Tetrahedron Letters No.47, pp. 3557-3561, 1964. Pergamon Press Ltd.
Printed in Great Britain.

SPINOCHROMES A(M) AND C(F)

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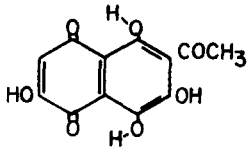
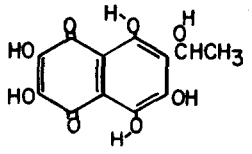
(Received 28 September 1964)

In a previous communication (1) we showed that spinochrome M possesses structure I. We also suggested, on the basis of a preliminary comparison, that spinochrome M is probably identical with spinochrome A, for which structure II had been suggested (2). We have now confirmed this point by reisolating spinochrome A from one of its original sources (3), the Mediterranean sea urchin Paracentrotus (Strongylocentrotus) lividus Lam. (4). The pigment was isolated as described earlier (1) and proved to be identical with M in all respects: m.p., mixture m.p., thin-layer chromatogram in two systems, u.v. spectra in three solvents, i.r. and n.m.r. spectra. The preferred trivial name of this pigment should be spinochrome A.



I

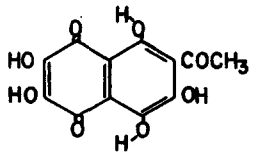


II

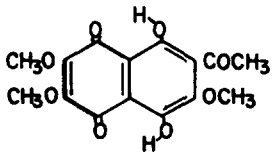
We further suspected that a purple spinochrome, m.p. 187-188°, which Tyler (5) had isolated from the Californian sea urchin Strongylocentrotus purpuratus might have been spinochrome A. We have now isolated this pigment from its original source (6) and have proved its identity with spinochrome A in the usual way. Spinochrome A thus emerges as one of the

most widely distributed spinochromes.

The Hawaiian sea urchin Echinometra oblonga Blainville, from which we first isolated spinochrome A, elaborates another pigment which appears as an orange band and trails the purple band of spinochrome A on deactivated silica gel columns during elution with benzene. We similarly encountered the identical pigment during the work-up of Paracentrotus lividus (vide supra). This spinochrome (ca. 0.01% yield from E. oblonga) was crystallized from methanol as red-orange needles, m.p. 246-248°. Combustion data (7) pointed to a molecular formula of $C_{12}H_8O_8$. We will show below that this pigment was described earlier as spinochrome C or F and we have assigned structure III to it on the basis of the following evidence. Its n.m.r. spectrum in dimethyl sulfoxide-d_6 showed only a



III



IV

sharp singlet at δ 2.58 (8) for the methyl protons of an acetyl group (9). The identical n.m.r. signal is shown by the acetyl group of spinochrome A (I) in dimethyl sulfoxide-d_6. The normal carbonyl absorption of the acetyl group in the infrared spectrum is shifted to longer wavelength because of intramolecular hydrogen bonding and is masked by the carbonyl absorption of the quinonoid system at 1665-1540 cm^{-1}. The ultraviolet spectrum is, for reasons not immediately apparent, not that of a typical naphthazarin: λ_{max}^{MeOH} 238.5 mu (log ε, 4.13), 293 (4.15), 348 (3.98), 460 (3.77). Also atypical are the instability (air oxidation) of this spinochrome in 0.05 N methanolic KOH and the small bathochromic shift in 0.005 N

methanolic KOH: $\lambda_{max}^{KOH/MeOH}$ 253.5 mu (log ε, 4.07) 306.5 (4.17), 365 (3.98), 466 (3.90).

Methylation of this spinochrome (III) with diazomethane in methanol-ether afforded a trimethyl ether, $C_{15}H_{14}O_8$, m.p. 116-117°, after chromatography on deactivated silica gel and crystallization from chloroform as dark-orange plates, and to which we have assigned structure IV. In contrast to its parent compound the trimethyl ether exhibits a typical naphthazarin spectrum in the ultraviolet: λ_{max}^{MeOH} 314 mu (log ε, 3.69), sh 469 (3.59), 494 (3.62), sh 529 (3.48), sh 591 (2.74); $\lambda_{max}^{0.05NKOH/MeOH}$ 296-318 mu (log ε, 3.88), 564 (3.95), 596 (3.93). The infrared spectrum of IV (KBr) now showed the carbonyl absorption of the acetyl group at 1704 cm^{-1} as expected. The n.m.r. spectrum in deuteriochloroform showed singlets at δ 13.07 (C_8-OH), 12.97 (C_5-OH), 4.10 (C_6-OCH_3), 4.07 (C_2-OCH_3 and C_3-OCH_3) and 2.50 (C_7-$COCH_3$).

Our contention that this spinochrome of structure III is the same as spinochromes C and F of the literature rests on the following points. Spinochrome F, m.p. 229°, was isolated in 1940 by Kuroda and Ohshima (10) from the spines of Heterocentrotus mammilatus Linn. and Hemicentrotus pulcherrimus Ag. In 1960 (11) Kuroda reported for spinochrome F a new m.p. of 245-247°, a molecular formula of $C_{12}H_8O_8$ and a trimethyl ether, m.p. 104°. Direct comparison of Kuroda's spinochrome F (12) with our spinochrome proved identity in all respects.

The historical background of spinochrome C is less straightforward (13). A dark red pigment, m.p. 229°, isolated from Arbacia pustulosa (also A. lixula or A. aequituberculata), was mentioned in 1939 by Kuhn and Wallenfels (14). In a subsequent publication these authors (15) called this same pigment, m.p. 229-230° (from dioxane-water), spinone A, $C_{12}H_8O_8$,

and assigned to it structure III. They assumed that spinone A might be an artefact which was formed during work-up of the true pigment, i.e. spinochrome A (air oxidation in basic medium), which then was assumed by Lederer and Glaser (3) to have structure II. Also in 1939, Glaser and Lederer (15) first mentioned a brown-red spinochrome, m.p. 247°, isolated from Arbacia, which they called isoechinochrome. In his detailed account of 1952 (17) Lederer supplied spectral data and a molecular formula of $C_{12}H_8O_8$. He suggested identity of spinone A and isoechinochrome on the basis of a comparison of physical data and adopted the new name of spinochrome C in accordance with an earlier nomenclature proposal for echinoid pigments (18). In addition Lederer (17) reported isolation of spinochrome C from the spines of P. lividus. In our own work-up of the spines of P. lividus (vide supra) we encountered spinochromes A and C thereby confirming Lederer's observation and establishing unequivocally structure III for spinochrome C, which should be the correct trivial name of this pigment.

Acknowledgment.- This work was supported by a PHS Grant GM-10413 from the Institute of General Medical Sciences, Public Health Service.

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4. We are grateful to Dr. S. J. Townsley for the collection of these animals in the Gulf of Naples.
5. A Tyler, Proc. Nat. Acad. Sci. U.S.A. 25, 523 (1939).
6. We are indebted to Dr. R. A. Boolootian for arranging for this collection in Southern California.
7. Combustion analyses were performed by Berkeley Analytical Laboratory. All compounds reported in this paper had satisfactory analyses.
8. Referred to TMS ($\delta = 0$) as the internal standard.
9. The signal is superimposed on the low field region of the quintet arising from the CHD_2 proton of the solvent.
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