Foliaxanthin

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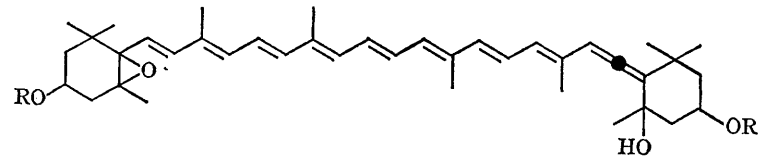
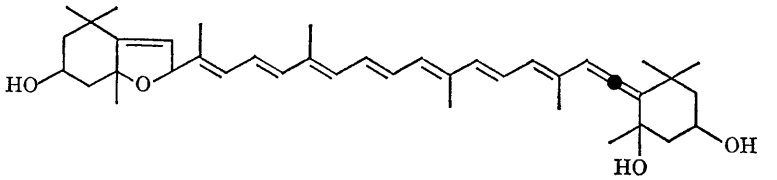
FOLIAXANTHIN was first isolated from paprika,[1] and has since been found in lucerne, maple, and other leaves.[2] It has now been shown to have the structure (I); an allenic carotenoid has not previously been reported in higher plants.

Foliaxanthin is an unstable amorphous solid, m.p. 128°, which exhibits the typical properties of a carotenoid epoxide.[1] Its light-absorption properties* reveal the presence of a conjugated nonaene chromophore [λ_{max} 467, 439, and 416 mμ, (10^{-3} ϵ, 120·6, 134·6, and 94 respectively); λ_{max} (C_6H_6) 478, 448, and 423 mμ], hydroxyl groups (ν_{max} 3597 cm.$^{-1}$), and an allene group (ν_{max} 1923 cm.$^{-1}$). Acetylation ($CH_3COCl/C_5H_5N/C_6H_6$) gives a crystalline derivative, m.p. 112° [λ_{max} (C_6H_6) 478, 448, and 423 mμ; ν_{max} 3590, 1923, and 1720 cm.$^{-1}$] in almost quantitative yield. Mass-spectral studies show foliaxanthin to be a trihydroxy-compound, $C_{40}H_{56}O_4$, and characterise its derivative as a (tertiary) hydroxy-diacetate, $C_{44}H_{60}O_6$. Dehydration ($POCl_3/C_5H_5N$) of this derivative gives an epiphasic pigment devoid of hydroxyl groups

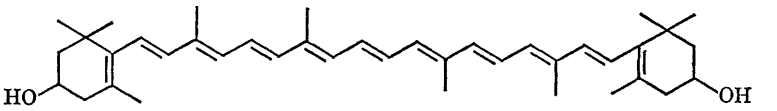
* Unless indicated to the contrary, visible and infrared absorption spectra were determined on solutions in 96% ethanol and in chloroform respectively.



(I)



(II)



(III)

(partition tests between petrol and 95% MeOH), but with the same visible light absorption [$\lambda_{max}(C_6H_6)$ 478, 448, and 423 mμ].

On treatment with *ca.* 0·01% ethereal or chloroformic hydrogen chloride foliaxanthin undergoes an epoxide–furanoid oxide rearrangement giving (crystalline) foliachrome, m.p. 148° [λ_{max} 451, 424, and 401 mμ, (10^{-3} ϵ, 131·5, 136·2, and 87 respectively); λ_{max} (C_6H_6) 459, 430, and 406 mμ; ν_{max} 3595 and 1923 cm.$^{-1}$]; mass spectral studies establish the formula $C_{40}H_{56}O_4$, and indicate the presence of at least 2 hydroxyl groups. Infrared irradiation of an ethereal solution of foliachrome and lithium aluminium hydride gives (crystalline) zeaxanthin (III) (similar reductions of the epoxides and furanoid oxides of β-carotene and zeaxanthin regenerate the parent carotenoids[3]).

The results summarised above lead to the structure (I, R = H) for foliaxanthin, (I, R = OAc) for its diacetate, and (II) for foliachrome. These conclusions are consistent with the n.m.r. spectrum of foliaxanthin, and its diacetate.

It has been suggested[4–6] that foliaxanthin is identical with neoxanthin, a common pigment of leaves.[5,7,8]

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