Mass Spectrometry of Carotenoid Epoxides and Furanoid Oxides

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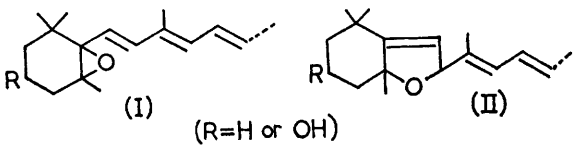
THE compounds listed in the Table have been examined by high-resolution mass spectrometry.* All exhibited molecular ions with the expected compositions. Some features of the spectra, notably peaks due to the loss of 92 and 106 mass units, are observed with most carotenoids.[1,2] Others appear to be specific for the carotenoid epoxides (I) and furanoid oxides (II), and to provide a valuable new method for the detection of these important pigments. Fortunately a distinction between the two classes can readily be made, even on a microgram scale, by virtue of the marked changes in visible light absorption properties which accompany the isomerisation of carotenoid epoxides to the corresponding furanoid oxides on exposure to traces of acid.[3,4]

* Mass spectra were determined on A.E.I. MS9 instruments. Samples were directly inserted into the source, which was operated at as low a temperature as possible (200–230°). Heptacosafluorotributylamine was used as a standard in high resolution studies.



TABLE

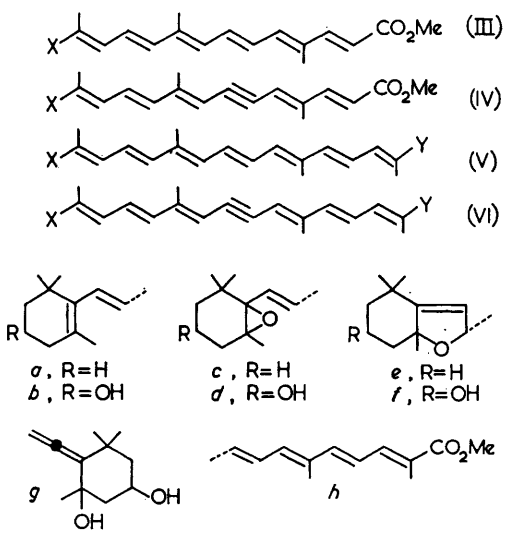
Epoxides

1. Methyl C_{27}-apo-10′-β-carotenoate epoxide (III; X = *c*).
2. Methyl 15,15′-dehydro-C_{27}-apo-10′-β-carotenoate epoxide (IV; X = *c*).
3. Torularhodin methyl ester epoxide (V; X = *c*, Y = *h*).
4. β-Carotene mono-epoxide (V; X = *c*, Y = *a*).
5. 15,15′-Dehydro-β-carotene mono-epoxide (VI; X = *c*, Y = *a*).
6. β-Carotene di-epoxide (V; X=Y = *c*).
7. 15,15′-Dehydro-β-carotene di-epoxide (VI; X=Y = *c*).
8. Foliaxanthin (V; X = *d*, Y = *g*).[5]

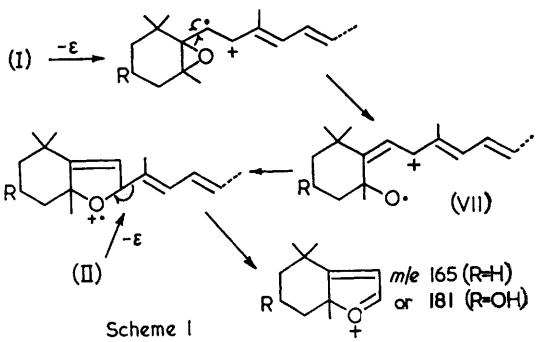
Furanoid oxides

9. β-Carotene mono-furanoid oxide (mutatochrome) (V; X = *e*, Y = *a*).
10. Lutein mono-furanoid oxide (flavoxanthin) (V; X = *f*, Y = *b*†).
11. β-Carotene di-furanoid oxide (aurochrome) (V; X = Y = *e*).
12. Zeaxanthin di-furanoid oxide (auroxanthin) (V; X = Y = *f*).[6]
13. Foliachrome (V; X = *f*, Y = *g*)[5].

† End group as in (*b*) except that the cyclic douole bond is in the unconjugated α-(4,5-)position.

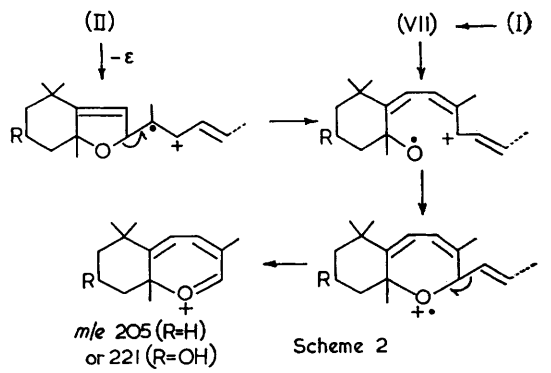


Peaks were observed at *m/e* 165 and 205 with compounds unsubstituted at C-3, and at *m/e* 181 and 221 with their 3-hydroxy-derivatives. High resolution mass spectrometry showed the composition of the corresponding ions to be $C_{11}H_{17}O$ and $C_{14}H_{21}O$ (compounds 9 and 11), and $C_{11}H_{17}O_2$ and $C_{14}H_{21}O_2$ (compounds 10 and 12) respectively. These peaks, which were strong with the furanoid oxides, may be attributed to normal α-fission (Scheme 1), and to a novel type of fission between sp^2 hybridised carbon atoms leading to a homopyrylium type ion (Scheme 2). With the epoxides these peaks were of more variable intensity, and the possibility of rearrangement on the probe cannot be excluded.



Scheme 1

All furanoid oxides, and some epoxides, showed a moderately strong peak at $M-80$. High-resolution studies (compounds 9—12), and the observation of the appropriate metastable ion (compounds 9 and 11), showed this to be due to the concerted loss of C_6H_8. This fragmentation, which has not been encountered with other classes of carotenoids, occurred twice with the di-furanoid oxides.



Scheme 2

Some of the epoxides showed a peak at $M-18$; the observation of such a peak does not, therefore,

necessarily indicate that the compound under investigation contains a hydroxy-group.

Other features of the mass spectra of carotenoid epoxides and furanoid oxides will be discussed in the full publication.

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[1] U. Schwieter, H. R. Bollinger, L. H. Chopard-dit-Jean, G. Englert, M. Kofler, A. König, C. v. Planta, R. Rüegg, W. Vetter, and O. Isler, *Chimia* (*Switz.*), 1965, **19**, 294.
[2] B. C. L. Weedon, in the press.
[3] P. Karrer and E. Jucker, "Carotinoide", Birkhäuser, Basle, 1948.
[4] B. C. L. Weedon in "Chemistry and Biochemistry of Plant Pigments", ed. T. W. Goodwin, Academic Press, London, 1965.
[5] Observations by L. Cholnoky, K. Györgyfy, J. Szabolcs, E. S. Waight, and B. C. L. Weedon, *Chem. Comm.*, 1966, 404.
[6] We thank Dr. E. S. Waight for the spectrum of this compound.