AN INVESTIGATION OF THE CHEMICAL COMPOSITION OF A CO_2 EXTRACT FROM A PULP OF *Hippophaë rhamnoides*

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We have studied for the first time the physicochemical indices and the vitamin and fatty acid compositions of a CO_2 extract from an air-dried pulp of sea buckthorn collected in Northern Ossetia and in the foothill regions of Stavropol krai in 1976. The CO_2 extract was obtained from the dried wastes from the production of juice, comminuted to flakes 0.12 mm thick, by extraction with liuqid carbon dioxide under a pressure in the system of 5.7 MPa at a temperature of +20°C. The yield of CO_2 extract was 7.5%. We give the physicochemical characteristics of the CO_2 extract:

Density at 20°C, g/cm^3	0.9069
Refractive index at 20°C	1.4830
Acid No., mg of KOH/g	118.50
Ester No., mg of KOH/g	22.56
Waxes and wax-like substances, %	21.60
Free acids, %	20.30
Bound acids, %	8.20
Unsaponifiable substances, %	37.00
Vitamins: tocopherols, mg %	455.00
carotenoids, mg %	2.10
essential fatty acids (vitamin F), %	13.00
ascorbic acid, mg %	21.02
steroids — determined qualitatively	

The composition and relative amounts of the higher fatty acids of the CO_2 extract were studied by gas—liquid chromatography on a Khrom-3 chromatograph with a flame-ionization detector using a column 180 cm long and 0.4 cm in diameter. The stationary phase was 15% of poly(ethylene glyol succinate) on Chromaton, the column temperature was 190°C, and the carrier gas was nitrogen at a rate of 1-1.2 mg/sec. The fatty acids were chromatographed in the form of their methyl esters.

Acid	Amounts of the Acids, %	
	free	bound
Unidentified	2.4	-
Myristic	2.3	7.0
Palmitic	16.1	11.1
Palmitoleic	5.2	5.1
Stearic	2.7	1.4
Oleic	22.5	36.9
Linoleic	26.8	26.2
Linolenic	21.0	8.6
Unidentified	0.9	3.7

The lipid fraction was investigated by thin-layer chromatography on "Silufol" in the solvent system hexane—diethyl ether—glacial acetic acid (80:15:1). This showed the presence in it of phospholipids, mono-, di-, and triglycerides, sterols, tocopherols, and carotenoids. The value of a CO_2 extract of *Caucasium* buckthorn consists in its high content of essential fatty acids (vitamin F), tocopherols (vitamin E), and ascorbic acid (vitamin C). Qualitatively, the fatty acid composition of a CO_2 extract of sea buckthorn differs little from the composition of the oil obtained by extraction with other solvents [1, 2].

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QUINOID PIGMENTS OF ECHINODERMATA.

VI. NEW ANTHRAQUINONE FROM THE STARFISH *Echinaster echinophorus*

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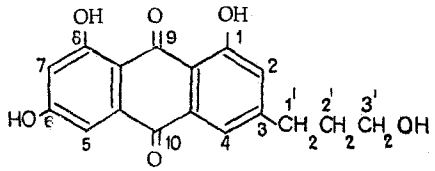
We have previously reported the isolation of anthraquinone pigments similar to the pigments of some sea lilies from the starfish *Echinaster echinophorus* [1]. In addition to the main components, in the mixture of pigments we have detected a fourth components, which is a new, previously undescribed,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



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