

BILLETER and MIESCHER<sup>1</sup> proposed a scheme to account for the oxidation products of cholesterol acetate dibromide. They assume that in the first place tertiary C-atoms are attacked by oxygen, thus yielding tertiary alcohols. These points are liable to further oxidations.

With the aid of these assumptions it is possible to explain the formation of the oxidation products isolated so far. All these substances are formed by the destruction of the side-chain or by the oxidation of ring D.

As yet, only one compound,  $\Delta$ -3,5-androstadiene-dione-7,17 (see above), where oxidation had occurred in ring B, had been isolated.

The formation of 7-oxo-dehydro-iso-androsterone acetate may be explained by the presence of unbrominated cholesterol acetate, which usually occurs in the starting material. This contamination will be oxidized at C7.

Other 5,6 unsaturated steroids as well yield 7-oxo-compounds on oxidation, for instance cholesterol acetate to 7-oxo-cholesterol acetate (WINDAUS, LETTRÉ and SCHENCK<sup>2</sup>).

The 7-oxo-cholesterol acetate on further oxidation will lose the side-chain to give 7-oxo-dehydro-iso-androsterone acetate.

Little can be said about the amount of this compound formed during the oxidation of dibromo-cholesterol acetate, but it will depend on the completeness of the bromination and thus widely vary.

C. C. BOLT

Research Laboratories, N. V. Organon, Oss, Holland, April 24, 1951.

#### Zusammenfassung

Bei der Reinigung von technischem Trans-Dehydroandrosteronazetat gelang es, durch Chromatographie der letzten Mutterlaugen  $\Delta$ 5-3 $\beta$ -azetoxy-androsten-dion-(7,17) zu isolieren. Diese Verbindung war bisher in den Oxydationsprodukten des Cholesterinazetatdibromids noch nicht gefunden worden. Wahrscheinlich ist sie bei der Oxydation von nicht bromiertem Cholesterolazetat entstanden.

<sup>1</sup> J. R. BILLETER and K. MIESCHER, *Helv. chim. acta* 30, 1414 (1947).

<sup>2</sup> A. WINDAUS, H. LETTRÉ, and FR. SCHENCK, *Ann. Chem.* 520, 98 (1935).

### The Nomenclature of the Spinochromes of Sea Urchins

The name echinochrome was coined in 1885 by MACMUNN<sup>1</sup> to designate the red pigment of the elaeocytes of sea urchin. The name spinochrome was given in 1938 by LEDERER and GLASER<sup>2</sup> for a similar darker pigment found in the spines of the sea urchin, *Paracentrotus lividus*. In 1939 KUHN and WALLENFELS<sup>3</sup> proposed to add suffixes to echinochrome and spinochrome to distinguish the various pigments found in the eggs and spines of different species. The pigment isolated from *Arbacia pustolusa* eggs was called echinochrome A and that from *Paracentrotus lividus* spines called spinochrome P. On the evidence available in 1940, LEDERER<sup>4</sup>

did not consider that this addition of suffixes was warranted; however later in 1940, KUHN and WALLENFELS<sup>1</sup> isolated, in small amounts, further echinochromes, B and C, from *Arbacia* eggs and in 1942 MUSAJO and MINCHILLI<sup>2</sup> isolated spinochrome P<sub>1</sub> from *Paracentrotus* spines. GOODWIN and SRISUKH<sup>3</sup>, in 1950 attempted to standardize the nomenclature by suggesting that KUHN and WALLENFELS<sup>4</sup> scheme regarding echinochromes be adopted but that the spinochromes should be renamed spinochrome A, B, etc., instead of P and P<sub>1</sub>; P and P<sub>1</sub> were used originally to indicate the origin of the pigment (*Paracentrotus*)<sup>5</sup>, but as these also occur in other species (e. g. *Echinus esculentus*) it was concluded that ambiguity would be avoided if these prefixes were dropped and A, B, C, etc., substituted.

The principle of the nomenclature suggested by GOODWIN and SRISUKH<sup>3</sup> is acceptable, but, as will be pointed out later, the details will have to be altered somewhat in the light of recent work. There does arise, however, a more important point as to whether the separate terms spinochrome and echinochrome are justified, because the work of LEDERER and GLASER<sup>6</sup> recently repeated by LEDERER<sup>7</sup>, and confirmed in the Liverpool laboratory, indicated that echinochrome A is not confined to the eggs and (or) perivisceral fluid of urchins, but also occurs in the test and spines. We feel that the differentiation is still valid for two main reasons (a) spinochromes have not as yet been observed in eggs or perivisceral fluid, (b) that LEDERER<sup>7</sup> has observed that the organic residue remaining after dissolution of the spines and test of *Paracentrotus* in HCl, contains both echinochrome A and spinochrome A, but in this case the echinochrome A is the major component. This organic residue, consisting of the bases and motor muscles of the spines, can quite reasonably be considered as the site of conversion of the echinochrome into spinochrome prior to the latter's incorporation into the calcified regions. It is possible then that the echinochrome found in spines comes from small amounts of organic residue (which would be extremely difficult to dissect out) and does not in fact occur in the calcified regions; it is also possible that both spinochrome and echinochrome are transferred to these regions (cf. MOORE<sup>8</sup>). In any case, whatever is the final explanation there is no reasonable doubt that the spinochromes are specifically incorporated into the test and spines, and thus one is justified in maintaining the distinction between spinochromes and echinochromes.

We therefore propose that the following nomenclature be adopted (Table) for spinochromes; further pigments when isolated could then be added to this list by adding the appropriate letter to spinochrome.

Apart from the inclusion of new pigments<sup>9</sup> this scheme differs from that of GOODWIN and SRISUKH<sup>3</sup> in two major details. Isoechinochrome, the occurrence of which

<sup>1</sup> R. KUHN and K. WALLENFELS, *Ber. Dtsch. chem. Ges.* 73, 458 (1940).

<sup>2</sup> L. MUSAJO and M. MINCHILLI, *Bol. sci. Fac. Chim. Ind. Bologna* 3, 113 (1942).

<sup>3</sup> T. W. GOODWIN and S. SRISUKH, *Biochem. J.* 47, 69 (1950).

<sup>4</sup> R. KUHN and K. WALLENFELS, *Ber. Dtsch. chem. Ges.* 72, 1407 (1939).

<sup>5</sup> L. MUSAJO and M. MINCHILLI, *Bol. sci. Fac. Chim. Ind. Bologna* 3, 113 (1942); *Gazz. Chim. Ital.* 70, 287 (1940).

<sup>6</sup> R. GLASER and E. LEDERER, *C. r. Acad. Sci. Paris* 208, 1939 (1939).

<sup>7</sup> E. LEDERER, *Biochim. biophys. acta* (1951) (in press).

<sup>8</sup> H. B. MOORE, *J. Mar. biol. Ass. U. K.* 21, 711 (1937).

<sup>9</sup> E. LEDERER, *Biochim. biophys. acta* (1951) (in press).

<sup>1</sup> C. A. MACMUNN, *Quart. J. Micr. Sci.* 25, 469 (1885).

<sup>2</sup> E. LEDERER and R. GLASER, *C. r. Acad. Sci. Paris* 207, 454 (1938).

<sup>3</sup> R. KUHN and K. WALLENFELS, *Ber. Dtsch. chem. Ges.* 72, 1407 (1939).

<sup>4</sup> E. LEDERER, *Biol. Rev.* 15, 273 (1940).

## Proposed nomenclature of spinochromes:

Suffix	m. p.	Formula	Previous name	Origin
A	185°	C <sub>12</sub> H <sub>10</sub> O <sub>8</sub>	Spinochrome . . . . .	North Atlantic <i>P. lividus</i> LEDERER and GLASER <sup>1</sup> GOODWIN and SRISUKH <sup>2</sup>
B	>300°*	C <sub>12</sub> H <sub>8</sub> O <sub>7</sub> **	Spinochrome P <sub>1</sub> . . . . .	<i>P. lividus</i> from Atlantic or Mediterranean MUSAJO and MINCHILLI <sup>3</sup> GOODWIN and SRISUKH <sup>2</sup>
C	247°	C <sub>12</sub> H <sub>8</sub> O <sub>8</sub>	iso-echinochrome; perhaps identical with spinon A .	<i>Arbacia pustulosa</i> and <i>P.</i> <i>lividus</i> Mediterranean GLASER and LEDERER <sup>4</sup> KUHN and WALLENFELS <sup>5</sup>
D	295°		Spinochrome Aka . . . . .	<i>Pseudocentrotus depressus</i> KURODA and OSHIMA <sup>6</sup>
E	>350°		new pigment . . . . .	<i>P. lividus</i> Mediterranean LEDERER <sup>7</sup>
F	229°		Spinochrome F . . . . .	<i>Heterocentrotus</i> <i>mammilatus</i> KURODA and OSHIMA <sup>6</sup>
G	>350°		new pigment . . . . .	<i>P. lividus</i> Mediterranean LEDERER <sup>7</sup>
M	193°		Spinochrome M . . . . .	<i>Anthocidaris crassispina</i> KURODA and OSHIMA <sup>6</sup>
P	188°	C <sub>12</sub> H <sub>10</sub> O <sub>7</sub>	Spinochrome P . . . . .	<i>P. lividus</i> Mediterranean MUSAJO and MINCHILLI <sup>8</sup>

\* MUSAJO and MINCHILLI found m. p. above 350°, GOODWIN and SRISUKH<sup>2</sup> found m. p. 283°. Our recent preparations melt above 300° with decomposition and partial sublimation. It is very difficult to state a definite melting point.

\*\* This is the formula suggested by MUSAJO and MINCHILLI<sup>3</sup> who obtained four concordant analyses.

<sup>1</sup> E. LEDERER and R. GLASER, C. r. Acad. Sci. Paris 207, 454 (1938).

<sup>2</sup> T. W. GOODWIN and S. SRISUKH, Biochem. J. 47, 69 (1950).

<sup>3</sup> L. MUSAJO and M. MINCHILLI, Bol. sci. Fac. Chim. Ind. Bologna 3, 113 (1942).

<sup>4</sup> R. GLASER and E. LEDERER, C. r. Acad. Sci. Paris 208, 1939 (1939).

<sup>5</sup> R. KUHN and K. WALLENFELS, Ber. dtsh. chem. Ges. 74, 1594 (1941).

<sup>6</sup> C. KURODA and H. OSHIMA, Proc. Imp. Acad. Tokyo 16, 214 (1940).

<sup>7</sup> E. LEDERER, Biochim. biophys. acta (1951) (in press).

<sup>8</sup> L. MUSAJO and M. MINCHILLI, Gazz. Chim. Ital. 70, 287 (1940).

LEDERER and GLASER<sup>1</sup> first reported in *Arbacia* without specifying the site of occurrence, was assumed from its name to occur in the eggs. LEDERER<sup>2</sup>, however, had pointed out in his review that this pigment does in fact occur in the spines of *Arbacia*, and has since confirmed this<sup>3</sup>. Isoechinochrome, which is probably identical with Spinon A<sup>4</sup> is thus renamed spinochrome C. Although recent work has confirmed the view of GOODWIN and SRISUKH<sup>5</sup> that spinochrome P<sub>1</sub> and B are identical, it has shown quite conclusively that spinochromes A and P are distinct pigments in spite of very similar properties<sup>3</sup>. The suffix P is therefore retained for the pigment of MUSAJO and MINCHILLI<sup>6</sup>.

Spinochrome Aka, isolated from Japanese urchins<sup>7</sup> has been renamed D; spinochrome F cannot, however, be as KUHN and WALLENFELS<sup>4</sup> suggest, spinochrome A, because of the very great differences in m. p.

T. W. GOODWIN, E. LEDERER, and L. MUSAJO

Department of Biochemistry, University of Liverpool, Institute for Physico-chemical Biology, Paris, and Institute for Pharmaceutical Chemistry, University of Padua, July 23, 1951.

## Résumé

La présente note contient une proposition de nomenclature des pigments naphthoquinoniques des parties

<sup>1</sup> E. LEDERER and R. GLASER, C. r. Acad. Sci. Paris 207, 454 (1938).

<sup>2</sup> E. LEDERER, Biol. Rev. 15, 273 (1940).

<sup>3</sup> E. LEDERER, Biochem. biophys. acta (1951) (in press).

<sup>4</sup> R. KUHN and K. WALLENFELS, Ber. dtsh. chem. Ges. 74, 1594 (1941).

<sup>5</sup> T. W. GOODWIN and S. SRISUKH, Biochem. J. 47, 69 (1950).

<sup>6</sup> L. MUSAJO and M. MINCHILLI, Gazz. Chim. Ital. 70, 287 (1940).

<sup>7</sup> C. KURODA and H. OSHIMA, Proc. Imp. Acad. Tokyo 16, 214 (1940).

calcaires d'Oursins. Les différents spinochromes sont désignés par des lettres majuscules, A, B, C, etc. Le tableau donne cette nomenclature.

Arenicochrome, a new Pigment from *Arenicola marina* L.

In a histological and histochemical investigation LIGNAC<sup>1</sup> some years ago described a pigment occurring as green granules in the epithelial cells of the worm *Arenicola marina* L. found off the Dutch coast at Den Helder.

This pigment, which was called arenicochrome by LIGNAC, showed some analogy to the melanins when judged by its granular form (0.25 to 1.30 μ) and localization within the cell. On treating a tissue-section with hydrogenperoxide the arenicochrome granules could be transformed into brown granules which in turn were made black by silvernitrate and could be decolorized by further treatment with hydrogenperoxide. The two latter reactions are also given by the melanins, so that it seemed that arenicochrome could be considered as a premelanin.

A search of the available literature revealed that the only two authors dealing with pigments in the skin of *Arenicola* species (FAUVEL<sup>2</sup> and ASHWORTH<sup>3</sup>) had probably not observed these green granules in their material.

The pigment could be extracted from the skin of *Arenicola* by means of an alkaline extraction-fluid but it proved to be very unstable in the crude extract. We

<sup>1</sup> G. O. E. LIGNAC, Proc. Kon. Acad. Wetensch. Amsterdam 48, 406 (1945).

<sup>2</sup> P. FAUVEL, C. r. Soc. Biol. 129, 1273 (1899).

<sup>3</sup> J. H. ASHWORTH, *Arenicola* (The lugworm) (London, 1904).