A NEW BINAPHTHOQUINONE FROM *Strongylocentrotus intermedius*

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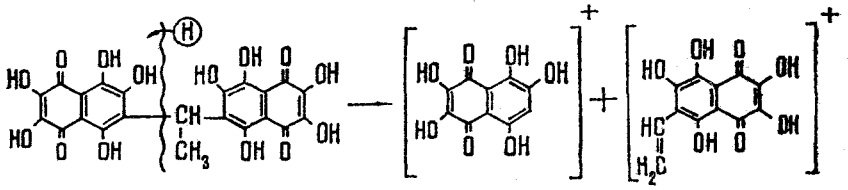
We have previously reported the isolation of spinochromes A, B, and C from the test and needles of the sea urchin *Strongylocentrotus intermedius* (Agas.) [1]. In the present paper we give information showing the presence in the total mixture of pigments from the same animal of spinochrome D (I) and of a new binaphthoquinone (II) having a binaphthazarin structure.

The composition and constants of substance (I) ($C_{10}H_6O_7$, sublimes at 285-290°C) and the results of absorption, NMR, and mass spectra correspond completely to the known spinochrome D (2,6,7-trihydroxynaphthazarin) [2-5].

Substance (II) was isolated with difficulty from the accompanying minor pigments. On repeated chromatography on acidic silica gel (see below), a loss of pigment was observed and the accompanying formation of substance (I), and also of brown products remaining at the starting line on TLC.

As the result of repeated separation by TLC, from the fraction with R_f 0.04, after crystallization from aqueous dioxane, we isolated substance (II) in the form of dark brown-red needles decomposing without melting at a temperature above 300°C. The pigment isolated has a typical naphthazarin spectrum in the UV and visible region. The main peak in the mass spectrum has m/e 238, and the nature of the decomposition under electron impact is similar to that of (I) with the exception of an additional peak with m/e 264.

The presence in the spectrum of fragments with m/e 124 and 125, and also a rearrangement of fragments with m/e 153 unambiguously shows the formation under electron impact of a fragment with the naphthazarin structure containing a proton in the aromatic nucleus, in accordance with the following scheme:



Two groups of peaks can be seen in the mass spectrum of the methylated product. One of them begins with a peak having m/e 586 (main peak) followed by the splitting out of methanol (m/e 554) and one of the methyl groups (m/e 539, while the other peaks of this group are inconsiderable and follow with a further decrease in intensity. This group can be assigned to the fragmentation of the molecular ion as a whole. The second must be assigned to a process of the primary decomposition of the molecule into two large fragments with their subsequent fragmentation. This group begins with peaks at m/e 308 and 280 (the main peak of this group); the subsequent fragmentation is similar to that of the decomposition of the trimethyl ether of spinochrome D.

A pigment of similar chemical structure has recently been isolated by Mathieson and Thomson [6] from the skeletal parts of the sea urchin *Spatangus purpureus*. It has been ascribed the structure of 3,3'-ethylidenebis(2,6,7-trihydroxynaphthazarin).

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The difference between this pigment and substance (II) reduces basically to the following fact. The binaphthequinone isolated by the British workers and its hexamethyl ether have much lower melting points (155-157°C and 44-47°C, respectively).

The mass spectrum of the hexamethyl ether showed only a weak molecular ion with m/e 586, while in the ether of substance (II) the molecular ion with the same m/e value was the main peak of the spectrum, which shows its greater stability under electron impact.

The absence of optical activity from substance (II) shows the symmetrical structure of the molecule. Of all the alternative structures, the most probable for substance (II) is therefore the structure 6,6'-ethylidenebis(2,3,7-trihydroxynaphthazarin).

EXPERIMENTAL

To separate the combined pigments, they were chromatographed on a column and in a thin layer of KSK silica gel containing 15% of a 0.1 N aqueous solution of oxalic acid (—0.08 mm for the thin layer and 0.08-0.15 mm for columns), using the following solvent systems (by volume): 1) benzene—methanol—0.1 N oxalic acid (10:1:0.05); and 2) benzene—methanol—0.1 N oxalic acid (5:1:0.025).

The pigments were purified additionally by chromatography on a column of Sephadex LH-20 in methanol and benzene—methanol.

The methyl ethers were chromatographed on KSK silica gel in chloroform. The absorption spectra were obtained on a Specord instrument in methanol, the NMR spectra on a Brüker HX-90E instrument with a working frequency of 90 MHz (δ, ppm, 0 — TMS), and the mass spectra on an LKB-9000S spectrometer with the direct introduction of the sample into the ion source at an ionizing voltage of 70 eV. The melting points were determined on a Kofler block.

For the isolation of the pigments, the needles and test of the sea urchins were dissolved in hydrochloric acid and the pigments were extracted with peroxide-free ether. The spinochrome D was isolated from the fraction with R_f 0.14 (system 1). After reprecipitation of methanol, small orange-red needles were obtained which sublimed without melting at 285-295°C. Absorption spectrum: λ_{max} 334, 460, 486_{sh}, 525_{sh} nm (log ε 3.59, 3.61, 3.56, 3.42). Mass spectrum: m/e 238, 210, 192, 181, 168, 153, 140, 136, 125, 124, 108.

The methylation of (I) with an ethereal solution of diazomethane led to the formation of a mixture of products from which a trimethyl ether was isolated by TLC (R_f 0.61), mp 161-162°C (from methanol).

Absorption spectrum; λ_{max}, nm: 233, 316, 470, 495, 525 (log ε 4.10, 3.68, 3.57, 3.63, 3.46). NMR spectrum ($CDCl_3$, ppm): 3.87; 4.00; 4.07 (3MeO), 6.33 (H_{ap}), 12.84; 12.96 (2αOH). Mass spectrum: m/e 280, 215, 237, 209, 181, 179, 168, 138.

From the fractions difficult to esterify we isolated the pigment (II): it decomposed at a temperature above 300°C without melting; λ_{max} 260, 346, 474, 540_{sh} nm (log ε 4.35, 3.93, 3.87, 3.51). NMR spectrum (C_5D_5N, ppm): 2.20 (doublet, J = 7 Hz, CH_3), 590 (q, J = 7 Hz, CH).

An ethereal solution of diazomethane was added dropwise to a suspension of pigment (II) in benzene until the evolution of bubbles of nitrogen ceased. The reaction mixture was separated by TLC; from the zone with R_f 0.57, by recrystallization from ethanol, we isolated the hexamethyl ether: mp 135-137°C, λ_{max} 235, 318, 480, 505, 540 nm (log ε 4.14, 3.87, 3.84, 3.91, 3.81). NMR spectrum ($CDCl_3$): 3.99, 4.06, 4.09 (6 MeO), 1.69 (doublet, J = 7 Hz, CH_3), 4.69 (q, J = 7 Hz, CH), 12.94, 13.36 (4α-OH). Mass spectrum: M 586 (main).

SUMMARY

From a mixture of the pigments of the sea urchin *Strongylocentrotus intermedius*, in addition to the known spinochrome D, we have isolated a new binaphthoquinone having the structure of 6,6'-ethylidenebis(2,3,7-trihydroxynaphthazarin).

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A STUDY OF THE STEROECHEMISTRY OF TERPENOID COUMARINS OF THE IRESANE SERIES BY PMR SPECTROSCOPY WITH ADDITIONS OF $Eu(DPM)_3$

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Four isomeric coumarins containing a terpenoid substituent of the iresane type in position 7 have been isolated from various representatives of the genera *Ferula* and *Colladonia*. The structure and absolute configuration of one of them [farnesiferol A (I)] were established mainly by chemical methods together with the ORD method [1]. Caglioti et al. [1] did not obtain unambiguous proofs for the configuration of C_1', but on the basis of indirect evidence they proposed the β-axial orientation as the most probable for the C_1'—CH_2 group. Scott et al., [2], by analogy with other diterpenoids, put forward the hypothesis of the equatorial orientation of the C_1'—CH_2 group in farnesiferol A.

Another coumarin, gummosin (II), is an epimer of farnesiferol A at C_6' and differs from it only by the orientation of the hydroxy group, which is axial in gummosin and equatorial in farnesiferol A [3].

Again, no proof of the configurations at C_1' has been obtained for the following pair of epimers at C_6', badrakemin (III) [4, 5] and colladonin* (IV) [6]. In addition, the nature of the linkage of the rings in the decalin nucleus has not been determined for these compounds. As well as this, on the basis of the PMR spectrum of badrakemin and a comparison of them with the corresponding characteristics of gummosin, the equatorial orientation of the C_1'—CH_2 group in it has been suggested.

Thus, the configuration at C_1' has not been established reliably for even one of the compounds mentioned.

We set ourselves the task of studying the relative configurations of these compounds by the PMR method using europium tris(dipivaloylmethanate) as paramagnetic shift reagent (PSR).

Below we give the PMR spectra of all four isomers (Figs. 1 and 2) and the chemical shifts (CSs) and spin—spin coupling constants of the main signals (Table 1). It can be seen from Figs. 1 and 2 and Table 1 that the epimeric pairs at C_6' — farnesiferol A and gummosin, on the one hand, and colladonin and badrakemin, on the other hand — differ, in the first place, as the positions of the signals of the exocyclic methylene group (the CS between the two signals for the first pair is 0.10 ppm and for the second pair 0.37 ppm), and, in the second place, by the shape of the signal from the C_1'—CH_2 grouping; in farnesiferol A and gummosin the latter appears in the form of two one-proton quartets with a distance of one from the other of 0.29-0.31 ppm, and in the pair colladonin—badrakemin they appear in the form of a two-proton multiplet.

Colladonin and badrakemin may differ from farnesiferol A and gummosin, respectively, either by the nature of the linkage of the decalin ring system or by the orientation of the methylene group at C_1', or by both these characteristics.

*Colladonin is identical with isobadrakemin, obtained from badrakemin [4].

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