The Structure of the Acetylenic Dehydrogenation Product of Canthaxanthin

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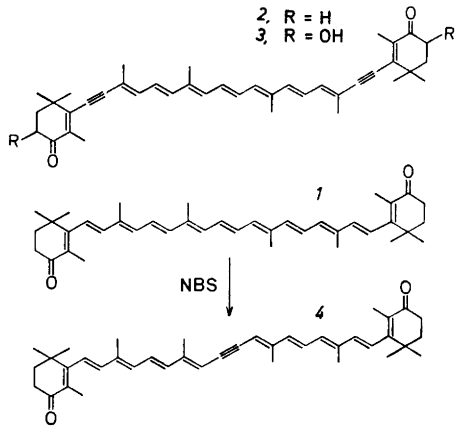
Some years ago Faigle and Karrer [1] reported on a remarkable acetylenic dehydrogenation product obtained in 21 % yield on treatment of canthaxanthin (*1*) with *N*-bromosuccinimide. At a time when proton magnetic resonance and mass spectrometry were not yet available the product was characterized as bisdehydrocanthaxanthin (*2*), the 7,8,7′,8′-positions being preferred for the acetylenic bonds.[1]

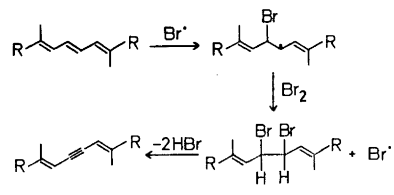


More recently structure *3* has been assigned to "asterinsäure" isolated from starfish.[2,3] The disagreement in visible light absorption properties between *3* and the NBS-dehydrogenation product called for a reinvestigation of the latter by modern spectrometric methods. It has now been demonstrated that the dehydrogenation product previously obtained [1] is pure monoacetylenic 15,15′-didehydrocanthaxanthin (*4*).

The IR-spectra (KBr) of the dehydrogenation product and canthaxanthin (*1*) were virtually identical, *cf.* Ref. 4, indicating that any acetylenic bonds were in a more remote position from the carbonyl groups than in *2*.[5,2] The bathochromic shift of the visible light absorption spectrum of the dehydrogenation product relative to canthaxanthin [2] (*1*) provided further supporting evidence. The mass spectrum (Fig. 1) had its molecular ion peak at *m/e* 562, demonstrating the presence of no more than one acetylenic bond. M−92 and M−158 ions, characteristic of the majority of carotenoids [6,7] were absent, but M−90 and M−156 ions were observed. An M−90 peak has previously been observed in carotenoids with a centrally located triple bond.[8] Peaks associated with in-chain and end group cleavages as indicated in Fig. 1 were further in support of structure *4*. The PMR-spectrum (Fig. 2) was fully consistent with this assignment with characteristic signals ($CDCl_3$) of the in-chain methyl groups at τ 7.88 (2 Me) and 8.00 (2 Me); *cf.* Ref. 9.

Authentic 15,15′-didehydrocanthaxanthin (*4*), prepared by total synthesis [10] was finally directly compared with the NBS-dehydrogenation product of canthaxanthin (*1*). Visible light,[1,10] IR, PMR, and mass spectra as well as chromatographic properties (R_F = 0.80 on kieselgur paper,[11] 10 % acetone in petroleum ether) were in complete agreement. A mixed melting point determination of totally synthetic *4* (found m.p. 195°C, reported 187−188°C [10]) and the dehydrogenation product (found m.p. 201°C, reported 201−202°C [1]) gave no depression (195−196°C).

The mechanism of the NBS-reaction has recently been discussed.[12] Generally the initial step is allylic bromination by a radical mechanism. In the case of canthaxanthin (*1*) the keto groups may prevent allylic bromination of the rings. The result could possibly be explained by Scheme 1. Whereas polar addition of bromine leads



Scheme 1

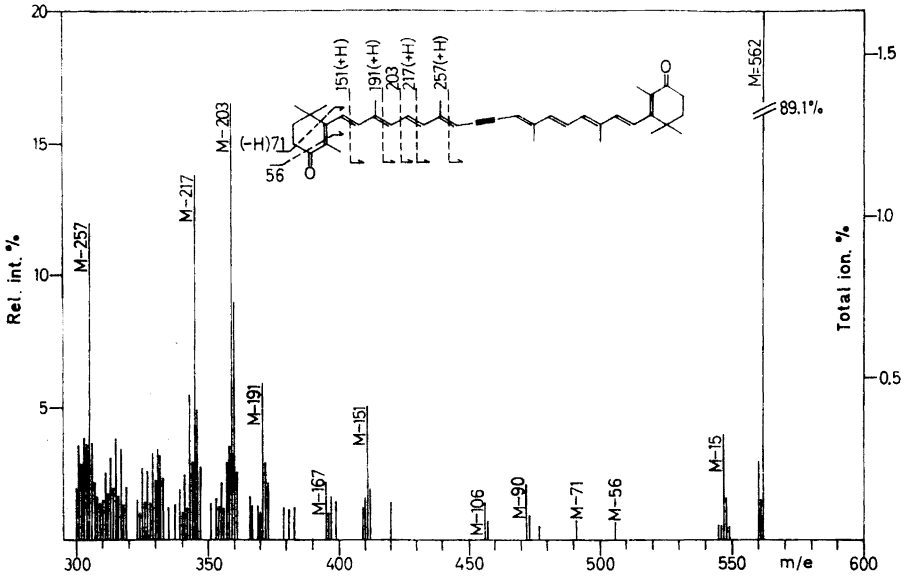


Fig. 1. Mass spectrum of 15,15′-didehydrocanthaxanthin (*4*) prepared by NBS-dehydrogenation of canthaxanthin (*1*).

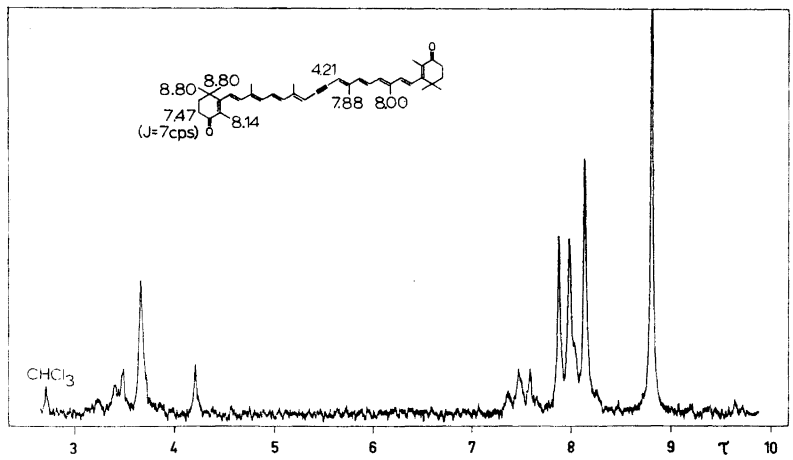


Fig. 2. Proton magnetic resonance spectrum ($CDCl_3$) of 15,15′-didehydrocanthaxanthin (4) prepared by NBS-dehydrogenation of canthaxanthin (*1*).

exclusively to *trans* dibromides,[13] addition by a radical mechanism could conceivably in part lead to a *cis* dibromide which by subsequent *trans* elimination of hydrogen bromide would result in the formation of the acetylenic bond.

Reasoning along similar lines was used by Faigle and Karrer.[1] Addition to the central position may be preferred for steric reasons.

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Animal Carotenoids

5.* The Carotenoids of Some *Anthozoa*

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Lower marine animals have offered interesting carotenoid chemistry. Thus acetylenic [1-4] and allenic [5] carotenoids and nor-carotenoids with ring contraction [6] have been isolated from marine invertebrates in recent years. Only few species of the class *Anthozoa* (phylum *Coelenterata*, subphylum *Cnidaria*), comprising sea anemones, sea pens, sea fans, and true corals, have so far been studied with respect to their carotenoids.[6-10] We now report on the carotenoid composition of some corals and sea anemones from Norwegian waters.

The corneous coral *Paragorgia arborea* (Linné) (610 g wet weight), Aasenfjord, October 1968, contained 0.002 % carotenoids of the acetone-extracted residue. Astaxanthin (*1*), isolated as astacene (*2*) after standard saponification, chromatography on cellulose columns and crystallization [11] was the single carotenoid. The identification was based on absorption spectrum in visible light, R_F-value, co-chromatography with authentic material, IR spectrum, and mass spectrum.

Another corneous coral *Primnoa resedaeformis* (Gunnerus) (530 g wet weight), source as above, contained 0.004 % carotenoids of the acetone-extracted residue. Astaxanthin (*1*), isolated as astacene (*2*), and identified on the basis of the above criteria and melting point, was the single carotenoid.

The stony coral *Lophelia pertusa* (Linné), above source, contained 0.0004 % carotenoids of the acetone-extracted residue (260 g). Astaxanthin (*1*) was the single carotenoid and was isolated as astacene (*2*) and identified by the above criteria.

Astacene (*2*), in each case crystallized from acetone-petroleum ether, had m.p. 215–216°C (reported 228°C),[12] $R_F = 0.68$ on kieselgur paper (10 % acetone in petroleum ether), λ_{max} (acetone) 472 nm (rounded spectrum), characteristic ν_{max} (KBr) 3400 (OH); 2920 (CH); 1620, 1535, 1250 and

* Part 4. *Acta Chem. Scand.* **24** (1970) 3050.