Mass Spectrometry of Carotenoid Ketones

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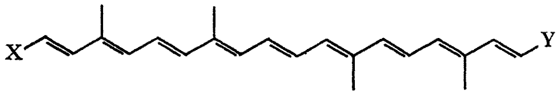
THE keto-carotenoids listed in the Table have been examined by high-resolution mass spectrometry,† and all displayed easily recognizable molecular ions. The diosphenols and cyclopentyl ketones also showed characteristic fragment ions; mass spectrometry is therefore useful in the identification of these classes of pigment. Diosphenol acetates undergo loss of keten upon electron impact and subsequently fragment in the same way as the parent hydroxy-compounds.

Diosphenols[a] *and their acetates*	(I)—(III)	Y	X
Astacene	(I)	*a*	*a*
Astacene diacetate	(I)	*b*	*b*
15,15′-Dehydroastacene	(II)	*a*	*a*
15,15′-Dehydroastacene diacetate ..	(II)	*b*	*b*
3-Oxocanthaxanthin	(I)	*a*	*c*
3-Oxocanthaxanthin acetate	(I)	*b*	*c*
15,15′-Dehydro-3-oxocanthaxanthin ..	(II)	*a*	*c*
15,15′-Dehydro-3-oxocanthaxanthin acetate	(II)	*b*	*c*
3-Oxoechinenone[b]	(I)	*a*	*g*
3-Oxoechinenone acetate	(I)	*b*	*g*
15,15′-Dehydro-3-oxo-echinenone[c] ..	(II)	*a*	*g*
4′-Hydroxy-3-oxo-echinenone[d]	(I)	*a*	*e*
4′-Methoxy-15,15′-dehydro-3-oxo-echinenone acetate	(II)	*b*	*f*
Apo-8′-15,15′-dehydroastacenal[e] ..	(III)	*a*	—
Cyclohexenones			
Canthaxanthin	(I)	*c*	*c*
15,15′-Dehydrocanthaxanthin	(II)	*c*	*c*
Echinenone	(I)	*c*	*g*
15,15′-Dehydroechinenone	(II)	*c*	*g*
3-Hydroxyechinenone	(I)	*d*	*g*
15,15′-Dehydro-3-hydroxyechinenone	(II)	*d*	*g*
Phoenicoxanthin	(I)	*d*	*c*
Astaxanthin	(I)	*d*	*d*
Cyclopentyl ketones			
Capsorubin	(I)	*i*	*i*
Capsorubindione..	(I)	*j*	*j*
Capsanthin	(I)	*i*	*h*
Capsanthinone	(I)	*j*	*h*

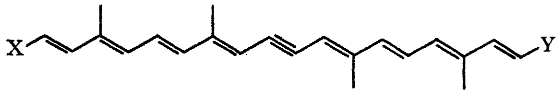
[a] Base peak *m/e* 203, unless stated otherwise.
[b] The ion *m/e* 203 was 30% of the base peak at *m/e* 159.
[c] The ion *m/e* 203 was 40% of *M* (the base peak).
[d] The ion *m/e* 203 was 9% of the base peak at *m/e* 159.
[e] The ion *m/e* 203 was 60% of the base peak at *m/e* 152.

The diosphenols give a strong ion (generally the base peak) at *m/e* 203 with the composition $C_{13}H_{15}O_2$. It is formulated as (IV), and its formation may be rationalised as shown in Scheme 1. Other benzonium ions have frequently been observed as stable species,[1] and, in the present series, the unpaired electron is well delocalized over the remainder of the polyene chain. With the acetates, as well as the peak at *m/e* 203, a weaker ion occurs at *m/e* 245, and is formulated as (V).

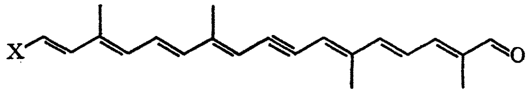
(I)

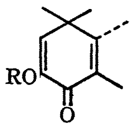


(II)

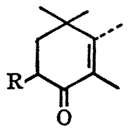


(III)

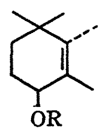




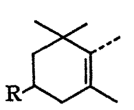
(*a*) R=H
(*b*) R=Ac



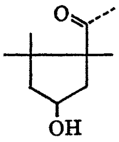
(*c*) R=H
(*d*) R=OH



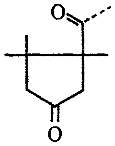
(*e*) R=H
(*f*) R=Me



(*g*) R=H
(*h*) R=OH

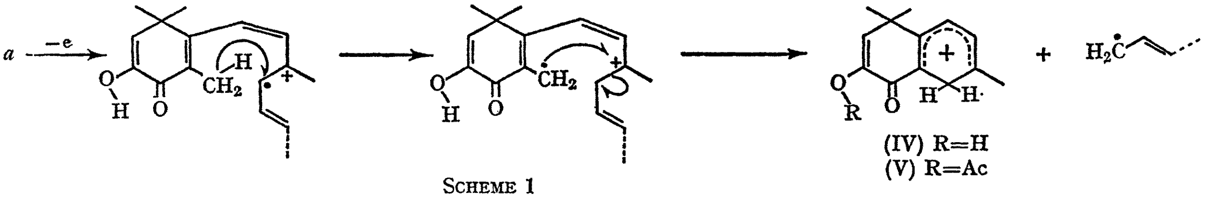


(*i*)



(*j*)

Other characteristic intense ions in the mass spectra of the



(IV) R=H
(V) R=Ac

SCHEME 1

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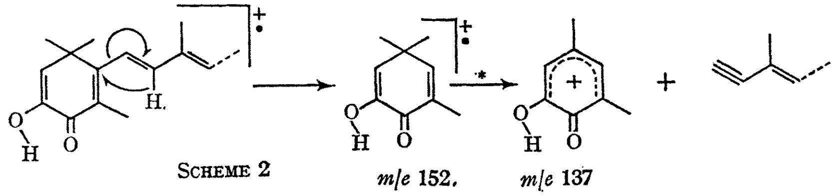
† Mass spectra were determined on an AEI MS9 or MS902 with direct insertion into the source. Heptacosafluorotributylamine was used as a standard in high-resolution studies.

diosphenols occur at *m/e* 152 and 137 and have the compositions $C_9H_{12}O_2$ and $C_8H_9O_2$, respectively. The latter ion is produced by loss of a methyl group from *m/e* 152, as is shown by the appearance of a metastable ion at *m/e* 123·5, and its formation is rationalised in Scheme 2.



SCHEME 2

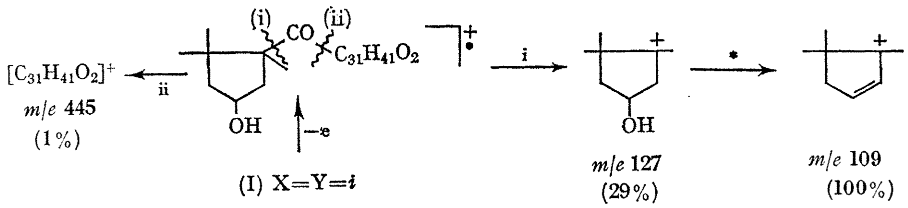
* Appropriate metastable ion observed

The cyclohexenones echinenone and canthaxanthin, and their 15,15′-dehydro-analogues, show little specific fragmentation, and their spectra at low *m/e* values are dominated by hydrocarbon ions $C_7H_7^+$, $C_8H_9^+$, and $C_9H_{11}^+$, which doubtless originate from the polyene chain and provide little useful structural information. The 3-hydroxy-derivatives show weak peaks at *m/e* 203, 152, and 137, indicating that some dehydrogenation or disproportionation may occur on the probe to give the corresponding diosphenols.

All compounds of type (I) show ions at $M-92$ (and at $M-42-92$ for the acetates), while with those of type (II) the corresponding ions are at $M-90$ (or $M-42-90$) indicating that in this skeletal rearrangement the elements of toluene or dehydrotoluene are lost from the central portion of the polyene chain. A similar loss of 92 mass units has been postulated in the mass spectrum of β-carotene and isomeric hydrocarbons.[2]

Capsanthin and capsorubin have mass spectra showing ions corresponding to $M-H_2O$ and $M-2H_2O$. The $M-92$ rearrangement ion discussed above is weak, but all the cyclopentyl ketones show strong ions at $M-106$, together with the conjugate hydrocarbon ions at *m/e* 106. This latter species subsequently decomposes to *m/e* 105 and 91 suggesting its formulation as a xylene radical cation.[3] The *m/e* 91 ion is the base peak of the spectra of capsanthin and capsanthinone.

As is usual for ketones,[4] fissions initiated by the in-chain carbonyl groups are important and characteristic. The expected acylium ions are, however, weak, and major charge retention occurs on the conjugate ions and their decomposition products. Thus with capsorubin the fragmentation shown in Scheme 3 is observed.

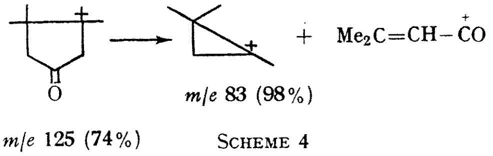


(I) X=Y=*i*

SCHEME 3

* Appropriate metastable ion observed

Fragmentation "i" with the tetra-one capsorubindione gives the species at *m/e* 125, which subsequently decomposes by losses of C_3H_6 and C_2H_2O to the isobaric ions at *m/e* 83 (Scheme 4). The base peak of the spectrum of capsorubindione is the hydrocarbon ion C_4H_8 (*m/e* 56). Capsanthin and capsanthinone fragment essentially by the pathways described for capsorubin and capsorubindione respectively.



SCHEME 4

(*Received, February 24th,* 1969; *Com.* 258.)

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[1] J. S. Shannon, *Austral. J. Chem.*, 1962, **15**, 265.

[2] 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.

[3] H. M. Grubb, and S. Meyerson, in "Mass Spectrometry of Organic Ions", ed. F. W. McLafferty, Academic Press, New York, 1963, p. 458.

[4] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Mass Spectrometry of Organic Compounds", Holden-Day, San Francisco, 1967, pp. 134—135.