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MYTILOXANTHIN AND ISOMYTILOXANTHIN, TWO NOVEL ACETYLENIC CAROTENOIDS

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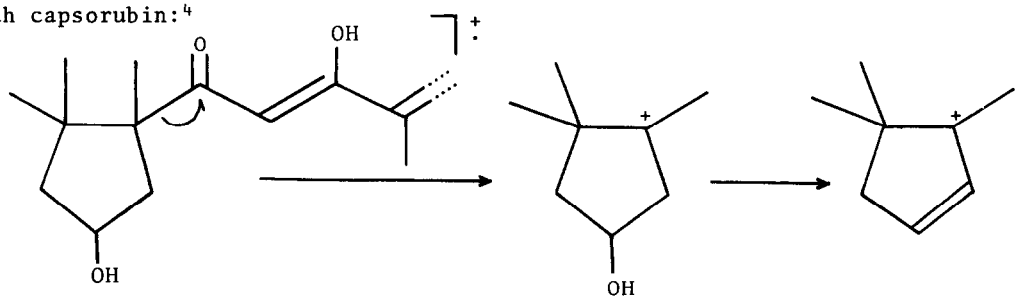
Two isomeric carotenoids, $C_{40}H_{54}O_4$, have been isolated from the edible mussel, Mytilus edulis, and are formulated as (1) and (2). The former is presumed to be identical with Sheer's mytiloxanthin from M. californianus.[1]

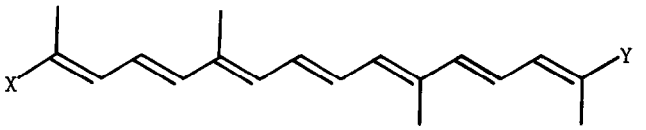
Both isomers are acetylenic (ν_{max} 2170 cm^{-1}), and have n.m.r. spectra which include bands (δ 1.14, 1.20, and 1.90) characteristic of the end group in alloxanthin (3). Both on reduction with sodium borohydride give a product with light absorption properties λ_{max}(EtOH) 455 and 428 nm, in good agreement with those predicted for a 7,8-acetylenic analogue of apo-8'-β-carotenol (4).[2]

Mytiloxanthin has m.p. 147°, λ_{max}(CS_2) 496, (PhH) 480, (EtOH) 470, and (EtOH-KOH) 455 nm, and is an enolic β-diketone, ν_{max} 1605 cm^{-1} (H-bonded C=O), δ 16.25 (enolic OH), 5.82 (CO.CH=COH). The n.m.r. spectrum includes an in-chain methyl band at δ 1.97, and also methyl bands at 0.85, 1.19 and 1.34 similar to those of capsorubin (5) (δ 0.94, 1.20, and 1.37).[3] The mass spectrum indicates the following transformations, analogous to those observed with capsorubin:[4]

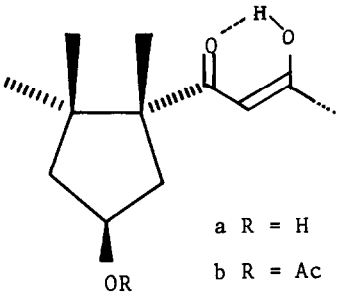


m/e 598.4014 m/e 127.1120 m/e 109.1012

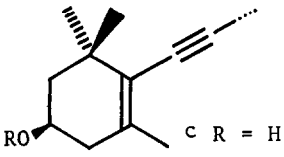
Cleavage of the 8,9 bond is significant giving the expected ions m/e 197.1168 and 401.2835.



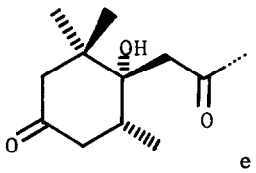
(1) X = a, Y = c
(2) X = e, Y = c
(3) X = Y = c
(4) X = CH_2OH, Y = g
(5) X = Y = f
(6) X = b, Y = d
(7) X = h, Y = d
(8) X = e, Y = d
(9) X = i, Y = c
(10) X = j, Y = c



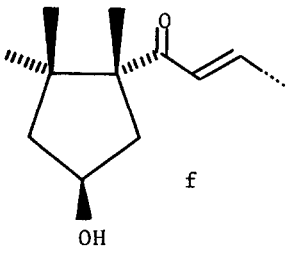
a R = H
b R = Ac



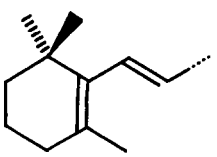
c R = H
d R = Ac



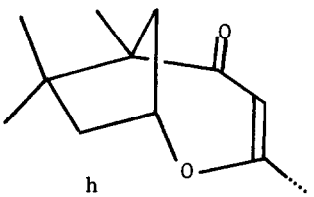
e



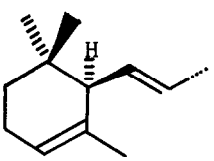
f



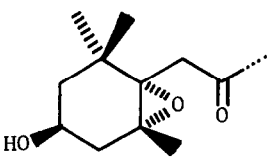
g



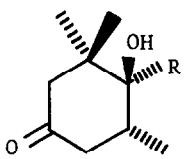
h



i



j



(11) R = CH_2.CHO
(12) R = CH_2.CO.Et
(13) R = H

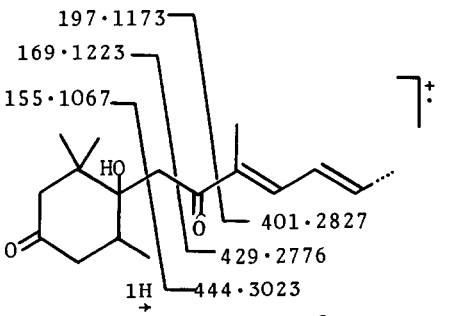
Acetylation (Ac_2O/py) of mytiloxanthin gives a diacetate, m.p.121° (δ 5.83, 16.28), with properties consistent with structure (6), and an anhydromonoacetate λ_{max} (PhH) 484 nm, as a minor by-product probably formed by intramolecular attack at C-3' by $-O^-$ at 8' (i.e. 7). The latter, unlike mytiloxanthin and its diacetate, is readily eluted from alumina and is therefore not pseudo-acidic.

Isomytiloxanthin has λ_{max} (CS_2) 504 and 476, (PhH) 486 and 459, (Hexane) 474 and 447, (EtOH) 452 nm; ν_{max} 1710 (unconjugated C=O), and 1640 cm^{-1} (conjugated C=O). Its ^{1}H-n.m.r. spectrum includes methyl bands at δ 0.98 (d, J = 6.5 Hz, 5'-Me), 1.09, 1.26 (1^{i}Me's), 1.94 (9'-Me), and 1.98 (9-, 13- and 13'-Me's); ^{13}C-n.m.r. δ(TMS) 201.0 (8'C=O), 208.6 (3'C=O). Acetylation gives a monoacetate with properties consistent with structure (8).

Treatment of isomytiloxanthin with alkali causes an irreversible bathochromic shift of 13 nm to λ_{max} (EtOH) 465 nm, which is attributed to dehydration of the β-hydroxy-ketone. Reduction of the product with sodium borohydride gives material with λ_{max} (EtOH) 472 (infl.) and 446 nm, suggesting that anionotropic rearrangement of the bisallylic alcohol formed initially occurs to give a chromophore identical with that of crocoxanthin (9) which has λ_{max} (EtOH) 477 and 447 nm.[5]

The mass spectrum of isomytiloxanthin contains a strong line at m/e 155 attributed to cleavage of the 6,7 bond. Charge retention on the other moiety with transfer of a hydrogen atom results in an ion at m/e 444. Cleavage on either side of the 8-ketone is also observed.

m/e 598·4014



(2)

Isomytiloxanthin acetate shows an analogous fragmentation pattern.

Reduction of isomytiloxanthin with lithium aluminium hydride gives a tetrahydr

derivative, $C_{40}H_{58}O_4$. Its mass spectrum includes lines at m/e 157.1225 ($C_9H_{17}O_2$) and 446.

The characteristic fragmentation of the 6,7 bond in isomytiloxanthin is paralleled in the model compounds (11) and (12). The stereochemistry of the models is assumed to be the same as that of the related alcohol (13). However, comparison of the ^{1}H-n.m.r. and ^{13}C-n.m.r. spectra of these compounds with those of isomytiloxanthin,[6] suggests that the carotenoid has the opposite relative configuration at 5,6.

The novel end groups of these two carotenoids may be biogenetically related to the epoxide end group (j) of the type present in fucoxanthin.[7] Pinacollic rearrangement of the epoxide (cf. capsorubin[3]) would then give the mytiloxanthin end group (a) whereas hydride (NADPH?) reduction of the epoxide and oxidation at C-3 would give the isomytiloxanthin end group (e). These routes predict relative stereochemistry consistent with the experimental results, and suggest the absolute configurations shown.

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