

exclusively to *trans* dibromides,<sup>13</sup> 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.<sup>1</sup> 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<sup>1-4</sup> and allenic<sup>5</sup> carotenoids and nor-carotenoids with ring contraction<sup>6</sup> 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.<sup>6-10</sup> We now report on the carotenoid composition of some corals and sea anemones from Norwegian waters.

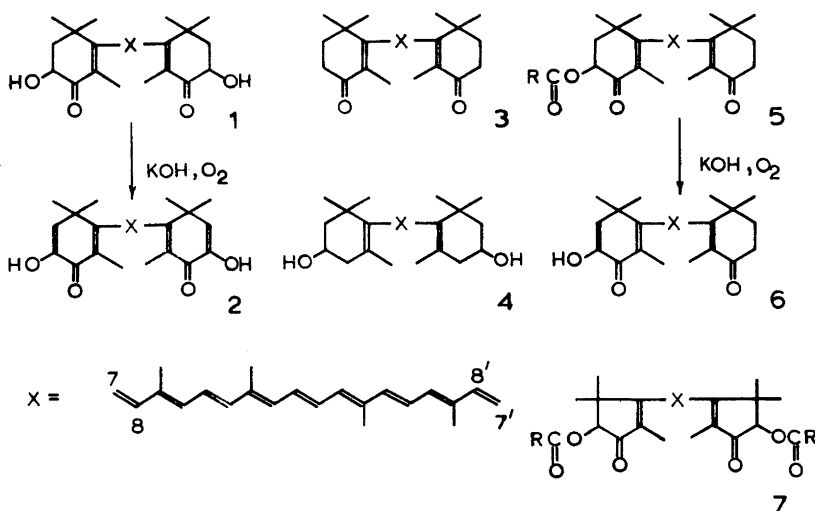
The corneous coral *Paragorgia arborea* (Linné) (610 g wet weight), Aasenfjord, October 1968, contained 0.002 % carotenoids of the acetone-extracted residue. Astaxanthin (1), isolated as astacene (2) after standard saponification, chromatography on cellulose columns and crystallization<sup>11</sup> was the single carotenoid. The identification was based on absorption spectrum in visible light,  $R_F$ -value, cochromatography 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),<sup>12</sup>  $R_F=0.68$  on kieselgur paper (10 % acetone in petroleum ether),  $\lambda_{\max}$  (acetone) 472 nm (rounded spectrum), characteristic  $\nu_{\max}$  (KBr) 3400 (OH); 2920 (CH); 1620, 1535, 1250 and

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



1060 (diosphenol); 1380, 1365 (*gem.* methyl) and 970 (*trans* disubst. double bond)  $\text{cm}^{-1}$  and *m/e* 592 (M), M-92, M-106, *m/e* 137, 152<sup>13</sup> in complete agreement with the properties of synthetic astacene (gift from Hoffmann-La Roche, Basel).

Preliminary studies on two other corals are also reported:

The corneous coral *Paramuricea* sp. (Kölliker), Aasenfjorden 1968, contained 0.0046% carotenoids of the acetone-extracted residue. Canthaxanthin (3) was the major component; zeaxanthin (4) was present and astaxanthin (1) was tentatively identified.

The soft coral *Alcyonium digitatum* (Linné) (980 g wet weight), Borgenfjord, July 1968, contained 2.7 mg carotenoids. Astaxanthin (1) was the major carotenoid besides the 7,8-didehydro and 7,8,7',8'-tetradidehydro derivative, previously encountered in the starfish *Asterias rubens* (Linné), and minor yellow components.

The results indicate that astaxanthin (1) is a characteristic carotenoid of several corals; the acetylenic derivatives being less abundant.

Sea anemones such as *Actinia equina* (Linné) are known to contain actinioerythrin (7 = 2,2'-bisnorastaxanthin diester) as the characteristic carotenoid, which is considered to be biosynthetically related to astaxanthin (1).<sup>14</sup> Preliminary results on some other sea anemones are now reported:

Actinioerythrin (7) was also encountered in *Bolocera tuediae* (Johnston) (Korsfjorden, October 1968), carotenoid content 0.01% of acetone-extracted residue) together with astaxanthin (1) esters.

From *Actinostola callosa* (Verrill) (same source, carotenoid content 0.007% of acetone extracted residue) astaxanthin (1) esters only were isolated.

*Metridium senile* (Linné), Korsfjorden, September 1968, contained 0.006% carotenoids of the acetone-extracted residue. Traces of canthaxanthin (3) and zeaxanthin (4) together with astaxanthin (1) esters (isolated as astacene (2)) were present. The major component was after saponification spectroscopically (visible light) identical with astacene (2) but less strongly adsorbed, possibly 5, which may be identical with metridin.<sup>9,10</sup> The naturally occurring ester is in case an adonirubin<sup>15</sup> = phoenicoxanthin<sup>16</sup> (6) ester.

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*cera tuediae* (Jan Olafsen) and *Actinostola callosa* (Grethe Kubberød).

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## Fluoroalcohols

### Part 13.<sup>1</sup> Solid-liquid Phase Equilibria of the System Hexafluoro-2-propanol—Water

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In Part 5 of this series, we reported<sup>2</sup> results of a study of the vapour-liquid equilibria in mixtures of 1,1,1,3,3,3-hexafluoro-2-propanol (HFP) and water. These mixtures were found to behave exceptionally; the liquid curves had a plateau at low alcohol contents, and the plot of the logarithm of the activity coefficient of HFP against mole fraction had a minimum and that for water a maximum when  $x_{\text{HFP}}$  was about 0.4. Thus it was thought worthwhile to study also the cryoscopic behaviour of the mixtures.

HFP was purified as previously.<sup>3</sup> Each sample (about 10 ml) was frozen in a large test tube while being mixed with a propeller. The sample tube was in a larger test tube with an air space between the inner and the outer tube which was immersed in a cold bath consisting of alcohol and dry ice. The temperature was read from a calibrated mercury thermometer. The differences between the maximum and minimum temperatures on cooling curves for each HFP-water mixture were plotted against the maximum temperatures and the melting point was obtained by extrapolation to zero difference as proposed by Hoare.<sup>4</sup>

The results are plotted in Fig. 1. It is seen that addition of HFP to water decreases the melting point relatively rapidly until the content of HFP is about 3 mole %. In this region also the boiling point decreases rapidly<sup>2</sup> and the molar volume of HFP passes through a deep minimum.<sup>3</sup> Between 3 and 17 mole % of HFP, the decrease of the melting point is smaller; this region corresponds to the plateau in the isobaric vapour-liquid diagrams.<sup>2</sup> In this region the viscosity and energy of activation of viscous flow for the liquid are maxima.<sup>3</sup> The eutectic curve has an inflexion point in the region where the plateau in the vapour-liquid plot begins. A cooling curve of the same type has been