LITERATURE CITED

1. Ya. Zham'yansan, Khim. Prirodn. Soedin., 133 (1978).
2. S. M. Aslanov and É. N. Novruzov, Khim. Prirodn. Soedin., 652 (1976).

QUINOID PIGMENTS OF ECHINODERMATA.

VI. NEW ANTHRAQUINONE FROM THE STARFISH *Echinaster echinophorus*

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UDC 547.673+593.93

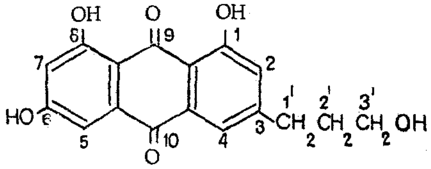
We have previously reported the isolation of anthraquinone pigments similar to the pigments of some sea lilies from the starfish *Echinaster echinophorus* [1]. In addition to the main components, in the mixture of pigments we have detected a fourth components, which is a new, previously undescribed, compound.

The evaporated ethanolic extract (50 g) from 2 kg of animals was dissolved in chloroform, and the pigments were extracted with a 5% aqueous solution of Na_2O_3. The sodium carbonate extract was acidified with dilute hydrochloric acid, and the pigments were extracted with diethyl ether. The total pigment extract (1.5 g) was separated on a column of acid-treated silica gel (Woelm) in the ether—hexane (2:1) system. Rechromatography of the fraction containing a pigment with R_f 0.1 (silufol) on a column of Sephadex LH-20 in chloroform gave 5 mg of a pigment with mp 229-230°C ($MeOH-CHCl_3$). The substance had an electronic spectrum typical for 1,6,8-trihydroxy-9,10-anthraquinones, λ_{max} (MeOH), nm: 224, 252, 262, 291, 437, 455 sh. (log ε 4.41, 4.17, 4.14, 4.17, 3.94, 3.89; Specord UV-VIS).

An intense peak of the molecular ion M^+ 314 (55%) showed the presence in the structure of the pigment of a side chain with the composition C_3H_7O. The formation of the main peak with m/e 270 (100%), and also the presence of ions with m/e 296 (15%) and 283 (13%), arising as the result of the elimination of a molecule of water and of $CH_2=\overset{+}{O}H$ from the molecular ion showed that there was a hydroxy group at C-3' of the side chain [2]. The absence from the mass spectrum of peaks with m/e 285 and 299 excluded the position of the hydroxy group at C-1' and C-2', respectively [3].

Analysis of the PMR spectrum of the pigment confirmed the structure of the hydroxypropyl substituent. PMR spectrum (C_5D_5N, 0 — TMS, Brüker HX-90E), δ, ppm: 2.04 (m, CH_2-2'), 290 (distorted t, CH_2-1'), 3.87 (t, J = 6.2 Hz, CH_2-3'), 6.97 (d, J = 2.3 Hz, H_{ar}), 7.28 (d, J = 1.5 Hz, H_{ar}), 7.69 (d, J = 2.3 Hz, H_{ar}), 7.86 (d, J = 1.5 Hz, H_{ar}). Under the action of an ethereal solution of diazomethane, the pigment readily formed a monomethyl ether at the β-hydroxy group with mp 162-163°C ($CHCl_3$—hexane). Absorption spectrum of the monomethyl ether in MeOH, λ_{max}, nm: 224, 252, 267, 291, 431, 445 sh. (log ε 4.65, 4.37, 4.34, 4.35, 4.18, 4.13); IR spectrum ($CHCl_3$, Specord IR-75), cm^{-1}: 3620 (alcoholic OH), 1676 (free C=O), 1626 (chelate C=O), 1611 (C=C).

On the basis of the results obtained, the structure of 1,6,8-trihydroxy-3-(3'-hydroxypropyl)-9,10-anthraquinone is proposed for the pigment.



LITERATURE CITED

1. N. K. Utkina and O. B. Maksimov, Khim. Prirodn. Soedin., 636 (1977).
2. A. A. Polyakova and R. A. Khmel'nitskii, Mass Spectrometry in Organic Chemistry [in Russian], Leningrad (1972), p. 97.

Pacific-Ocean Institute of Bioorganic Chemistry, Far-Eastern Scientific Center of the Academy of Sciences of the USSR, Vladivostok. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 651-652, September-October, 1978. Original article submitted May 24, 1978.

0009-3130/78/1405-0561$07.50

3. G. L. Bartolini, T. R. Erdman, and P. J. Sheuer, Tetrahedron, 29, 3699 (1973).

A COUMARIN FROM THE ROOTS OF *Ferula nevskii*

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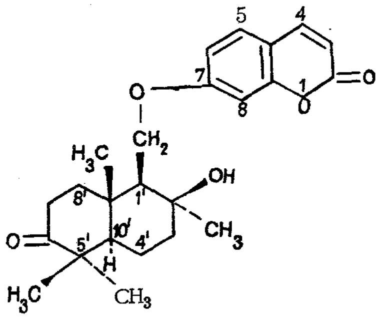
From the total extractive substances of the roots of *Ferula nevskii* by preparative separation on Silufol UV-254 plates (chloroform system) we have isolated a terpenoid coumarin with the composition $C_{24}H_{30}O_5$ (I), M^+ with m/e 398, mp 180-181°C (ethanol), R_f 0.09, not previously described in the literature, which we have called nevskone.

The IR spectrum of (I) has absorption bands at (cm^{-1}) 3510, 3470 (hydroxy group), 1720 (CO of a ketone in a six-membered ring), 1705 (CO of an α-pyrone), 1613, 1560, and 1510 (C=C of a coumarin system).

The NMR spectrum of nevskone (Varian JNM-4H 100/100 MHz, $CDCl_3$, 0 — TMS, δ scale) contains the signals of protons at 1.09 and 1.11 ppm ($CH_3-\overset{\diagdown\,\diagup}{C}-CH_3$, 3 H each, singlets), 1.22 ($-\overset{|}{\underset{|}{C}}-CH_3$, 3 H, singlet), 1.28 ($-\overset{|}{\underset{OH}{C}}-CH_3$, 3 H, singlet), 4.36 (Ar—O—CH—C$\underline{H}$<, 1 H, quartet, J_{gem} = 10.0 Hz, J_{vic} = 4.0 Hz), 4.15 ppm (Ar—O—C$\underline{H}$'—CH<, 1 H, quartet, J_{gem} = 10.0 Hz, J_{vic} = 3.0 Hz).

The signals of the protons of the coumarin system (5 H) resonate in the 6.20-7.70-ppm region. According to its composition and spectral characteristics, compound (I) is a new natural ketone of nevskin [1, 2]. The oxidation of nevskin formed nevskone. On the basis of the facts given, the following structure is suggested for the coumarin nevskone:



LITERATURE CITED

1. V. Yu. Bagirov and N. P. Kir'yalov, Khim. Prirodn. Soedin., 387 (1972).
2. V. Yu. Bagirov, V. I. Sheichenko, and A. A. Ban'kovskii, Khim. Prirodn. Soedin., 450 (1976).

V. L. Komarov Institute of Botany, Academy of Sciences of the Azerbaidzhan SSR, Baku. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 652-653, September-October, 1978. Original article submitted May 22, 1978.

0009-3130/78/1405-0562$07.50