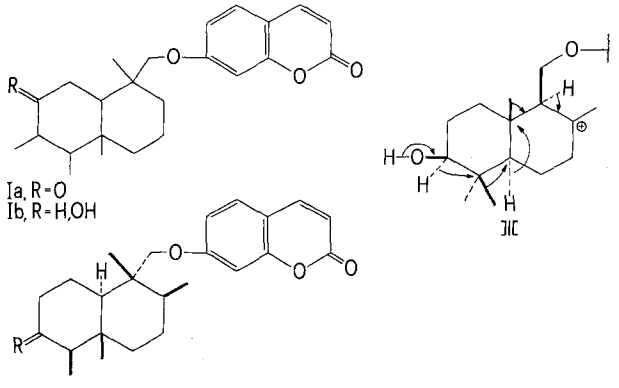
(IIb) are fully consistent with all the reported spectral (Figure) and chemical data[3,4]. It is to be noted that kamolone bears the same relationship to kamolol as friedelin to friedelenol, the latter two co-occurring in *Clusea rosea*[7]. Finally, it remains to be stressed that the stereochemical details may be as indicated by (IIa) and (IIb) or their mirror images.



Zusammenfassung. Neue Strukturvorschläge für den terpenoiden Teil zweier Inhaltsstoffe aus *Ferula penninervis*.

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[1] For a recent illustrative review, see S. Dev, in *Some Recent Developments in the Chemistry of Natural Products* (Ed. S. Rangaswami and N. V. Subba Rao; Prentice-Hall, India 1972), p. 308.
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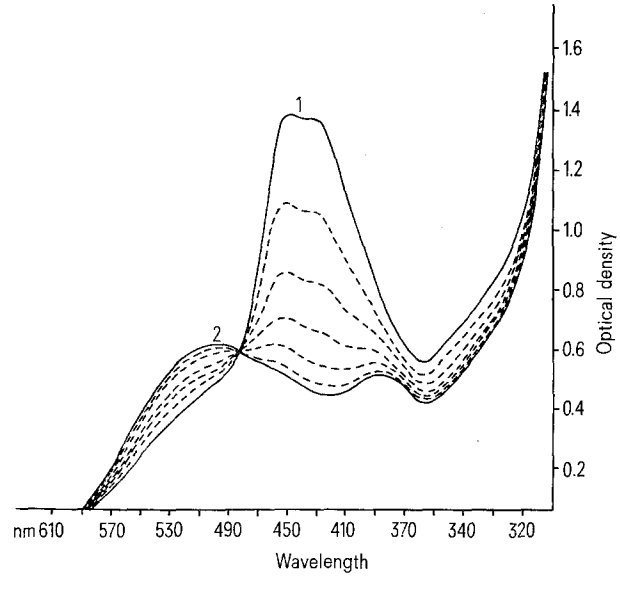
Occurrence and Characterization of a Labile Xanthommatin Precursor in some Invertebrates

In a previous paper[1] we reported that a labile yellow pigment was detected, by extraction at low temperature, in the eyes of *Octopus vulgaris* and *Sepia officinalis*. When left standing this pigment is rapidly converted into dihydroxanthommatin and by subsequent air oxidation into xanthommatin.

In this paper we intend to examine the eyes and skin of *Loligo vulgaris*, *Sepia officinalis*, *Octopus vulgaris*, the eyes of *Homarus gammarus* and, in addition, the heads of *Musca domestica* and *Apis mellifera*. In all these animal species the presence of xanthommatin was known[2]. All results are reported in Table I.



Absorption spectra of the labile pigment in buthanol-acetic acid, 0.5*N* HCl (60:15:25) (curve 1) and its spectrophotometric transformation into dihydroxanthommatin (curve 2).

The animals were frozen to death and the structures containing the photoreceptors were carefully separated from animals and potterized at −5 °C in acetone. After several washings with acetone, at low temperature, the materials were extracted with buthanol-acetic acid-0.5*N* HCl (60:15:25 v/v) and were examined spectrophotometrically (Figure).

The UV-spectrum of crude extract from the eyes of *Octopus* displayed absorption maxima at 450 and 430 nm. In all the cases reported in Table I, it is possible to note the presence of the labile pigment with UV-maxima at 450 and 430 nm. It is noteworthy that the spectrophotometric curves of the extracts from the eyes of *Homarus* and heads of *Musca* and *Apis* are not so well defined, owing to the presence of impurities[3].

Table I. Composition of extracts in buthanol-acetic acid-HCl 0.5 *N* (60:15:25 vv) at −5 °C

Octopus	eyes skin	labile pigment, ommin
Sepia	eyes skin	labile pigment, ommin
Loligo	eyes skin	labile pigment, ommin
Homarus	eyes	labile pigment, ommin
Apis	heads	labile pigment, ommin
Musca	heads	labile pigment, little xanthommatin

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Table II

Mixture	Labile pigment		Xanthommatin		Dihydroxan.		I		II	
ButOH-AcH-0.5N HCl (60:15:25)	450	430	460	390	498	385	450	430	450	430
2N HCl	500	460	470	390	500 (I)	470	495	462	495	462
							435 (I)		430 (I)	

(I) = inflection

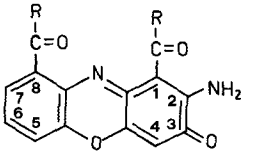
At room temperature, this labile pigment with UV-maxima at 450 and 430 nm is rapidly converted into a red substance with UV-maxima at 498 and 385 nm which, in turn, is transformed into a product with UV-maxima at 460 and 385 nm. It should be noted that the presence of an isosbestic point indicates the complete transformation of the labile pigment into the product with maxima at 498 and 385 nm. This isosbestic point is also observed in the extracts from all animals reported in Table I. In all the cases examined, both products of transformation were isolated and purified by chromatography column on carboxy-methyl-cellulose (Whatman CM 23) using buthanol-acetic acid-H_2O (60:15:25 v/v) as eluent. They were identified, as dihydroxanthommatin and xanthommatin, by comparison of their chromatographic properties with those of authentic samples[4].

The conversion of labile pigment into dihydroxanthommatin did not involve an oxidative reaction as it occurred also in the presence of reducing agents (SO_2, ascorbic acid) which of course inhibited the subsequent transformation of dihydroxanthommatin into xanthommatin.

As shown in Table I, after exhaustive extraction of labile pigment from the animal tissues, generally no xanthommatin can be detected.

Taking into consideration these results, we suggest that xanthommatin probably arises from the labile precursor. In order to obtain information on the nature of this labile ommochrome, we compared its electronic spectrum with those of two phenoxazinic substances obtained by oxidation of 3-hydroxyanthranilic acid and its methylester.

A solution of 0.04 mole of $K_3[Fe(CN)_6]$ in 20 ml of phosphate buffer pH 6.8 was added to a solution of 1.5 g (0.01 mole) of 3-hydroxyanthranilic acid in 10 ml of the same buffer, at 25 °C with agitation. Stirring was continued for 1 h, after which the solution, acidified with acetic acid, was extracted with ethyl acetate. The organic phase was concentrated and purified by chromatography column 2 × 30 cm on polyamide (Macerey, Nagel and Co.) using benzene as eluent. The fraction containing product I, which emerged from the column after about 200 ml, was identified as cinnabarinic acid[3] by mass spectroscopy ($M^+ = 320$).



I R=OH
II R=OCH_3
III R=CH_2–CH(NH_2)–COOH

The ester II[5] of cinnabarinic acid ($M^+ = 328$) was characterized by spectral data. NMR-spectrum in CD_3SOCD_3 shows signals due to OCH_3 groups at δ 3.85 and δ 3.90 (each 3H, s) to C(4)-proton at δ 6.5 (1H, s), to aromatic protons at δ 7.6 (3H, s) and to aminic protons at δ 7.8 (2H, by D_2O exchanged). IR-spectrum shows the C(8)-carbomethoxy C = O stretching band at 1724 cm^{-1}; C(1)-carbomethoxy C = O at 1670 cm^{-1}; C = O quinonic at 1640 cm^{-1}.

The Table II shows the UV-maxima of the labile pigment in two extracting mixtures and those of products I and II, dihydroxanthommatin and xanthommatin in the same solvents.

The values reported in Table II indicate that the behaviour of the chromophore of the labile pigment corresponds to those of compounds I and II. These results support the hypothesis that the pigment has a chromophore of type III. In nature the two uncyclized aminoacidic chains are plausibly stabilized.

Riassunto. Un nuovo ommocromo labile è stato rinvenuto in alcuni invertebrati. Sulla base del suo comportamento chimico e spettrale si puó ritenere che sia un precursore della xantommatina.

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[6] Acknowledgement. The authors wish to express their thanks to Prof. R. A. NICOLAUS for his interest in this work.

Imidazole Nucleoside Analogues Possessing a Non-Glycosidic Link between Sugar and Base

A number of analogues of most of the important naturally occurring imidazole ribofuranosides have been prepared[1,2,3] for use in studies of the *de novo* biosynthesis of purines and as potential anti-virus and anti-cancer compounds. Most of them have the same carbohydrate component as the natural purine precursors and all contain a glycosidic link between sugar and base. Recently[4] we synthesized an imidazole nucleoside (I) in which