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Applications of Natural Purple from *Dolabella Auricularia*: Colouration of Cholesteric Liquid Crystals

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ABSTRACT

Hydroxypropyl cellulose (HPC) as a cholesteric liquid crystal was coloured with purple ink from *dolabella auricularia* as a sea hare. Optical texture of the liquid crystal mixture was confirmed with a polarising optical microscope.

1. INTRODUCTION

Dye chemistry and engineering have been developed to electric communications, new display devices, solar cells, and energy conversion system. Today, highly development of synthetic dyes is mainly employed for industrial applications. However, the natural purple recently paid attention from viewpoints of medicine [1-3] and information science, and reconsidered for their functionalities.

Purple as a glace colour has been used for dyeing of textiles since Greek and Roman time. Tyrian purple (6,6-dibromoindigo) has been obtained from murex purpuream (shellfish), as shown in Figure 1. Sea hares release purple ink against predators such as crabs in the sea. The ink plays roles of screening and toxin to protect themselves.

We have studied on synthesis and electro-magnetic properties of π-conjugated polymers, especially conducting polymers. Our present attempt directs to learn from natural dyes after reconsideration of the fact that the conducting polymers are polymer dyes. At the present stage, we proceed for an interface study on marine biology and polymer science. In this research, liquid crystal colouring is carried out by using natural purple from *dolabella auricularia*.

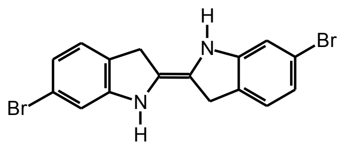

Figure 1. Chemical structure of tyrian purple (6,6-dibromoindigo).

Figure 2. Scenery of Shimoda gulf.

Dolabella auricularia was obtained in Shimoda (Japan) with a support and instruction of diving by Shimoda Marine Research Center, University of Tsukuba on August, 2015. Photograph of the sea at the Shimoda gulf is shown in Figure 2. Shimoda area in Japan is shown in Figure 3. The purple ink was sampled from the shellfish. *Dolabella auricularia* discharges relative materials of this compound.

Figure 4 shows *Dolabella Auricular*ia beneath of the sea. Sea hare *Aplysia californica* discharges purple ink. *Dolabella auricularia* collects molecules from the sea weeds in the sea and stores the compounds. Secretion of the ink from *dolabella auricularia* contains several molecules, such as aplysioviolin [4], dolabellin [5,6], auriside A and dolastatin 10 [7] (Figure 5). In the case of auriside A, synthesis of C1-C9 of the molecule was carried out with Meinwald reaction of alkyl propionate [8]. Total synthesis of auriside A has been performed [9]. Molecules from sea hares and cyanobacteria show pharmacodynamics effect, and are expected for application of medical science. Potent antimitotic activity of dolastatin 10 has been reported [10].

So, sea weeds such as red alga have originally synthesise pharmacodynamics compounds in the sea. Application of sea weeds may open a new avenue for materials science and medical science.

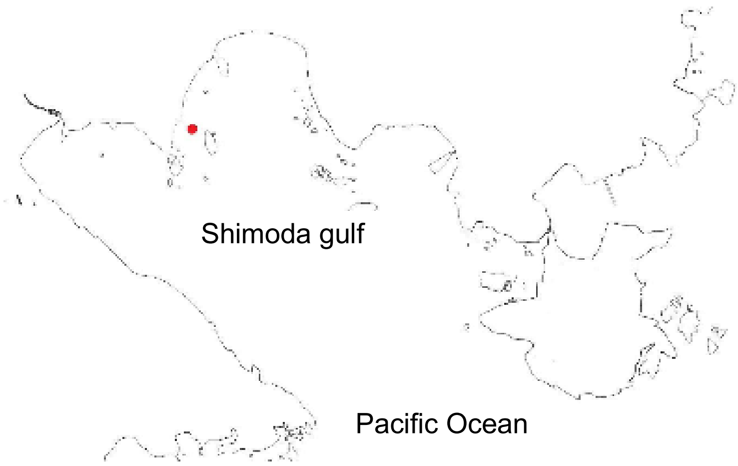

Figure 3. Shimoda in Japan. Red point = sampling area.

Hydroxypropyl Cellulose (HPC)

HPC (150-400 cP, cP (centipoise) = mPa·s) was purchased from Wako Chemical (Japan), and used without further purification. HPC shows lyotropic liquid crystal with helical structure at appropriate concentration in the water. Chemical structure of the HPC is shown in Figure 6. Hydroxypropyl group are partly substituted onto the main-chain. The substitution rate is described by degree of substitution. The entire sample of the HPC can form liquid crystal as a chiral aggregation form.

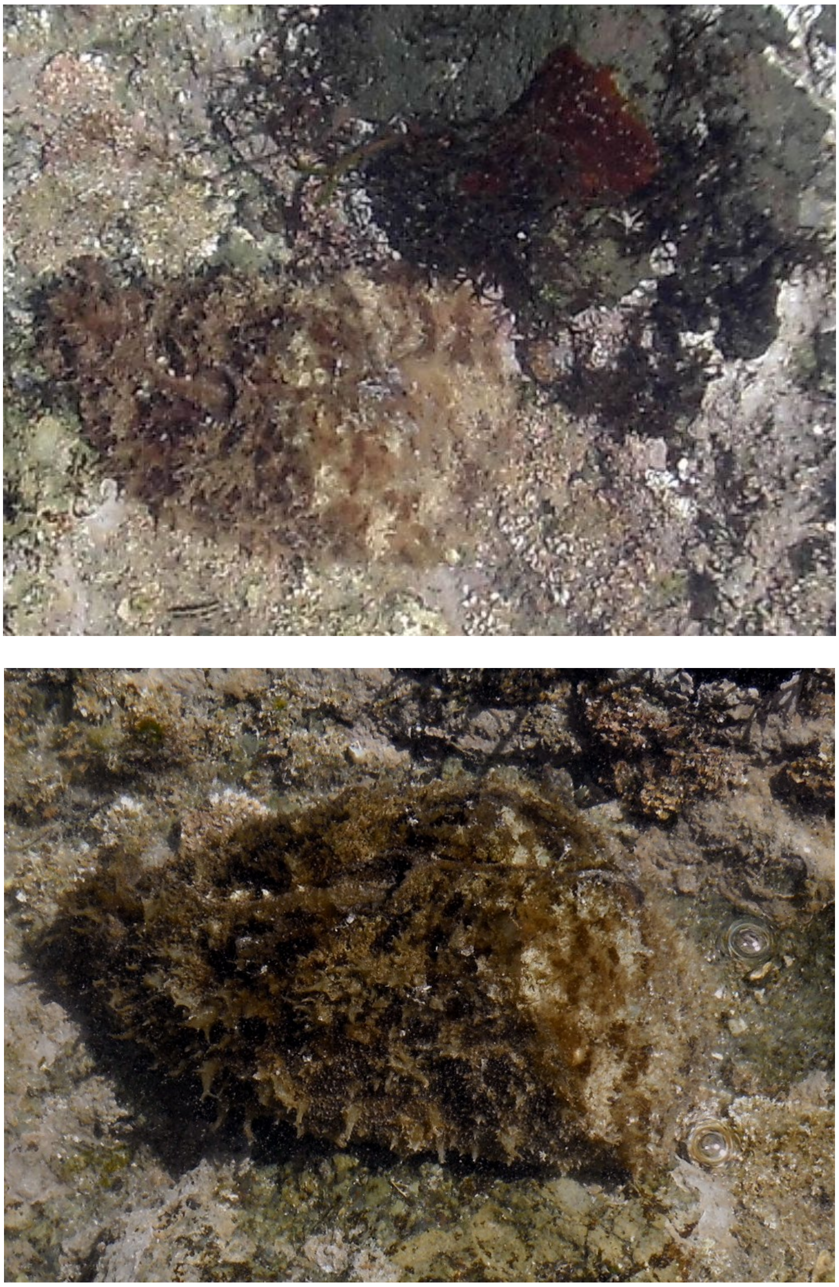

Figure 4. *Dolabella Auricularia* (top): top view, (bottom): side view.

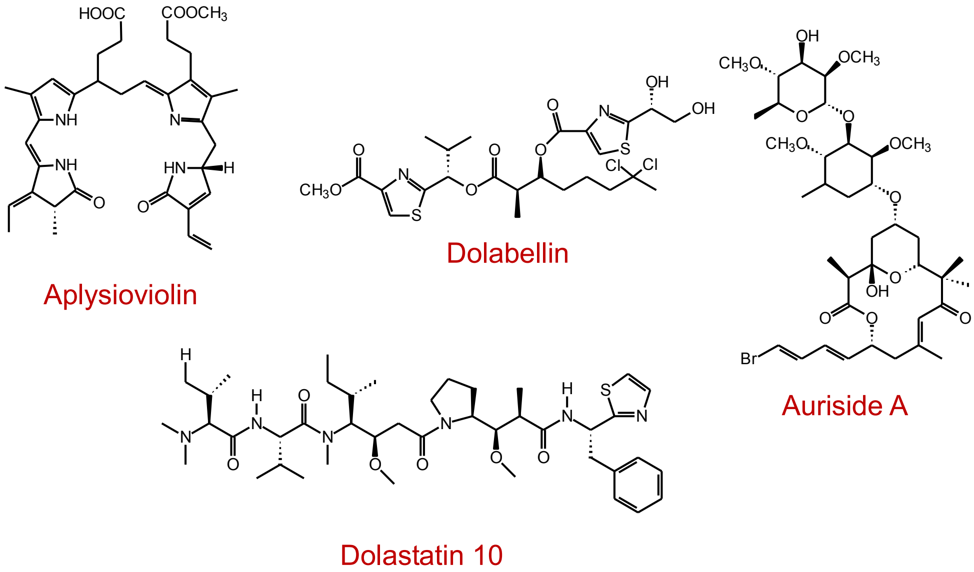

Figure 5. Chemical structure of aplysioviolin, dolabellin, auriside A, and dolastatin 10.

2. EXPERIMENT

The purple ink in the marine water from the *dolabella auricularia* was mixed with HPC. After ca. 24 h, optical texture of the purple liquid crystal mixture is examined.

3. RESULT AND DISCUSSION

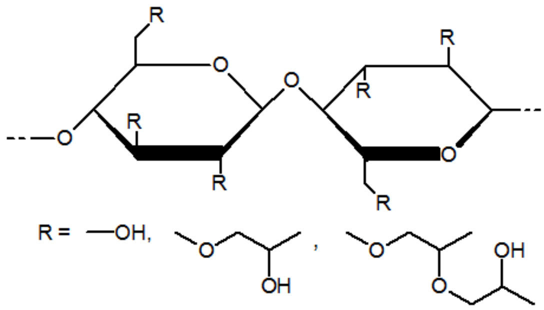

Figure 6. Chemical structure of hydroxypropyl cellulose (HPC).

Figure 7 shows polarising optical microscopy image of the coloured HPC with the ink. After the mixed, the liquid crystallinity of the purple HPC was confirmed because the product shows numerous lines derived from helical half-pitch of the cholesteric liquid crystal. This result indicates that the purple ink from *dolabella auricularia* is good affinity with HPC. Plausible helical aggregation structure of the HPC in the liquid crystal state is shown in Figure 8(left). The purple ink can align helical manner along to the helical aggregation structure of the matrix HPC, as shown in Figure 8(right). The colouring by using the purple ink from the sea sell may allow us to apply the coloured liquid crystal for production of light selective materials or gratings.

We confirmed good affinity of the purple ink from *dolabella auricularia* (originally from sea weeds) with HPC as a cholesteric liquid crystal, through the field-study and the research in laboratory. A significance of this attempt is colouring of polymer liquid crystal with natural functional dye from the sea. The ink molecule may align along the helical order of the cholesteric liquid crystal. The natural dye chemistry may extend to liquid crystal science.

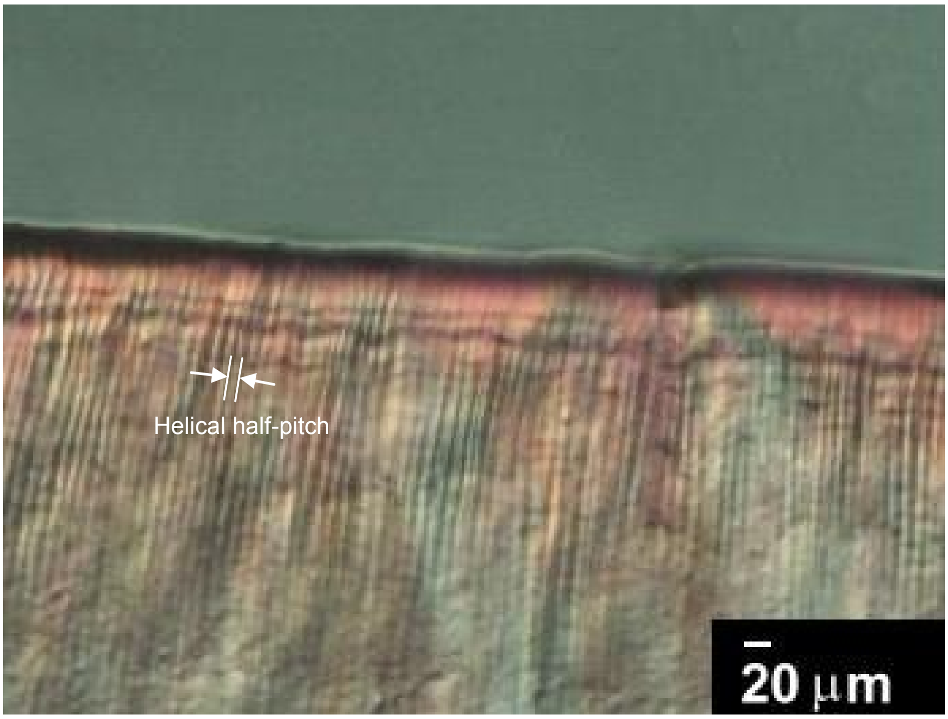

Figure 7. Polarising optical micrograph of hydroxypropyl cellulose (HPC)/purple ink from *dolabella auricularia* at room temperature.

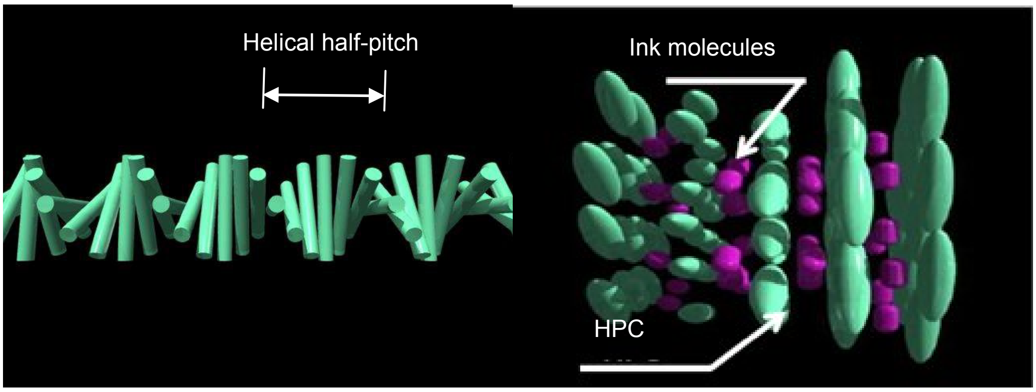

Figure 8. An illustration of HPC in cholesteric liquid crystal stare.
(Left): Helical arrangement of HPC in the cholesteric liquid crystal state.
(Right): The ink in the HPC.

Marine organisms show unknown optical and chemical properties. Recently, new functions of bio-materials have been found. For example, green fluorescent protein (GFP) shows circular polarised luminescence [9]. Combination of natural products and polymers can be expected to lead development for new opto-electro-functional materials.

Finally, an importance of sea weeds for application of materials science and medical science may need to be enhanced because these plants in the sea synthesise valuable molecules with numerous chiral centres, which can show high performance in technology and medical science.

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