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ANTHRAQUINOID PIGMENTS FROM THE DEEP-WATER STARFISH *Henricia* SP.

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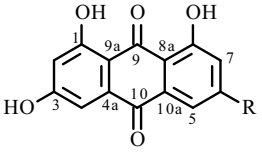
Previous studies have shown that starfish of the family Echinasteridae collected in shallow waters contain a series of anthraquinoid pigments [1–4]. In continuation of the search for biologically active metabolites in marine organisms, we studied the alcohol extract from a deep-water starfish of the genus *Henricia* that was collected in Okhotsk Sea at a depth of 200 m during the 31st cruise of Research Ship Akademik Oparin.

Starfish (10 g) was extracted with EtOH. The extract was separated over a column of Sephadex LH-20 using $CHCl_3$:MeOH (3:1) to produce **1** (5 mg), **2** (1 mg), **3** (0.6 mg), and **4** (0.5 mg). Compounds **1**–**4** were identified by comparison of their spectral characteristics with the literature for 1,3,8-trihydroxy-6-propyl-9,10-anthraquinone (crinoemodin, **1**) [1, 3–5]; 1,3,8-trihydroxy-6-(2′-hydroxypentyl)-9,10-anthraquinone (**2**) [1, 4, 6]; 1,3,8-trihydroxy-6-(2′-hydroxypropyl)-9,10-anthraquinone (isorhodoptilometrin, **3**) [1, 3, 4]; and 1,3,8-trihydroxy-6-(3′-hydroxypropyl)-9,10-anthraquinone (*ω*-rhodoptilometrin, **4**) [2, 4], respectively.



1 - 4

1: R = $CH_2CH_2CH_3$; **2:** R = $CH_2CH(OH)CH_2CH_2CH_3$
3: R = $CH_2CH(OH)CH_3$; **4:** R = $CH_2CH_2CH_2OH$

Compounds **1–4** (0.1 mM) were checked for ability to inhibit oxidation of linoleic acid (5 mM) induced by 2,2′-azobis(2-amidinopropane) dihydrochloride (AAPH) (1 mM). The oxidation process was monitored by the absorption increase at 234 nm from linoleic acid diene hydroperoxides formed during it (Fig. 1). It was found that **1**–**4** exhibited under these conditions weak anti-oxidant properties with a decrease of the linoleic acid oxidation rate by 2.6, 1.8, 1.7, and 1.9 times, respectively. Standard antioxidants trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid) and ionol (2,6-di-*t*-butyl-4-methylphenol, BHT) (0.1 mM) reduced the oxidation rate by 17.4 and 13.2 times, respectively.

Methylation of **1**–**4** by diazomethane in ether gave the corresponding C-3 methyl ethers, the spectral characteristics of which agreed with the literature [1, 2]. Monomethyl ethers of **1**–**4** (0.1 mM) did not reduce the oxidation rate of linoleic acid. Thus, the observed antioxidant activity of these compounds was related to the C-3 hydroxyl, which is capable of donating a proton to the peroxyl radical.

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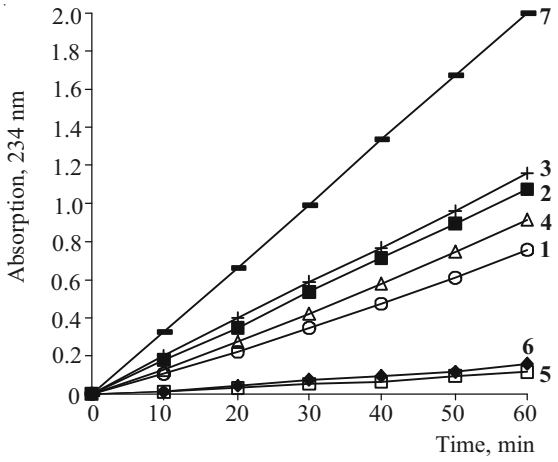

Fig. 1. Oxidation of linoleic acid induced by AAPH without antioxidants (control, **7**) and with **1**–**4**, trolox (**5**), and ionol (BHT, **6**).

ACKNOWLEDGMENT

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