Short Paper

Isolation of Three Stereoisomers, Tunaxanthin A, B and C from Tunaxanthin Fraction in Japanese Fishes*¹

Tunaxanthin, a common carotenoid found in marine fishes, was first isolated ($C_{40}H_{56}O_2$, mp. $196^\circ C$) by HIRAO *et al.*,^{1,2)} and the chemical constitution of this carotenoid was proposed as ϵ, ϵ -carotene-3, 3'-diol by CROZIER *et al.*³⁾

This paper reports the isolation of three stereoisomeric tunaxanthins in tunaxanthin fraction from the integuments of Japanese fishes (marine fishes: 4 species, fresh water fishes: 7 species).

Tunaxanthin fraction obtained by the same method as previously described⁴⁾, showed one spot on t.l.c. of silica gel G with 30% acetone in pet. ether. However, on t.l.c. of either silica gel G (35% ethylacetate in benzene) or $Mg_2(OH)_2CO_3$ (10% acetone in pet. ether), this fraction was separated into three compounds showing the same visible absorption spectrum (λ_{max} . 414, 437, 467 nm in pet. ether). All these compounds gave dimethyl ethers and diacetates. From the results described above, it seems reasonable to suppose that they have the same constitution of ϵ, ϵ -carotene-3, 3'-diol and are stereoisomers. So, we designated them tunaxanthin A, B and C as shown in Fig. 1. In 1978, tunaxanthin B, a major carotenoid in these stereoisomers, was assigned 3R, 6S, 6'S, 3'S- ϵ, ϵ -carotene-3, 3'-diol by stereochemical examinations⁵⁾. (Fig. 2) The

Fig. 1. Thin-layer chromatograms of tunaxanthin fraction from the integuments of fishes on silica gel G (I) with 35% ethylacetate in benzene and on $Mg_2(OH)_2CO_3$ (II) with 10% acetone in pet. ether.

1: tunaxanthin A, 2: tunaxanthin B, 3: tunaxanthin C.

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*¹ 魚類ツナキサントン画分より立体異性体、ツナキサンテン A, B および C の分離、確認。

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Fig. 2. Absolute configuration of tunaxanthin B.

absolute configurations of the other stereoisomers, tunaxanthin A and tunaxanthin C have not yet been established.

On the other hand, BINGHAM has made an independent study of tunaxanthin fraction from marine Californian fishes and reported⁶⁾ the presence of four stereoisomers, oxyxanthin-45, oxyxanthin-51, oxyxanthin-58 and chiriquixanthin B. The first three of them, from the senorita fish (*Oxyjulis californicus*), were assigned 3S, 6S, 6'S, 3'S-, 3S, 6S, 6'S, 3'R- and 3R, 6S, 6'S, 3'R- ϵ, ϵ -carotene-3, 3'-diol respectively. The last stereoisomer from the yellow-tail rockfish (*Sebastes flavidus*) was identical to chiriquixanthin B (3S, 6R, 6'R, 3'S- ϵ, ϵ -carotene-3, 3'-diol) isolated from the yellow Costa Rican frog⁷⁾.

From the evidence of thin-layer chromatography, we have concluded that tunaxanthin fraction from Japanese fishes is a mixture of three stereoisomers of ϵ, ϵ -carotene-3, 3'-diol, namely, tunaxanthin A, tunaxanthin B and tunaxanthin C. In correlation with the results of BINGHAM⁶⁾, we have deduced that tunaxanthin B is identical to oxyxanthin-51 and that either of tunaxanthin A and tunaxanthin C may well agree respectively with one of three stereoisomers, oxyxanthin-45, oxyxanthin-58 and chiriquixanthin B although no direct comparison has been made.

A detailed study on three stereoisomers in Japanese fishes will be reported soon elsewhere.

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