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NEW CAROTENOIDS, PARASILOXANTHIN AND 7,8-DIHYDROPARASILOXANTHIN

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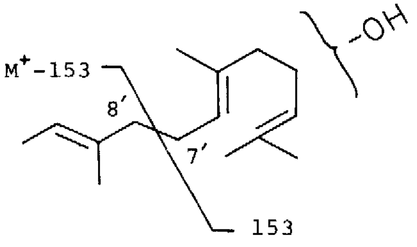
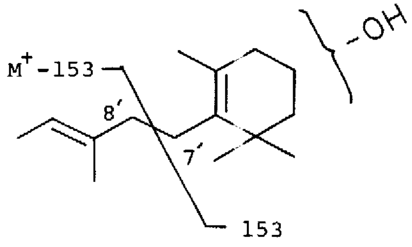
Two new carotenoids, parasiloxanthin and dihydroparasiloxanthin have been isolated from the fin and skin of Japanese common catfish <u>Parasilurus asotus</u>.[1] In the present study the structures of parasiloxanthin (1) and dihydroparasiloxanthin (2) have now been established by visible, ms, nmr spectra and chemical properties.

Both (1) and (2) were isolated as orange yellow needles (5 mg, 0.00001% yield, 2.5 mg, 0.000005% yield of the whole body weights), mp 202°, $C_{40}H_{58}O_2$ (M^+ 570), mp 197°, $C_{40}H_{60}O_2$ (M^+ 572), respectively. Their visible light absorption spectra (petroleum ether) showed absorption maxima at 405, 427, 452 nm, and at 380, 401, 426 nm, indicating the presence of aliphatic octaene and heptaene chromophores, respectively. The presence of two secondary hydroxy groups in (1) and (2) was demonstrated by nmr spectra (90 MHz) in DMSO-d_6 solution, and the hydroxy groups were not methylated with 0.01 N-HCl methanol solution at room temperature[2]. These facts indicated the presence of two secondary hydroxy groups at non-allylic positions in each compound. On treatment of (1) and (2) with conc. HCl in ether, no blue color change was observed (negative for epoxide test).

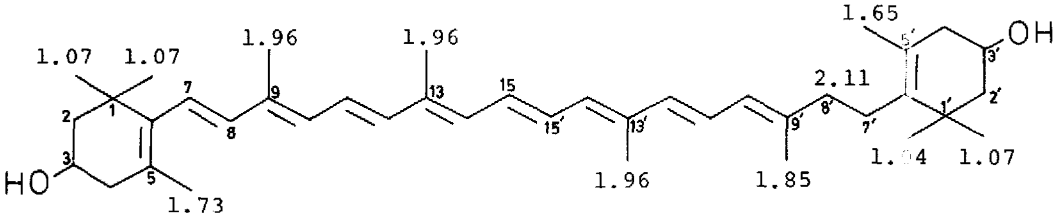
The mass spectrum of (1) showed abundant peaks at m/e 570 (M^+), 552 (M^+-18), 478 (M^+-92), 417 (M^+-153), 399 (M^+-153-18), and 325 (M^+-153-92). The characteristic fragment ion, m/e 417 (M^+-153), was associated loss of $C_{10}H_{17}O$, which corresponds to either 7′,8′-dihydro-monohydroxy acyclic end group (A) in 3-hydroxy-β-zeacarotene (3)[3] or 7′,8′-dihydro-monohydroxy cyclic end group (B), from the molecular ion.



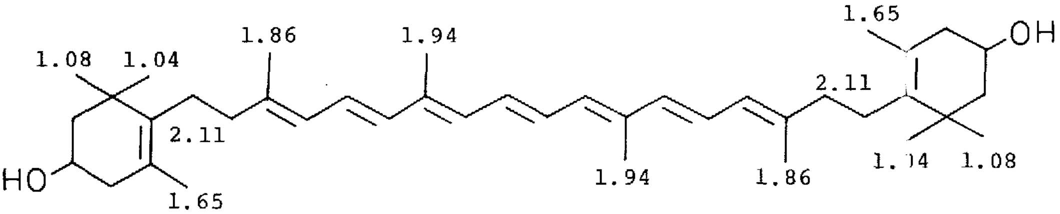
(A)



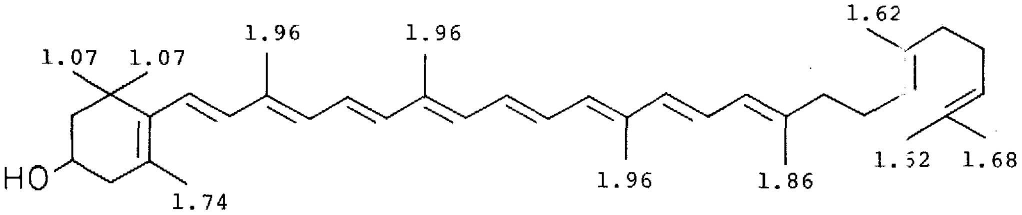
(B)



parasiloxanthin (1)



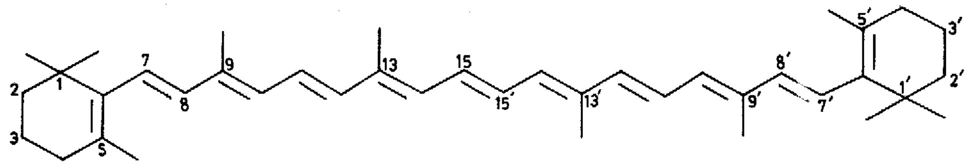
7,8-dihydroparasiloxanthin (2)



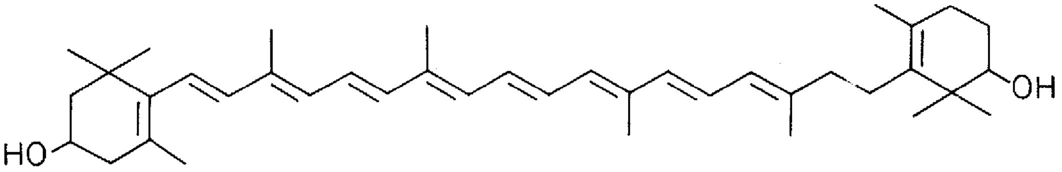
3-hydroxy-β-zeacarotene (3)

On the other hand, the nmr spectrum (100 MHz, $CDCl_3$) of (1) showed 10 methyl signals at δ 1.04 (C-1′ methyl, 3H), 1.07 (C-1, C-1, C-1′ methyls, 9H), 1.65 (C-5′ methyl, 3H), 1.73 (C-5 methyl, 3H), 1.85 (C-9′ methyl, 3H), 1.96 (C-9, C-13, C-13′ methyls, 9H), and methylene signal at 2.11 (C-7′, C-8′ methylenes, 4H). The signals at δ 1.07 (6H) and 1.73 (3H) are very similar to those recorded for C-1, C-1, C-5 methyl resonances in the one β-ionone ring of 3-hydroxy-β-zeacarotene (3)[3] and zeaxanthin (3,3′-dihydroxy-β-carotene)[4], and accordingly the presence of one 3-hydroxy-β-ionone ring was established. The other signals at δ 1.04 (3H), 1.07 (3H), and 1.65 (3H) did not agree with those of 3-hydroxy-β-zeacarotene (3) which have signals at δ 1.62 (C-1′ and C-5′ methyls, 6H) and 1.68 (C-1′ methyl, 3H). This excluded the possibility that the structure of parasiloxanthin might be a dihydroxy derivative of β-zeacarotene having a structural moiety (A).

Therefore, the remaining probable structure for parasiloxanthin compatible with ms, nmr spectral observations and the presence of two non-allylic OH groups should be limited to 3,2′-dihydroxy-7′,8′-dihydro-β-carotene (4) or 3,3′-di-



β-carotene



3,2'-dihydroxy-7',8'-dihydro-β-carotene (4)

Table. Observed relative shifts for the methyl signals of some hydroxylated carotenoids upon addition of Eu(dpm)$_3$ to the nmr samples

Carotenoid	Methyl groups									
	1	1	5	9	13	13'	9'	5'	1'	1'
2-hydroxy-β-carotene	100	67.5	29.4	13.6	3.53	0.81	0.81	0.27	0.27	0.27
parasiloxanthin	100	100	65	29	12	12	24	69	100	100
3,3'-dihydroxy-β-carotene	100	92	64	26	8	8	26	64	92	100

hydroxy-7',8'-dihydro-β-carotene (1) having a structural moiety (B).

In order to determine the possible structure (4 or 1), the ^{1}H nmr Eu-shift technique was applied to this carotenoid.[5] The relative values of induced shifts of methyl signals are given in the Table together with those of 3,3'-dihydroxy-β-carotene (zeaxanthin) and 2-hydroxy-β-carotene.[6] Above results supported the symmetrical attachment of two secondary hydroxy groups at C-3, C-3' like zeaxanthin.

Consequently, the structure of parasiloxanthin was determined to be 3,3'-dihydroxy-7',8'-dihydro-β-carotene (1). This is the first example of 7',8'-dihydro-β-carotene derivative in naturally occurring carotenoids.

The mass spectrum of dihydroparasiloxanthin (2) showed abundant peaks at m/e 572 (M^+), 554 (M^+-18), 480 (M^+-92), 419 (M^+-153), and 327 (M^+-153-92). These fragments were analogous to those observed with parasiloxanthin (1).

The nmr spectrum (90 MHz, $CDCl_3$) of (2) showed 10 methyl signals at δ 1.04 (C-1, C-1′ methyls, 6H), 1.08 (C-1, C-1′ methyls, 6H), 1.65 (C-5, C-5′ methyls, 6H), 1.86 (C-9, C-9′ methyls, 6H), 1.94 (C-13, C-13′ methyls, 6H), and methylene signal at 2.11 (C-7, C-8, C-7′, C-8′ methylenes, 8H). These chemical shifts were in good agreement with those of methyls (C-1′, C-1′, C-5′, C-9′, C-13′) and methylenes (C-7′, C-8′) of (1), and relative intensities of methyl signals at δ 1.04, 1.08, 1.65, 1.86, 1.94 and methylene signal at δ 2.11 of (2) showed twice those of methyl signals at δ 1.04 (C-1′), 1.07 (C-1′), 1.65 (C-5′), 1.85 (C-9′), 1.96 (C-13′) and methylene signal at δ 2.11 (C-7′, C-8′) of (1), respectively. This means that dihydroparasiloxanthin must be a symmetrical carotenoid.

Therefore, the structure of dihydroparasiloxanthin was concluded to be 3,3′-dihydroxy-7,8,7′,8′-tetrahydro-β-carotene (7,8-dihydroparasiloxanthin).

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