

A NOVEL MARINE CAROTENOID, MACTRAXANTHIN FROM THE JAPANESE EDIBLE SURF CLAM

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Summary: A new hexaol carotenoid, mactraxanthin [(3S,5S,6S,3'S,5'S,6'S)-5,6,5',6'-tetrahydro- $\beta,\beta$ -carotene-3,5,6,3',5',6'-hexaol] has been isolated from the Japanese edible surf clam, Mactra chinensis.

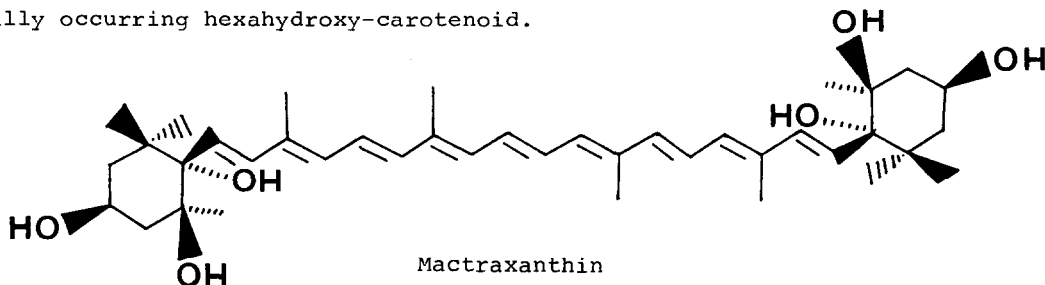
As a series of comparative biochemical studies of carotenoids from marine animals, recently our laboratory has reported the isolation of three new marine carotenoids, pectenol<sup>1</sup> (from the Japanese sea mussel), halocynthiaxanthin<sup>2</sup> (from the Japanese sea squirt), and mytiloxanthinone<sup>3</sup> (from the Japanese sea squirt). In this paper, the authors report the isolation of another novel marine carotenoid, mactraxanthin from the Japanese edible surf clam, Mactra chinensis.

A new hexaol carotenoid, mactraxanthin (major carotenoid) was isolated as deep orange needles (3 mg from 1000 specimens), m.p. 232-233 °C, C<sub>40</sub>H<sub>60</sub>O<sub>6</sub> (M<sup>+</sup> 636), along with fucoxanthin, zeaxanthin, and unidentified carotenoids. The VIS spectrum (ether) showed absorption maxima at (394), 416, 439, and 469 nm, indicating the presence of aliphatic nonaene chromophores, that is to say, suggesting the presence of two  $\epsilon$ -end groups or 5,6-dihydro- $\beta$ -end groups. The MS spectrum showed abundant peaks at m/z 636 (M<sup>+</sup>, 100%), 618 (M<sup>+</sup>-18, 10%), 600 (M<sup>+</sup>-36, 14%), 582 (M<sup>+</sup>-54, 7%), 564 (M<sup>+</sup>-72, 3%), 546 (M<sup>+</sup>-90, 2%), 544 (M<sup>+</sup>-92, 10%), 538 (M<sup>+</sup>-98, 6%), 528 (M<sup>+</sup>-108, 1%), 526 (M<sup>+</sup>-110, 5%), 508 (M<sup>+</sup>-128, 6%), 493 (M<sup>+</sup>-143, 2%), 465 (M<sup>+</sup>-171, 3%), 221 (homopyryllium, 28%), and 181 (furyllium, 31%). The MS spectrum contained typical fragment ion peaks (M<sup>+</sup>-143, M<sup>+</sup>-171, m/z 181, and 221) attributed to 3,5,6-trihydroxy- $\beta$ -end group as in heteroxanthin<sup>4</sup> [(3S,5S,6S,3'R)-7',8'-didehydro-5,6-dihydro- $\beta,\beta$ -carotene-3,5,6,3'-tetraol]. The fragment ion peak at M<sup>+</sup>-108 that indicated the presence of six hydroxy-groups was also observed. The IR spectrum showed no carbonyl, no allene, and no acetylenic groups. The <sup>1</sup>H NMR spectrum gave the signals (200 MHz, C<sub>5</sub>D<sub>5</sub>N, TMS) at  $\delta$  1.360 and 1.682 [s, 12H, H<sub>3</sub>C(16), H<sub>3</sub>C(16'), H<sub>3</sub>C(17), and H<sub>3</sub>C(17')], 1.748 [s, 6H, H<sub>3</sub>C(18) and H<sub>3</sub>C(18')], 2.007 [s, 12H, H<sub>3</sub>C(19), H<sub>3</sub>C(19'), H<sub>3</sub>C(20), and H<sub>3</sub>C(20')], 2.110 [d,d; J<sub>gem</sub>=12.5 Hz, J<sub>2,3</sub>=J<sub>2',3'</sub>=3.5 Hz, 2H, H<sub>ax.</sub>-C(2) and H<sub>ax.</sub>-C(2')], ca. 2.40-2.75 [m, 6H, H<sub>eq.</sub>-C(2), H<sub>eq.</sub>-C(2'), H<sub>2</sub>C(4), and H<sub>2</sub>C(4')], ca. 4.93 [m, 2H, H<sub>eq.</sub>-C(3) and

$H_{eq}$  - C(3')], and ca. 6.39–7.11 [m, 14H, olefinic-H]. The  $^1H$  NMR data revealed that mactraxanthin was a symmetrical carotenoid. The positions of six hydroxy-groups were determined to be located at C-3,5,6,3',5',6' by the  $^1H$  NMR data.

The CD spectrum [Ethanol, 20 °C,  $\lambda$  ( $\Delta\epsilon$ ); 328 (-1.1), 266 (-10.4), 230 (-0.2)] was closely similar in shapes and wavelengths to that of violaxanthin, (3S,5R,6S,3'S,5'R,6'S)-5,6,5',6'-diepoxy-5,6,5',6'-tetrahydro- $\beta,\beta$ -carotene-3,3'-diol, [Ethanol,  $\lambda$  ( $\Delta\epsilon$ ); 328 (+5.8), 266 (-29.4), 230 (+11.6)].<sup>5</sup> The CD results indicated same chirality at C-3,3' in violaxanthin (3S,3'S) and in mactraxanthin. The strong hydrogen bonding in the near-IR ( $\Delta\nu$  ca. 150)<sup>6</sup> spectrum revealed 3(3'),5(5')-cis-diol arrangement. The 5(5'),6(6')-diol was proved to be trans arrangement by no acetonide formation<sup>7</sup> and no hydrogen bonding of 1,2-cis-glycol.

Therefore, from the data described above, the absolute configuration of mactraxanthin was established to be (3S,5S,6S,3'S,5'S,6'S)-5,6,5',6'-tetrahydro- $\beta,\beta$ -carotene-3,5,6,3',5',6'-hexaol. This is the first report of a naturally occurring hexahydroxy-carotenoid.



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