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SPINOCHROME E

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SPINOCHROME E was first isolated, along with several other pigments, by Lederer,[1] from the calcareous parts of Mediterranean specimens of the sea urchin *Paracentrotus lividus* (Lam.), but insufficient material was available for chemical investigation. It has been obtained recently by Yoshida[2] from the species *Psammechinus miliaris* (Gemelin), in larger quantity. The pigment was isolated by treatment of the spines and test (shell) with hydrochloric acid, followed by dilution with methanol, and precipitation with pyridine. This product was then taken up in methanol, containing hydrochloric acid, from which spinochrome E separated. Recrystallization from acidified methanol gave brownish red needles, m.p. 320°. Carbon and hydrogen analysis indicated the formula $C_{10}H_{11}O_{10}$. We are greatly indebted to Dr. M. Yoshida for a gift of 200 mg. of this material.

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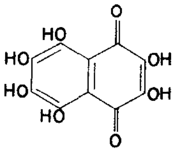
[1] E. Lederer, *Biochim. Biophys. Acta* **9**, 92 (1952).

[2] M. Yoshida, *J. Mar. Biol. Ass. U.K.* **38**, 455 (1959).

The specimen received contained 2.3% N and 3.3% Cl. These impurities were probably introduced during the previous treatment. Conversion to the acetate, and subsequent hydrolysis with methanolic sulphuric acid gave material free from nitrogen and chlorine, having C, 47.0; H, 2.5%. $C_{10}H_6O_8$ requires C, 47.2; H, 2.4%. (The product of hydrolysis with methanolic hydrochloric acid gave C and H figures very similar to those of Yoshida.$^{2)}$ The pigment gave the following colour reactions:

NaOH - deep orange, becoming green and then vanishing
$NaHCO_3$ - light brown precipitate (in MeOH)
$Na_2S_2O_4$ - decolourized, in MeOH, colour returned slowly in air
$FeCl_3$ - green (in MeOH)
$Pb(OAc)_2$ - violet precipitate (in MeOH)

Spinochrome E formed a yellow hexa-acetate, m.p. 192°, a colourless leuco-octa-acetate, m.p. 265° (decomp.), and, with diazomethane, a brown tetramethyl ether, m.p. 185°. The latter gave no colouration with aqueous sodium bicarbonate but formed a blue-violet solution in aqueous sodium hydroxide, and a violet solution with methanolic lead acetate. The ultraviolet absorption of the hexa-acetate showed maxima at 247 and 360 mμ (log ε 4.22 and 3.79 respectively) in methanol, and the curve was very similar to that of spinazarin tetra-acetate (2,3,5,8-tetra-acetoxy-1,4-naphthaquinone); the leuco-octa-acetate had $\lambda_{max.}$ 296 mμ (log ε 3.9) and $\lambda_{infl.}$ 286 mμ (log ε 3.87) (in chloroform), the spectrum closely resembling that of leucospinazarin hexa-acetate (1,2,3,4,5,8-hexa-acetoxynaphthalene). The leuco-octa-acetate has Mol. wt. 556 (ebullioscopic in benzene); octa-acetoxynaphthalene requires 592.



I

From these data we conclude that spinochrome E is hexahydroxynaphthaquinone (I). Experiments leading to the synthesis of this compound will be initiated shortly.

Satisfactory analyses were obtained for all derivatives.