

A NEW CAROTENOID, HALOCYNTHIAXANTHIN FROM THE SEA SQUIRT, HALOCYNTHIA RORETZI

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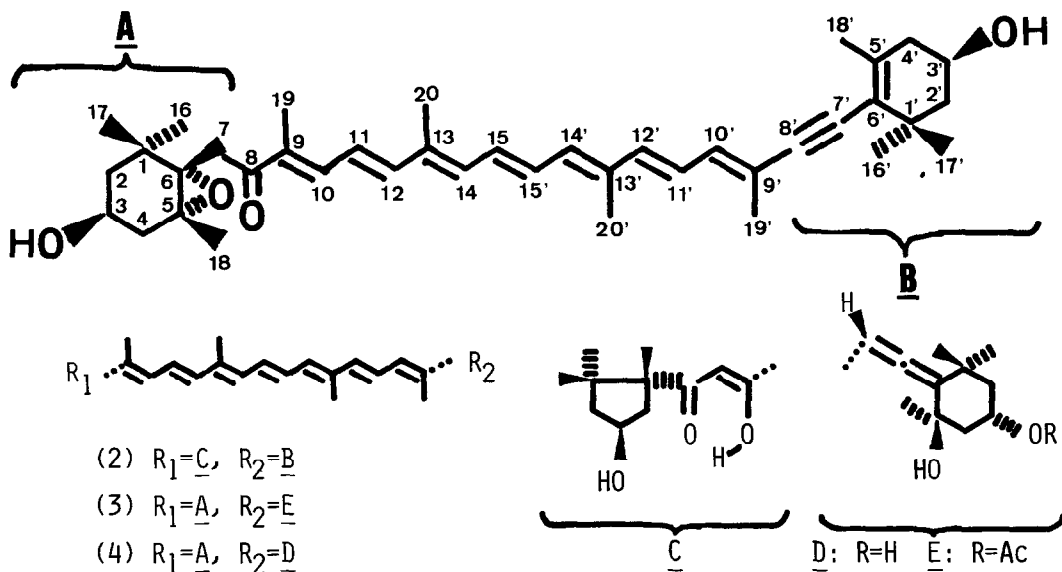
Summary: A new carotenoid, halocynthiaxanthin (5,6-epoxy-3,3'-dihydroxy-7',8'-didehydro-5,6,7,8-tetrahydro- β,β -caroten-8-one) has been isolated from the Japanese sea squirt, Halocynthia roretzi.

A new carotenoid, halocynthiaxanthin (1) was isolated as reddish needles (3 mg from 150 specimens), mp 158-160°C, $C_{40}H_{54}O_4$ (M^+ 598) from the sea squirt, Halocynthia roretzi along with mytiloxanthin (2), fucoxanthin (3), and fucoxanthinol (4). Its visible light absorption spectrum (ether) showed absorption maxima at (430), 452, 470 nm. The presence of two primary or secondary hydroxyl groups in (1) was demonstrated by acetylation and silylation, and the hydroxyl groups were not methylated with 0.01N-HCl methanol solution at room temperature¹. These facts indicated the presence of two primary or secondary hydroxyl groups at non-allylic position in (1). Iodine catalyzed stereomutation by light in p.e. solution was carried out by standard methods.² A hypsochromic shift (6 nm) proved the presence of one acetylenic end group. After treatment with ethereal hydrogen chloride, visible light absorption spectrum of (1) showed a hypsochromic shift of 25 nm. This indicates the presence of one rearrangeable epoxide end group. On sodium borohydride reduction, (1) gave a product with visible light absorption maxima at (405), 427, 454 nm (ether). The spectral changes on sodium borohydride reduction are consistent with the reduction of a single in-chain carbonyl and octaene chromophore. The infrared spectrum (KBr) of (1) showed distinctive absorption band at ν max 3350 (OH), 1645 (conj.C=O), and 2160 (weak, C \equiv C) cm^{-1} [no allene group, no unconjugated carbonyl group]. The mass spectrum of (1) showed abundant peaks at m/e 598 (M^+ , 45%), 582 (M^+-16 , 52), 580 (M^+-18 , 100), 565 ($M^+-18-15$, 20), 562 ($M^+-18-18$, 7), 506 (M^+-92 , 8), 490 ($M^+-92-16$, 20), and 488 ($M^+-92-18$, 15). The 80 MHz ¹H-NMR spectrum [δ (CDCl₃) 0.96 (s, 3H, 16-CH₃), 1.03 (s, 3H, 17-CH₃), 1.22 (s, 3H, 18-CH₃), 1.93 (s, 6H, 19- and 18'-CH₃), 1.20 (s, 3H, 16'-CH₃), 1.14 (s, 3H, 17'-CH₃), 1.99 (s, 9H, 20-, 20'- and 19'-CH₃), 2.59 and 3.66 (both d, 1H each, 7-CH₂, J=18Hz), 6.0-7.0 (m, 10H, olefinic-H)] confirms the presence of the epoxide end group A [the signals at δ 0.96, 1.03, 1.22, 1.93, 1.99, 2.59, and 3.66 agreed with those recorded for the half molecule of (3S,5R,6S,3'S,5'R,6'R)-fucoxanthin (3)³] and the acetylenic end group B (the signals at δ 1.20, 1.14, and 1.93 are similar to those recorded for C-16', C-17', C-18' methyl resonances of cynthiaxanthin⁴).

Consequently, the structure of halocynthiaxanthin was determined to be 5,6-epoxy-3,3'-dihydroxy-7',8'-didehydro-5,6,7,8-tetrahydro- β,β -caroten-8-one.

It is interesting from the biosynthetic point of view^{5,6,7} that this new carotenoid, halocynthiaxanthin is an intermediate of pathway⁸ from fucoxanthin (3) to mytiloxanthin (2) via fucoxanthinol (4).

From the biosynthetic point of view and the relative stereochemistry obtained from its ¹H-NMR measurement, the authors suggest the absolute configuration of halocynthiaxanthin as shown in (1).



References

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