

From the quantity of electricity used, the isotopic composition and the total amount of lithium along the anodic end of the rod both before and after the electrolysis, the mass effect,  $\mu^+$ , for lithium as the hydride can be calculated according to Klemm.<sup>11</sup> An enrichment of lithium-7 was always found at the anodic end. The experimental difficulties mentioned above allowed the passage of only a small quantity of electricity, resulting in a small total enrichment. Therefore only the very approximate minimum value,  $\mu^+ = -0.04$ , could be obtained. This value is, however, in agreement with Klemm's empirical relationship for the halides.<sup>3</sup> A small enrichment of lithium-7 at the cathodic end of the hydride rod was also found.

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## Algal Carotenoids

### III. The Oxygen Functions of Fucoxanthin

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**F**ucoxanthin, the characteristic carotenoid of brown algae and of diatoms, has been given the chemical composition  $C_{40}H_{54-60}O_6$ .<sup>1-5</sup> Except for one sample

of fucoxanthin which analysed as  $C_{40}H_{54}O_6$ , in the hands of Willstätter,<sup>1</sup> the analytical data given in the literature agree fairly well and indicate a content of six oxygen per forty carbon atoms for this pigment. Heilbron and Phipers<sup>4</sup> suggested that two of the oxygen atoms were present in carbonyl groups while four formed secondary hydroxyl functions. Retrovsky<sup>6</sup> has proposed a hexaol structure for fucoxanthin. On the basis of infra-red absorption data Liaaen and Sørensen<sup>7</sup> and Torto and Weedon<sup>5</sup> proposed the presence of one conjugated keto group and one isolated carbonyl function (or unsaturated ester<sup>5</sup>) in fucoxanthin. In two previous communications<sup>8,9</sup> we have shown that fucoxanthin contains one secondary (or primary) hydroxyl group, and we obtained evidence for the presence of at least two tertiary hydroxyl functions in the molecule. The presence of one carbonyl group in conjugation with the polyene chain was proven, and the presence of an absorption band at  $1732\text{ cm}^{-1}$  (isolated carbonyl function) in the infra-red spectrum of the pigment was verified.

We now want to present evidence to show that the isolated carbonyl absorption band at  $1732\text{ cm}^{-1}$  in the infra-red spectrum of fucoxanthin is associated with an acetoxy group. The infrared spectrum of fucoxanthin monoacetate<sup>8</sup> already indicated that fucoxanthin contained an acetoxy group, as the acetylation led to an increase in the intensity of the  $1732$  and  $1240\text{ cm}^{-1}$  bands without introducing any new bands. In addition, perhydrofucoxanthin obtained in our laboratory by catalytic hydrogenation (Adams catalyst) of fucoxanthin in ethyl acetate as well as in acetic acid showed absorption peaks at  $1735$ ,  $1245$  (acetate) and  $1720\text{ cm}^{-1}$  (isolated carbonyl). The first two peaks disappeared upon saponification.

The nuclear magnetic resonance spectrum of fucoxanthin in deuteriochloroform was kindly recorded by Dr. A. Melera on a Varian A-100 spectrometer and showed the presence of eleven methyl groups in the molecule; one more than the ten methyls of a normal carotenoid. One sharp peak with a  $\tau$ -value of 7.97 clearly indicated the presence of a methyl group in an acetoxy function.<sup>10</sup> This was confirmed by quantitative determination of acetyl groups according to the method of Pregl-Roth<sup>11</sup> which gave 0.8 mole of acetic acid per mole of fucoxanthin (calc. as  $C_{44}H_{62}O_6$ ; average of four determinations). The volatile acid

was identified by column chromatography according to a modified Swim and Krampitz procedure,<sup>12</sup> by paper chromatography of the ammonium salt<sup>13</sup> ( $R_F = 0.30, 0.35, 0.40,$  and  $0.35$  for the ammonium salts of formic, acetic, propionic acids and acid from fucoxanthin, respectively) and by paper chromatography of the hydroxamic derivative ( $R_F = 0.60, 0.41, 0.60,$  and  $0.75$  for the unknown, formic, acetic and propionic acid derivatives, respectively).

Fucoxanthin thus contains an acetoxy group, and the analytical data of the fucoxanthols previously reported by us<sup>9</sup> showed too high oxygen contents and led us to the erroneous conclusion that fucoxanthin could not be an ester. The fact that fucoxanthin is an acetate explains why Karrer *et al.*<sup>3</sup> obtained seven moles of acetic acid upon chromic acid oxidation of one mole fucoxanthin, as against six moles of acetic acid per mole of lutein and  $\beta$ -carotene.

The present evidence indicates that the oxygen functions of fucoxanthin are: one secondary (or primary) hydroxyl group, one conjugated keto function, one acetoxy group and two tertiary hydroxyl functions. The presence of the last mentioned is inferred from the partition data of fucoxanthol b acetate, and is compatible with the infra-red spectra of fucoxanthin and its derivatives.<sup>8</sup>

A detailed report of this work will be given elsewhere. Further studies on the structure of fucoxanthin are in progress.

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## The Crystal Structure of L-Ascorbic Acid, "Vitamin C"

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The crystal structure of vitamin C as proposed by Cox and Goodwin<sup>1</sup> in 1936 has been considered to be insufficiently accurate by modern standards. A revision seemed therefore appropriate, also in view of the biological importance of the substance. The author's main interest lies in the field of hydrogen bonding as studied by neutron diffraction methods, and it was felt that vitamin C might reveal some interesting features also in this respect.

In addition to X-ray data, neutron data were collected with the intention to study the positions of the hydrogen atoms. To permit a detailed investigation of the hydrogen atoms attached to oxygen atoms, and to avoid overlap in projections of these hydrogens with other atoms, two sets of neutron data were collected. The first set was recorded from a single crystal of the usual L-ascorbic acid. The second set was recorded from a crystal where the hydrogen atoms attached to oxygen were exchanged by deuterium atoms. The scattering amplitudes for these isotopes of hydrogen have different values and even different signs. A Fourier synthesis based upon the difference between the structure factors of these compounds is thus expected to give only the scattering density from the hydroxyl hydrogen atoms.

The space group is  $P2_1$ , as found by Cox and Goodwin. The unit cell dimensions