloroform—ethanol (18:1) and chloroform—ethyl acetate mixtures with a ratio changing gradually from 30:1 to 30:15. Two main fractions of aglycons were obtained: A (1.200 g) and B (0.420 g).

Fraction A was chromatographed again on a column of silica gel in the chloroform—ethyl acetate system, beginning with a ratio of 30:1 and gradually increasing the proportion of ethyl acetate to 100%. Further purification was achieved by high-performance liquid chromatography (Du Pont chromatograph, refractometer as detector) on a Zorbax ODS (5 μm, 4.6 × 250 mm) column with ethanol—water (63:37) as eluent and a Separon SGX (5 μm, 3 × 150 mm) column with chloroform—ethyl acetate (1:1) as eluent. The individual compounds were identified with known aglycons for starfish by comparison of their PMR and ^{13}C NMR spectra with those given in the literature, and also by the GLC-mass spectrometry of their acetates. We isolated 120 mg of 3β,6α-dihydroxy-5α-pregnen-9(11)-en-20-one (asterone, I) [2], 3 mg of the 17α- isomer of asterone (II) [3], 35 mg of (20E)-3β,6α-dihydroxy-5α-cholesta-9(11),20(22)-diene-23-one (isomarthasterone, III) [2], and 16 mg of (17E)- and (17Z)-3β,6α-dihydroxy-5α-cholesta-9(11),17(20)-dien-23-ones (VI) [2].

Fraction B was crystallized from ethanol—chloroform, to give 200 mg of aglycon (V), with mp 240-242°C, $[\alpha]_{Hg}$ +56.6° (c 0.24; ethanol). This aglycon was identified as 3β,6α,23ξ-trihydroxy-5α-cholest-9(11)-ene on the basis of the following spectral characteristics.

PMR spectrum (C_5D_5N, 250 MHz): 0.73 (s, CH_3-18); 1.02 (d, J = 6.0 Hz, CH_3-27); 1.04 (d, J = 6.0 Hz, CH_3-26); 1.09 (s, CH_3-19); 1.16 (d, J = 6.0 Hz, CH_3-21); 3.08 (dm, J = 10.8 Hz, H-4e); 3.93 (m, H-3, H-6); 4.10 (m, 1/2W = 19.2 Hz, H-23); 5.41 (d, J - 6.0 Hz, H-11). The recording of the nuclear Overhauser effect on irradiation of the multiplet at 4.10 ppm showed an enhancement of the H-21 and H-26 signals, which demonstrated the presence of a hydroxy substituent at C-23.

^{13}C NMR spectrum (C_5D_5N, 62.9 MHz): 36.6 (C-1); 32.5 (C-2); 70.9 (C-3); 34.1 (C-4); 50.9 (C-5); 68.6 (C-6); 43.7 (C-7); 36.2 (C-8); 116.3 (C-9); 38.7 (C-10); 146.7 (C-11); 42.3 (C-12); 41.5 (C-13); 54.0 (C-14); 25.7 (C-15); 28.9 (C-16); 57.7 (C-17); 11.8 (C-18); 19.7 (C-19); 34.3 (C-20); 19.8 (C-21); 46.2 (C-22); 68.0 (C-23); 47.6 (C-24); 25.0 (C-25); 24.1 (C-26); 22.2 (C-27). The assignment of the signals in the ^{13}C NMR spectrum of (V) was made on the basis of an experiment with incomplete decoupling from protons and by comparison with the corresponding spectra of aglycons (I) and (III).

Aglycon (V) has been isolated previously from a hydrolysate of the total asterosaponins of the starfish Asterias amurensis [4]. However, it was not possible to compare the characteristics of the compound that we had isolated with literature values since they were not given in the Japanese authors' paper.

Pacific Ocean Institute of Bioorganic Chemistry, Far Eastern Branch, Russian Academy of Sciences, Vladivostok. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 145-146, January-February, 1992. Original article submitted April 12, 1991.

LITERATURE CITED

1. A. A. Kicha, A. I. Kalinovskii, and V. A. Stonik, Khim. Prir. Soedin., No. 4, 520 (1991).
2. F. De Simone, A. Dini, E. Finamore, L. Minale, C. Pizza, and R. Riccio, Comp. Biochem. Physiol., 64B, 25 (1979).
3. J. A. Findlay and V. K. Agarwal, J. Nat. Prod., 46, No. 6, 876 (1983).
4. S. Ikegami, Y. Kamiya, and S. Tamura, Tetrahedron Lett., No. 35, 3725 (1972).

ALKALOIDS OF THE CULTIVATED SPECIES Aconitum chasmanthum AND Delphinium elatum

L. N. Samusenko, D. M. Razakova,
I. A. Bessonova, and A. P. Gorelova

UDC 547.944/945

Representatives of the genera Aconitum and Delphinium belong to the most valuable alkaloid-bearing plants of the Ranunculaceae family [1]. The hypogeal organs (rhizomes with roots) of Aconitum chasmanthum Stapf and Delphinium elatum L. cultivated in the Polar-Alpine Botanical Garden (Kirovsk) have been analyzed for their alkaloid content. The first of them – a species of the Himalayan flora – was grown from seeds of culture origin obtained from Munich. The second is a Eurasian species that has become naturalized during cultivation for many years under the environmental and climatic conditions of the Khibiny mountains. In this introduction region, both plants have bound a second homeland, which has been shown above all in their resistance to unfavorable factors of the external environment of the subarctic and in their capacity for vegetative and seed reproduction.

Aconitum chasmanthum is a most valuable medicinal plant that is widely used in the scientific and folk medicines of a number of countries of South-East Asia [2]. Delphinium elatum is a source of raw material for obtaining drugs used in the treatment of diseases accompanied by a pathologically elevated muscular tonus. Insecticide [3].

Alkaloids were isolated from the air-dry comminuted raw material of Aconitum chasmanthum (200 g) that had first been treated with sodium carbonate solution by extraction with chloroform and the subsequent treatment of the concentrated chloroform solution with acid. The acid solution, after being made alkaline, yielded 2.6 g of total alkaloids (1.3% on the mass of dry raw material). By column chromatography on alumina with elution by hexane-ether a base (I) (157 mg) was obtained with mp 199-201°C (acetone), composition $C_{34}H_{47}NO_{11}$, M^+ 645, and base (II) (182 mg) and mp 115-117°C (acetone), composition $C_{23}H_{37}NO_5$, M^+ 407. Analysis of the ^1H and ^{13}C NMR spectra of these alkaloids ($CDCl_3$, Bruker WM, 400 and 100.61 MHz, respectively) showed that they were close to those published for aconitine and isotalatisidine [4]. A direct comparison with authentic specimens showed the identity of (I) with aconitine and of (II) with isotalatisidine [5] (mixed melting points, TLC, and IR spectra). This is the first time that either alkaloid has been isolated from this plant.

In a similar way to that described above, the air-dry rhizomes with roots of Delphinium elatum (966 g), gathered in the period of complete withering of the epigeal part of the plant, yielded 1.68 g of alkaloids from the acid solution and 22.43 g from the alkaline solution. The total amount of alkaloids was 2.5% of the mass of the dry raw material.

The chromatographic separation of the weakly basic fraction gave an amorphous base (III) (yield 0.5 g) the perchlorate of which had mp 215-219°C (from ethanol).

From the total basic alkaloids (22.43 g) was obtained a crystalline perchlorate with mp 215-219°C (ethanol) identical with the perchlorate of base (III). Its yield was 22 g.

Institute of Chemistry of Plant Substances, Uzbek Academy of Sciences, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 146-148, January-February, 1992. Original article submitted April 29, 1991.

0009-3130/92/2801-0125$12.50