

## The Identity of Neoxanthin and Foliaxanthin

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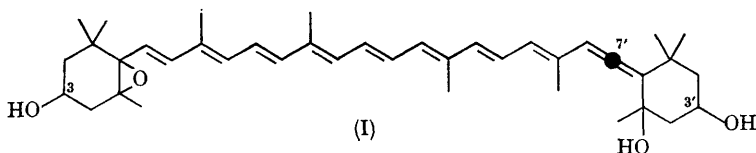
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NEOXANTHIN was first isolated from the green leaves of barley by Strain<sup>1</sup> in 1938, and was subsequently shown to be one of the principal xanthophylls in a wide variety of seed plants and spore-bearing plants.<sup>2</sup> Foliaxanthin was first isolated from paprika by Cholnoky *et al.*<sup>3</sup> in 1956, and has since been found in spinach, maple, and other leaves. It was shown to have the allenic structure (I)<sup>4</sup> whereas the corresponding formula containing a (7',8') double bond in place of the allenic group, and hence two extra hydrogen atoms, had been entertained for neoxanthin.<sup>5-8</sup>

It has often been suggested that neoxanthin and foliixanthin are identical.<sup>4-6,9</sup> and recent spectral studies on neoxanthin support this view.<sup>10</sup> It has now been established unambiguously that the two pigments have the same structure (I) and stereochemistry.

A sample of "foliixanthin", isolated from spinach and maple in Pécs, has been compared with one of "neoxanthin" isolated from the alga *Euglena gracilis* in Boston (and which has previously been compared with neoxanthin from barley leaves<sup>6</sup>), and one of "neoxanthin" isolated from spinach and maple leaves in Davis. All exhibited  $\lambda_{\max}$  (EtOH) 467, 438, and 415 m $\mu$  (in good agreement with the values observed by Strain for his original neoxanthin,<sup>1</sup> and by Curl for "neoxanthin" from leaves of elm, apricot, orange, spinach, and acacia, and from green bell peppers<sup>5,7</sup>), and an infrared absorption maximum near 1920 cm.<sup>-1</sup> attributable to an allenic group. Both foliixanthin (Pécs) and neoxanthin (Davis) had  $\tau$  (CDCl<sub>3</sub>)<sup>†</sup> 8.99, 8.92, 8.82, 8.79, 8.66, 8.19, and 8.05 (relative intensities *ca.* 1:1:1:1:2:1:3 respectively), consistent with formula (I). All

† Methyl bands only.



three samples were converted into the isomeric furanoid oxides by solution in "AnalaR" chloroform from which traces of acid had not been removed; precision mass-spectrometry (A.E.I. MS9) on the products revealed molecular ions ( $m/e$  600·417, 600·416, and 600·416 respectively) corresponding to  $C_{40}H_{56}O_4$  ( $M = 600·418$ ) and the characteristic fragmentation pattern<sup>11</sup> of a 3-hydroxyfuranoid oxide ( $m/e$  181, 221,  $M - 92$ ,  $M - 80$ ).

Folioxanthin did not separate from either neoxanthin samples in mixed thin-layer chromatograms on alumina or Kieselgel H (using ~35% acetone in light petroleum or 15% methanol in benzene as eluent). All three exhibited similar optical rotatory dispersion curves (for which we thank Professor W. Klyne) with a negative extremum near 235  $m\mu$  and a positive extremum

near 220  $m\mu$ ; a difference in absolute stereochemistry can therefore be excluded. An S-configuration is assigned to the asymmetric centres at C-3 and C-3' since the zeaxanthin prepared<sup>4</sup> from folioxanthin is identical<sup>12</sup> in all respects with natural zeaxanthin.<sup>13</sup>

Both "neoxanthin" and "folioxanthin" have been crystallised; the m.p. ca. 134° is common, but a higher value (143—145°) observed by Strain<sup>1</sup> suggests polymorphism. A geometrical isomer of "neoxanthin" has been reported by Curl in cling peaches.<sup>7,14</sup>

In future publications we shall refer to this widespread natural epoxide as neoxanthin, and to the related furanoid oxide as neochrome.

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