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THE STRUCTURE OF SIPHONAXANTHIN

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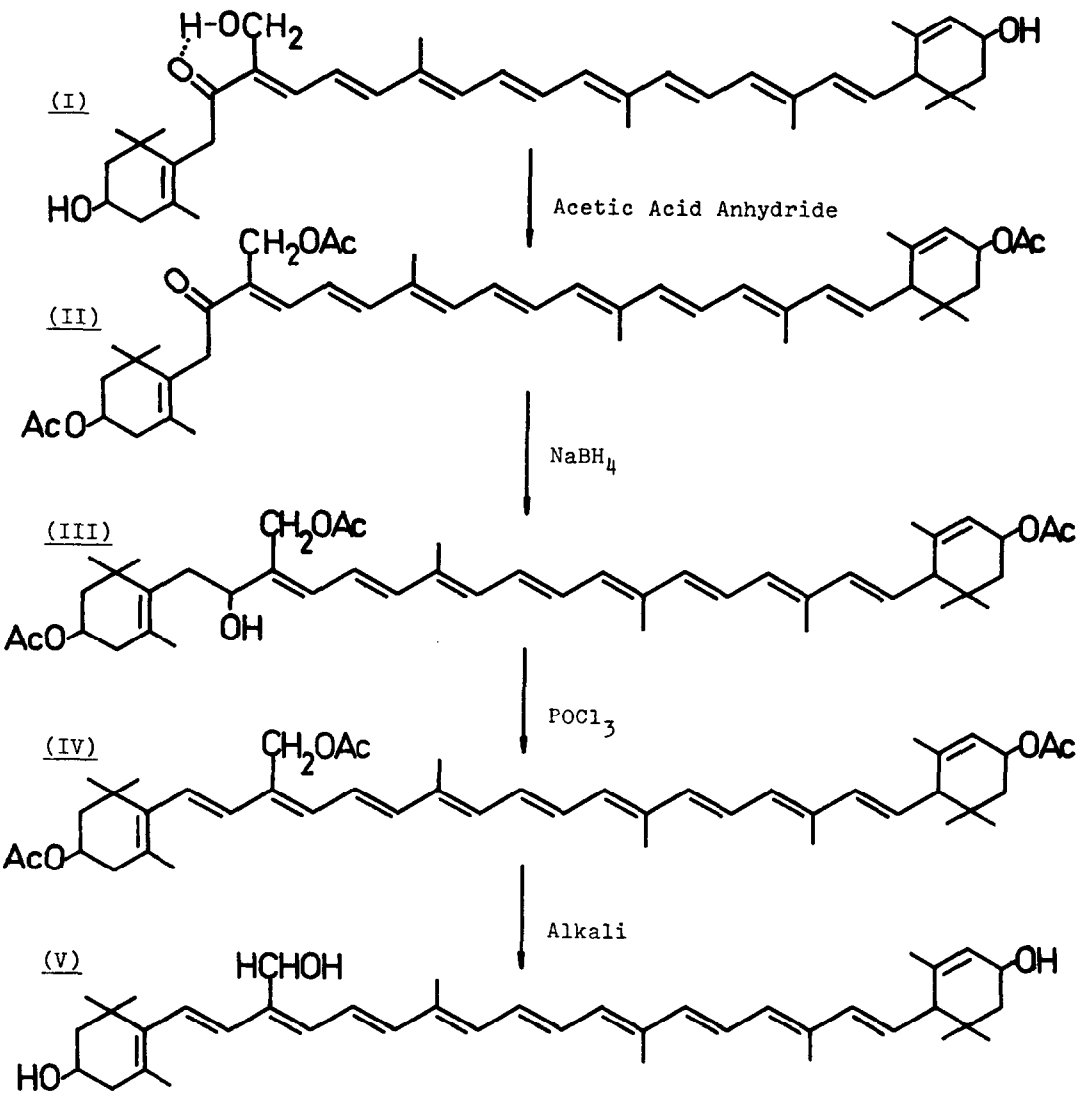
The carotenoids siphonaxanthin and siphonein were first detected by Strain[1,2] in some siphonous green algae. Preliminary structure formulae have been proposed[3] and a detailed survey of the natural distribution of these pigments was given[4]. In the present study the structure of siphonaxanthin was established by the conversion of the pigment into loroxanthin which has been isolated recently from green algae[5].

In a previous publication[3] we have not been able to determine the exact position of the primary hydroxyl group. There are three possible positions, namely, on the methyl groups at C1, C5 or C9. The probability of a C9 position is evident from sterical consideration of the hydrogen bond of this hydroxyl to the carbonyl group[3]. Using a Dreiding molecular model, the distance from this hydroxyl oxygen to the carbonyl oxygen was found to be about 2.5 Å. Structure I could now be confirmed by some typical reactions of siphonaxanthin (I). Attempts to eliminate the carbonyl function by dehydration of the reduced derivative with $POCl_3$ (according to ref. 6) were successful.


(I)
H-OCH2
O
OH
HO
Acetic Acid Anhydride
(II)
CH2OAc
OAc
AcO
NaBH4
(III)
CH2OAc
OAc
AcO
OH
POCl3
(IV)
CH2OAc
OAc
AcO
Alkali
(V)
HCHOH
OH
HO

The free hydroxyls were masked before the reduction by esterification with acetic acid anhydride (II). The resulting compound IV is then easily converted into loroxanthin (V) by saponification. The identification of V with loroxanthin (isolated from Cladophora spec.) was checked by comparison of the absorption spectra and by cochromatography of the free pigments, of the acetates, and of the allylic ethyl ethers (formation of the ethers according to ref.7). Partition chromatography[8] and chromatography on basic magnesium carbonate layers which separate isomeric carotenoids[9] were used. No differences in the chromatographic behaviour of the corresponding derivatives could be detected. The absorption spectra of compound V and loroxanthin are identical (maxima at 473 and 446 nm, shoulder at 425 nm; solvent ethanol).

Structure I for siphonaxanthin is also supported by the formation of an allylic diether with 0.01 N methanolic HCl when held at 40°C for 30 min. This indicates two allylic hydroxyl groups and excludes the position of the primary hydroxyl at a methyl group at C1.

With respect to the position of the carbonyl function of siphonaxanthin (I) there exists a remarkable similarity to fucoxanthin[10]. However, no allene group is present in siphonaxanthin as is inferred from the IR spectrum (no absorption at 1935 cm^{-1}; compare ref. 11).

Siphonein is an ester of siphonaxanthin characterized by the esterification of the primary hydroxyl group with a fatty acid[3].

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