Biochemical Studies on the Carotenoids in Porifera.
The Structure of a New Carotenoid, Tedaniaxanthin in Sea Sponge, *Tedania digitata*

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A new aromatic carotenoid isolated from the sea sponge, *Tedania digitata*, was confirmed to be a 3-hydroxy-2, 3-didehydro-β, γ-carotene. The name tedaniaxanthin is proposed for this aromatic carotenoid.

Karrer et al. confirmed the existence of astaxanthin in red sea sponge, *Axinella cristagalli*. Drumm et al. reported the presence of echinenone, γ-carotene in *Hymeniacidon sanguineum*. In 1957 Yamaguchi first isolated the aromatic carotenoids, renieratene, isorenieratene and renierapurprin from *Reniera japonica*.

The existence of mono-hydroxy-β-isorenieratene and β-renieratene was recently isolated by Smith.

A new undescribed aromatic carotenoid was isolated from the sea sponge, *Tedania digitata*.

Materials and Methods

The sea sponges were collected from the littoral zone of Sakurajima, Kagoshima and the carotenoids were extracted with acetone in a Waring blender. The crude carotenoids of acetone solution were transferred to petroleum ether by the addition of water. The petroleum ether solution of the crude carotenoids was washed with water to remove trace of acetone, dried over anhydrous sodium sulphate, and evaporated under reduced pressure.

The adsorbents for column chromatography were carefully selected according to the carotenoids under investigation, because some kinds of carotenoids were decomposed while they are in contact with some adsorbents. The crude carotenoids thus obtained were initially separated on a MgO column (magnesium oxide: Hyflo Super Cel=1:2). The pigment solution of petroleum ether was placed on the column and developed with 30% acetone in petroleum ether. The seven resulting bands were obtained and the orange band (Fr-5) was eluted with acetone. The carotenoids were transferred to petroleum ether by the addition of water. The petroleum ether solution of the carotenoids was repeatedly washed with water to remove trace of acetone, dried over anhydrous sodium
sulphate and evaporated under reduced pressure. The carotenoids which were thus extracted were rechromatographed on a dried, powdered sugar column, using petroleum ether as developing solvent. Three bands were obtained and the orange band was eluted with acetone. The carotenoid was transferred to petroleum ether from acetone with water and evaporated to dryness under vacuum. Thus obtained pigment was saponified by dissolving it in 100 ml of absolute ethyl alcohol, adding 10 ml of 60% (w/v) aqueous potassium hydroxide and leaving it overnight under nitrogen at room temperature. The saponified pigment was transferred to petroleum ether with water, dried over anhydrous sodium sulphate and concentrated under vacuum. The pigments were repurified on a dried, powdered sugar column, using petroleum ether as developing solvent. Only one band was obtained. The isolated pigment was crystallized from n-
hexane-ethyl ether and had the following characteristics: m. p. 164–165°C, λ max in petroleum ether 433, 459, 486 nm (Fig. 1).

The crystalline pigment was ground with potassium bromide, passed into a pellet and the infrared spectrum was measured in an IR-specrophotometer (Fig. 1). Characteristic absorption bands were obtained at 3440 cm⁻¹ (hydroxyl), and 975 cm⁻¹ (trans double bonds).

The NMR spectrum of the pigment was obtained at 100 MHz and was determined
in CDCl₃ relative to internal TMS (Fig. 3). The NMR spectrum revealed C-methyl resonances at 7.74 and 7.84, indicating the aromatic end group of renierapurpurin⁸⁻⁹. The signals at 8.78 and 7.96 suggest the existence of 3-hydroxy-2, 3-didehydro-β-carotene end group.

High resolution mass measurements of the pigment indicated a molecular formula: C₄₈H₆₀O= 546.38617 (sample: 546.386044). Mass spectrum shows the presence of peaks at M−92, M−106, M−133 and M−151 (Fig. 4). The peak at M−133 shows the existence of the carotenoids having the aromatic end group such as isorenieratene, renierapurpurin, chlorobactene and okenone¹⁰⁻¹³. The peaks at M−92 and M−106 are typical ones of the carotenoids. The peaks at M−151, M−191 and M−217 show the presence of 3-hydroxy-2, 3-didehydro-β-carotene end group.

The proposed structure of this carotenoid based on the visible absorption spectrum, IR, NMR and mass spectrum is shown in Fig. 5.

Fig. 5. Structure of tedaniaxanthin

Results

A new aromatic carotenoid, 3-hydroxy-2, 3-didehydro-β, χ-carotene was identified in sea sponge and the name tedaniaxanthin was proposed.

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References