THE OCCURRENCE AND INTERCONVERSION OF VARIOUS FUCOXANTHINS

Sir:

Many polyene compounds occur as two or more spatial or *cis-trans* forms, some of which are interconvertible.[1,2,3] Among the carotenoid pigments of green leaves, only the high-melting, stable polyene isomers have been observed.[3] Now, however, additional observations on algal carotenoids indicate that fucoxanthin, which participates in photosynthesis,[4] occurs in at least three interconvertible modifications.

By means of chromatographic adsorption,[5] we have prepared these isomeric fucoxanthins, in addition to smaller quantities of other xanthophylls, from brown algae (*Phaeophyceae*) and the diatom *Nitzschia closterium*. The principal fucoxanthin, here called *fucoxanthin a*, comprises about nine-tenths of the total fucoxanthins and forms an orange band on adsorption columns of powdered sugar. Above this, *fucoxanthin b* forms a smaller, slightly yellower zone. Immediately above fucoxanthin *b*, there occurs another pale orange zone containing *fucoxanthin c*. Traces of similar pigments appear higher on the column.

When pigments were extracted rapidly from *Nitzschia* and adsorbed under mild conditions, the same mixture of fucoxanthins was always obtained. Fucoxanthin *a* treated similarly gave only traces of its isomers. Unless a rapid conversion takes place immediately upon death of the cells, fucoxanthins *b* and *c*, as well as *a*, probably represent normal constituents of brown algae and diatoms.

Interconversion of the fucoxanthins occurs very slowly in ethanol at 20°, rapidly at 76°. It appears to be catalyzed by substances upon which the pigments are strongly adsorbed. Iodine dissolved in petroleum ether containing dimethylaniline[1] causes rapid interconversion of fucoxanthins *a*, *b* and *c*, yielding a mixture similar to that found in the algae. Acids, or iodine with little or no dimethylaniline,[1,2,3] form additional pigments (adsorbed above fucoxanthin *c* and below fucoxanthin *a*).

Isomeric fucoxanthins exhibit similar spectral absorption curves. In alcohols, each pigment has a single definite absorption maximum: λ max. (ethanol), fucoxanthin *a*, 452 mμ; *b*, 445 mμ; *c*, 446 mμ. Each isomer is decomposed by alkalies and is converted into water-soluble, blue products by concentrated hydrochloric acid. Fucoxanthin *a* represents the bulk of the fucoxanthin ordinarily prepared by crystallization[3] (p. 27) and probably corresponds to the fucoxanthin α detected by adsorption on filter paper.[6] A second more strongly adsorbed pigment (fucoxanthin β),[6] also observed by adsorption,[7] was likely a mixture of our fucoxanthins *b* and *c*.

By analogy with other xanthophyll pigments,[1,2,3] fucoxanthin *a* should be the stable, *trans* form. Isomers *b* and *c* presumably contain an unknown arrangement of hydroxyl groups and *cis* double bonds. If this be true, the original appellation of alpha and beta given to fucoxanthin isomers[6] is the inverse of that employed with isomeric polyene acids. Moreover, there is no rational system of nomenclature for various *cis* and *trans* carotenoid isomers; hence, use of Latin rather than of Greek letters to designate the various fucoxanthins seems desirable[3] (pp. 68–73).

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(1) Strain, THIS JOURNAL, **63**, 3448 (1941); and included refs.

(2) Zechmeister and Schroeder, *Science*, **94**, 609 (1941); Zechmeister, Le Rosen, Went and Pauling, *Proc. Nat. Acad. Sci.*, **27**, 468 (1941).

(3) Strain, "Leaf Xanthophylls," Carnegie Inst. of Wash., Publication No. 490, 1938, p. 29.

(4) Dutton and Manning, *Am. J. Bot.*, **28**, 516 (1941).

(5) Strain, "Chromatographic Adsorption Analysis," Interscience Publishers, Inc., New York, N. Y., 1942.

(6) Kylin, *Z. physiol. Chem.*, **166**, 39 (1927).

(7) Pace, *J. Biol. Chem.*, **140**, 483 (1941); and included refs.