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A NEW MARINE CAROTENOID, MYTILOXANTHINONE FROM THE SEA SQUIRT, HALOCYNTHIA RORETZI

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A new marine carotenoid, mytiloxanthinone (3,8'-dihydroxy-7,8-didehydro-β,κ-carotene-3',6'-dione) has been isolated from sea squirt, Halocynthia roretzi.

In the previous communication, we reported the isolation of a new carotenoid, halocynthiaxanthin from a sea squirt, Halocynthia roretzi ("Maboya" in Japanese).[1)] In the course of this investigation, another new marine carotenoid mytiloxanthinone (1), was isolated as reddish needles (5 mg from 1.8 Kg tunics, 100 specimens), $C_{40}H_{52}O_4$, mp 226-228°C (evacuated tube, corrected), by repeated preparative thin layer chromatography on silica gel G of acetone extract, along with fucoxanthin, fucoxanthinol, halocynthiaxanthin, mytiloxanthin (2), pectenolone and astaxanthin.

Astaxanthin has been reported as principal keto-carotenoid in the sea squirt, Halocynthia roretzi.[2)] In this experiment, the principal keto-carotenoid was not astaxanthin (5 %), but mytiloxanthinone (1) (10 %). 1 shows a remarkable lability toward base [10% KOH/MeOH (the usual saponification procedure of the carotenoid-esters]; therefore, it may have been overlooked till now.

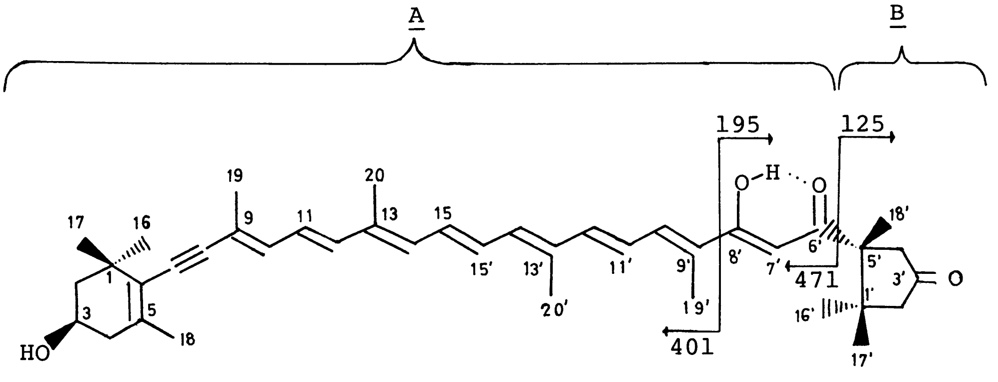
1 had λmax (petroleum ether) 474, (CS_2) 505, (benzene) 489, ($CHCl_3$) 485, (EtOH) 475, and (EtOH-KOH) 455 nm. On treatment of 1 with conc. HCl in ether, no blue coloration was observed (negative for epoxide test). Acetylation (Ac_2O/py) of 1 gave a monoacetate, trimethylsilylation [$(CH_3)_3SiCl/(CH_3)_3SiNHSi(CH_3)_3$] furnished a mono-TMS ether, and the hydroxyl group was not methylated with 0.01 N-HCl methanol solution at room temperature[3)]. These facts indicated the presence of one primary or secondary hydroxyl group in 1 at non-allylic position. The presence of a -C≡C- group in 1 was verified by the weak absorption at 2165 cm^{-1} in its IR (KBr) spectrum. The IR absorptions at 3390, 1610[4)], 1595, and 1588 cm^{-1} and ^1H-NMR signals at δ 5.90 (s,1H), 16.25 (s,1H)[4)] indicated the presence of enolic β-diketone group ($O{=}\underset{|}{C}{-}CH{=}C{\genfrac{}{}{0pt}{}{\diagup}{\diagdown OH}}$) in the molecule of 1. The ^1H-NMR spectrum exhibited methyl signals [δ ($CDCl_3$) 1.14 (s,3H,16-CH_3), 1.20 (s,3H,17-CH_3), 1.92 (s,3H, 18-CH_3), and 1.99 (s,12H,19-,20-,19'-, and 20'-CH_3)] due to the group A (The signals at δ 1.14, 1.20, 1.92, and 1.99 are very similar to those recorded for 16-, 17-, 18-, 19-, 20-, 19'-, and 20'-CH_3 resonances in the molecule of mytiloxanthin (2)[4)]). The MS spectrum of 1 showed m/e 596 (M^+,94%), 578 (M^+-18,100), 560 (M^+-18-18,16), 504 (M^+-92,6), 486 (M^+-92-18,3), 401 (M^+-195,8), and 195 (M^+-401,8).

The presence of the ions m/e 401 and 195 was attributed to the cleavage of the 8', 9' bond. Accordingly the presence of the structural moiety A in the molecule of mytiloxanthinone was established.

The IR (ν_{max} 1738 cm^{-1}), the MS [m/e 471 (M^+-125,2) and 125 (M^+-471,8)], and ^1H-NMR [δ ($CDCl_3$) 1.03 (s,3H,16'-CH_3), 1.22 (s,3H,17'-CH_3), and 1.34 (s,3H,18'-CH_3) (The signals at δ 1.03, 1.22, and 1.34 are similar to those recorded for the compound 3[5])] spectra revealed the presence of a cyclopentanone end group B.

The $NaBH_4$ reduction product of 1 exhibited the same vis. spectrum [λmax (ether) (405), 426, and 454 nm] as that of the compound 4 [the $NaBH_4$ reduction product obtained from mytiloxanthin (2)], and did not separate from 4 on mixed t.l.c.

On the basis of the accumulated evidences described above, the structure of mytiloxanthinone was determined to be 3,8'-dihydroxy-7,8-didehydro-β,κ-carotene-3',6'-dione (1). From the aforementioned results and biosynthetic point of view, it is suggested that the absolute configuration of mytiloxanthinone is visualized as shown in 1.



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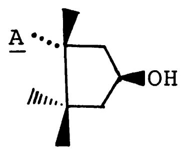

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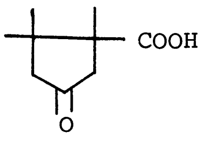

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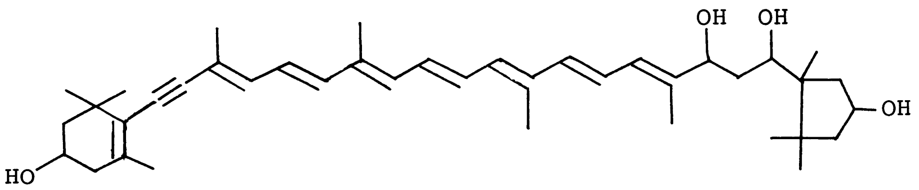

4

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