(30 min). The mixture was heated at 75° for 2 h to complete the reaction. The toluene was then filtered off (N_2-atm.) and 150 ml of tetrahydrofuran (dried and distilled over $LiAlH_4$) was added. The resulting solution (partly suspension) of indenylsodium was used in the preparation of deuterated indenes.

1,3-Dideutero-indene (III). The solution of indenylsodium prepared from trideuterated indene (11.9 g), was poured in a thin stream into excess water (ice-cooling, stirring). The reaction mixture was acidified with acetic acid a few seconds after the addition of indenylsodium. (Alternatively, the indenylsodium solution may be added to dilute acetic acid). The product was extracted with ether, the ether dried with $MgSO_4$ and evaporated in vacuum. Fractionation of the residue in vacuum (10 mm Hg, N_2-atm.) gave 6.5 g of the dideuterated indene (III).

1-Deutero-indene (I). This substance was prepared in the same way as (III) by adding the solution of indenylsodium (from ordinary indene) to excess D_2O.

The NMR-spectra were recorded with a Varian A-60 high resolution spectrometer. The kinetic runs were made at 30°C with 2 M indene concentration. Pyridine was used as a solvent and triethylamine as a catalyst.

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Algal Carotenoids

IV. On the Structure of Fucoxanthin

ARNE JENSEN

Norwegian Institute of Seaweed Research, N.T.H., Trondheim, Norway

Evidence for the chemical constitution of fucoxanthin has been presented [1-6] which allows a formula (I) to be proposed as a reasonable working hypothesis.

This structure is based on the assumption that fucoxanthin is closely related to the other carotenoids of brown algae, especially to violaxanthin (3,3′-dihydroxy-5,6,5′,6′-diepoxy-β-carotene), all of which are bicyclic. Considered together, the results of oxidative degradation,[3,7] the presence of two tertiary hydroxy groups and the NMR-evidence (methyl peaks at τ-values: 9.03 (3H), 8.98 (3H), 8.94 (3H), 8.78 (3H), 8.66 (3H), 8.62 (3H), 8.19 (3H), 8.08 (3H), 8.02 (6H) and 7.97 (3H); no isopropylene methyls) revealed the presence of at least one cyclic end-group, and are best accounted for by a bicyclic structure of the pigment. The chromophore of fucoxanthin (λ_{max} 449 mμ) requires the equivalent of 8 C=C and 1 C=O, all of which must be conjugated in an aliphatic system.[5] The moderate fine-structure of the spectrum together with the normal shift (25 mμ) in absorption maximum upon reduction of the conjugated keto group indicates that the chromophore is not cross-conjugated.

If the allene grouping [2,3] of fucoxanthin is to be accommodated in a bicyclic carotenoid structure, it has to be placed at one end of the active chromophore, and in ω-position to the conjugated carbonyl group. The relatively high stability of the allene group is best accounted for if it is placed in an exocyclic position as shown in structure I.

The structural formula suggested requires an uptake of 9 moles of hydrogen upon catalytic hydrogenation. Karrer, Helfenstein, Wehrli, Pieper and Morf [7] reported the absorption of 10 moles when acetic acid was used as solvent. Heilbron and Phipers [8] managed to remove four of the six oxygen atoms of fucoxanthin by hydrogenation in moderately forcing conditions. Thus hydrogenolysis may easily take place.

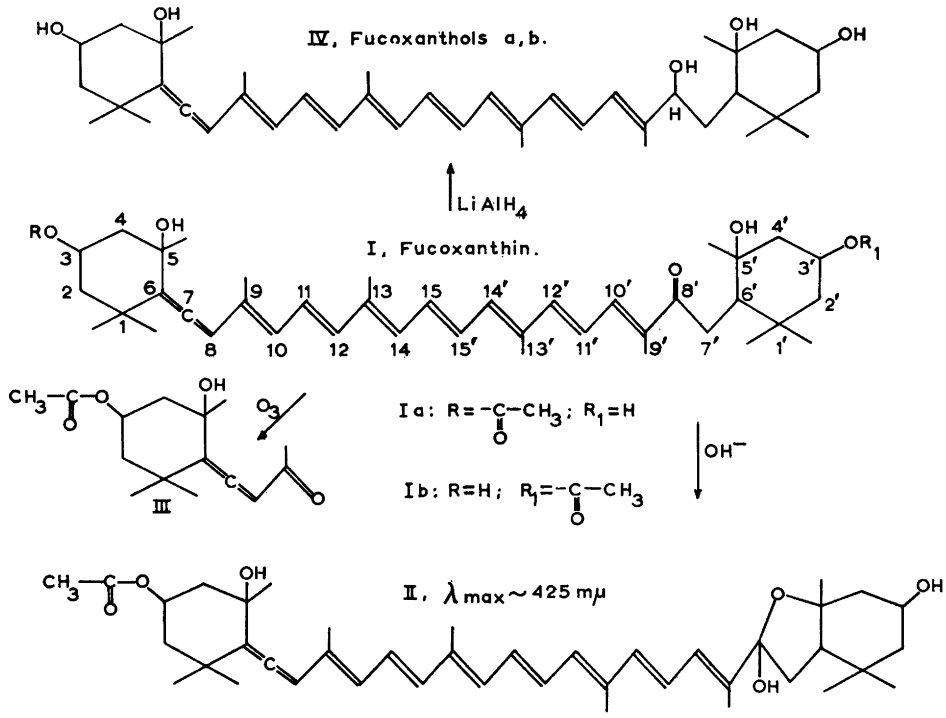

Fig. 1.

We repeated the catalytic hydrogenation using milder conditions. With ethyl acetate as solvent, fucoxanthin (m.p. 159°C, $E^{1\%}_{1cm}$ = 1610) absorbed between 8 and 9 moles of hydrogen (Adam's catalyst). This is in accordance with the number of olefinic protons (10—12) found in the NMR-spectrum of fucoxanthin. The semicrystalline, colourless oil obtained after chromatography of perhydrofucoxanthin on aluminium oxide gave two bands in the carbonyl region of the infrared spectrum (at 1740 and 1725 cm^{-1}). Saponification resulted in the loss of the 1740 (and 1250) cm^{-1} peaks. Hydrogenolysis of the acetoxy group had therefore not taken place during hydrogenation. This indicates a non-allylic nature of this group.

Fucoxanthol b [5] was not attacked by periodate in conditions which usually give quantitative oxidation of *vic-cis*-glycols.[9] Moreover, all the eleven methyl groups of fucoxanthin seem to be located on fully substituted carbon atoms (no coupling of methyl signals with protons in α-position in the NMR-spectrum). Comparison of the NMR-spectra of fucoxanthin and its reduction product ($LiAlH_4$) showed that the methyl signal of the acetoxy group (7.97 τ) disappeared and that the signal at 8.08 (tentatively assigned to the methyl group in 9′-position) moved to 8.15 upon reduction. These observations are compatible with the structures given in Fig. 1.

Further support for the structure (I) suggested was obtained by ozonization of fucoxanthin benzoate, prepared by treatment of fucoxanthin with benzoyl chloride in pyridine at room temperature over-night. Ozonization at −70°C and cleavage of the ozonides with boiling water gave a yellow oil. From the neutral fraction of this it was possible to isolate, after repeated chromatography on aluminium oxide, magnesium oxide and calcium oxide, some 20 mg (from 250 mg of fucoxanthin benzoate, $E^{1\%}_{1cm}$ = 1440) of a slightly yellow oil. The product showed

spectroscopic properties indicative of structure III (λ_{max} 215, 282 mμ: ν_{max} 3450 (OH and overtone of C=O), 1955 (−C=C=C−), 1730 (ester C=O), 1675 (conj. C=O), 1605 (−C=C−C=O), 1455 (CH_2), 1365 (broad $-CH_3$ >$C(CH_3)_2$), 1240 (ester −C−O−C−), 1160 (tert. OH), 1070 (−C=C=C−), 1025 (−C−O−C− in carotenoid acetates), 850 (>C=CH−C−) and 820 cm^{-1} (>$C(CH_3)_2$); τ-values 8.85 (3H), 8.58 (6H), 7.97 (3H), 7.91 (3H) and 4.29 (1H)). The above data rule out the presence of any aromatic ester in product III, and show that the acetoxy function and the allene group of fucoxanthin belong to the same end of the molecule. The acetoxy group therefore seems to be located in the 3-position rather than in the 3′-position, and fucoxanthin should probably be represented by structure Ia. It should be mentioned that the choice of the 3,3′-positions for the acetoxy and the secondary hydroxy group is based on the substitution pattern commonly found in algal carotenoids, and is in accordance with the results of the oxidative degradation of fucoxanthin.[7]

The observation of Stene Sørensen reported by Liaaen and Sørensen [2] that fucoxanthin, upon treatment with weak base, gave, among several products, a pigment with λ_{max} = 425 mμ which had lost the infrared absorption band at 1660 but retained the one at 1735 cm^{-1}, may be explained by assuming a semi-acetal formation (II).

The characteristic blue colour-reaction given by fucoxanthin with strong hydrochloric acid may be explained by rearrangement of Ia to produce furanoid rings at one or both ends.

According to the structure given in Ia, the fucoxanthols obtained by reduction of fucoxanthin with lithium aluminium hydride must be C_8' epimers (IV).

The structure Ia corresponds to $C_{42}H_{58}O_6$ which requires C 76.55; H 8.88 and O 14.57 %. Willstätter and Page [10] reported C 76.39 and H 8.77 % (C 76.17−76.55 and H 8.61−9.03) for highly purified samples. Torto and Weedon [3] obtained 14.9 % oxygen by direct determination. The revised formula Ia is therefore in good agreement with analytical data obtained for fucoxanthin. In fact, all the data presented above are in full accord with the structure (Ia) suggested for the pigment. The unequivocal proof has, however, still to be presented.

A detailed report on this work will be published elsewhere. Further studies on the structure and stereochemistry of fucoxanthin are in progress in our laboratory.

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On the Structural Relation between Niobium- and Tantalum-Wolfram Oxides and the Tetragonal Potassium Wolfram Bronze

ARTHUR SLEIGHT and ARNE MAGNÉLI

Institute of Inorganic Chemistry, University of Stockholm, Stockholm, Sweden

The existence of a phase in the Ta_2O_5—WO_3 system structurally similar to the tetragonal wolfram bronzes of the K_xWO_3 type [1] was first pointed out by Banks and Noval.[2] They stated that the phase has a range of homogeneity, while Kovba and Trunov [3] reported it to have the stoichiometric composition $Ta_2O_5 \cdot 3\,WO_3$. Goldschmidt [4] found the phase $Nb_2O_5 \cdot 3\,WO_3$, and Mohanty and Fiegel [5] indicated that this is also structurally related to tetragonal K_xWO_3.