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Animal Carotenoids

2.* Actinioerythrin and Related Compounds — Novel Nor-carotenoids with Ring Contraction

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Actinioerythrin, first isolated by Lederer [1] in 1933 from the sea anemone *Actinia equina* has only been partly characterized.[1-3] Following alkali treatment this red pigment was converted to the blue-coloured violerythrin.[2] It has been questioned whether these compounds belong to the carotenoid series.[4]

We now conclude that actinioerythrin is a 2,2'-bis-nor-astaxanthin diester (*1*) and violerythrin the corresponding tetraketone (*2*), the extraordinary light absorption properties of the latter being caused by the conjugated cyclopentenedione rings. Simple cyclopent-3-en-1,2-dione derivatives are yellow compounds.[5,6]

Actinioerythrin, m.p. 91°C, λ_{max} 505 and (536) mμ (all visible light absorption maxima refer to acetone solutions), ν_{max} (KBr disc) 1740, 1695, 1528 cm^{-1}; τ 7.97 (4 Me), 8.08 (2 Me), 8.57 (2 Me), and 8.83 (2 Me), methyl signals only are quoted; M > 800, gave a mono- and dioxime, no product under conditions for acetal formation and no product with *o*-phenylenediamine, acetylating, silylating, or methylating reagents. Sodium borohydride reduction furnished a mono-ol (*3*), a diol (*4*), a triol (*5*), and a tetraol (*6*, 3 *trans* stereoisomers). The mono-ol (*3*, λ_{max} 489 and (525) mμ) gave a monoacetate and was oxidized with air in the presence of iodine [7] (subsequent oxidations refer to this method) to actinioerythrin (*1*). The diol (*4*, λ_{max} (444), 470 and 499 mμ) gave a mono- and a diacetate and was oxidized to the mono-ol (*3*) and actinioerythrin (*1*). Both the diol (*4*) and the triol (*5*, λ_{max} (444), 470 and 499 mμ) on further treatment with lithium aluminium hydride or alkali were transformed to the tetraol (*6*). The triol (*5*) furnished on oxidation two products more polar than

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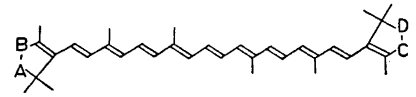
actinioerythrin (*1*), *7* (λ_{max} 489 and (525) mμ) and *8* (λ_{max} 504 mμ). Product *8* provided a monoacetate. The tetraol (*6*, λ_{max} (444), 470 and 499 mμ, M=472 corresponding to $C_{38}H_{72}O_4$), containing according to its R_F-value, acetylation, and silylation evidence four hydroxy groups, on oxidation provided actinioerythrol (*9*, λ_{max} 504 and (535) mμ), a diol according to acetylation evidence. In contrast to violerythrin below, actinioerythrol (*9*) reacted only slowly, and then differently, with *o*-phenylenediamine.

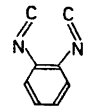
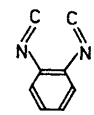
Actinioerythrin (*1*) on treatment with strong alkali in the absence of oxygen gave a dark blue compound, considered to be the alkali salt of the tetra-enolate,[8] subsequently converted to violerythrin (*2*) on access to oxygen. Alternatively careful alkali treatment of actinioerythrin (*1*) according to the method of Heilbron *et al.*[2] gave hypophasic products, which in the presence of oxygen on acidification provided the epiphasic, blue violerythrin (*2*), m.p. 236–238°C, λ_{max} 554 mμ, ν_{max} 1750, 1680, 1520 cm^{-1}. Violerythrin (*2*) could not be acetylated, silylated, or methylated. Absence of rapid acetal formation precluded aldehyde groupings. Treatment with *o*-phenylenediamine gave smooth formation of a mono- and bisquinoxaline derivative (*10*, λ_{max} 530 and (565) mμ, M=708, corresponding to $C_{50}H_{52}N_4$). A corresponding reaction has been reported for simple cyclopent-3-en-1,2-dione derivatives.[5,6]

Borohydride reduction of violerythrin (*2*) gave the intermediate diol actinioerythrol (*9*), the diacetate of which had M=652, corresponding to $C_{42}H_{52}O_6$. The diol *9* on alkali treatment in the presence of air autoxidized to the triketone *11* (λ_{max} 530 mμ) and violerythrin (*2*). Complete reduction of violerythrin (*2*) gave the tetraol *6* (3 *trans* stereoisomers).

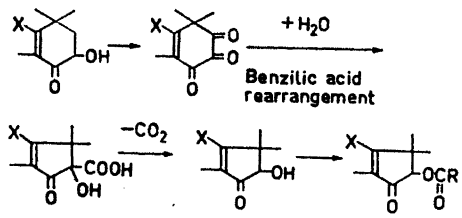
The visible light absorption spectrum reflects the planarity of the undecaene chromophore — the trimethylcyclopentene ring being better conjugated with the aliphatic polyene chain than the common 1,1,5-trimethylcyclohexene ring.[9] The observed carbonyl frequencies of the IR spectra are compatible with published data.[6,10] The methyl signals of the NMR-spectrum support a symmetrical molecule; 4 in-chain methyl groups (7.97 τ) and 2 end-of-chain ring methyl groups adjacent to the 4,4′-carbonyl groups (8.06 τ) are in accordance with previous findings,[11] and the 8.57, 8.83 τ signals are in likely positions for the *gem.* methyl groups on the cyclopentenedione rings.

The remarkable colour shift of the blue violerythrin (*2*) on treatment with weak alkali to yellow products, partly revertible to violerythrin on acidification will be discussed elsewhere.



	A	B	C	D
1	CHOCR (=O)	C=O	C=O	CHOCR′ (=O)
2	C=O	C=O	C=O	C=O
3	CHOCR (=O)	C=O	CHOH	CHOCR′ (=O)
4	CHOCR (=O)	CHOH	CHOH	CHOCR′ (=O)
5	CHOCR (=O)	CHOH	CHOH	CHOH
6	CHOH	CHOH	CHOH	CHOH
7	CHOCR (=O)	C=O	CHOH	CHOH
8	CHOCR (=O)	C=O	C=O	CHOH
9	CHOH	C=O	C=O	CHOH
10				
11	CHOH	C=O	C=O	C=O

It is suggested that actinioerythrin (*1*) is formed *in vivo* from astaxanthin as follows:



X: polyene chain

Support for this hypothesis is derived from the presence in *Actinia equina* of minor carotenoids containing 6-membered rings, one of which giving rise to astacene on alkali treatment.

Actinioerythrin (*1*) and violerythrin (*2*) are the first examples of bis-nor-carotenoids with ring contraction. Further details will be published.[12]

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