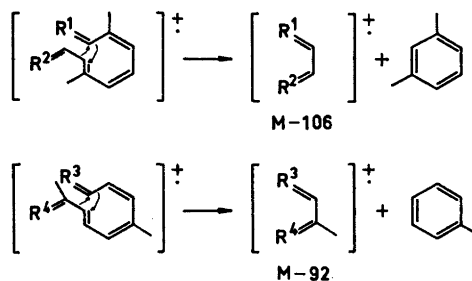


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Received March 12, 1968.



## Mass Spectrometric Studies of Carotenoids

### I. Occurrence and Intensity Ratios of M - 92 and M - 106 Peaks

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This communication discusses some preliminary findings of an investigation of the scope and limitations of mass spectrometry in the structural elucidation of carotenoids.

A previous study by Schwieter *et al.*,<sup>1</sup> has shown that various carotenes give rise to abundant M - 92 and M - 106 ions on electron impact. The formation of these was ascribed to the elimination of part of the central acyclic chain of the carotenoid skeleton, and the mechanism below was invoked to account for these losses. M - 92 and M - 106 ions have also been encountered in a later study of the mass spectra of carotenoid epoxides and furanoid oxides<sup>2</sup> and it has been claimed that these ions are a typical feature of the mass spectra of carotenoids.<sup>3,4</sup>

Examination of a wide variety of carotenoids, mainly of natural occurrence, shows that all those with C<sub>40</sub>-skeletons and an acyclic chain of at least 9 conjugated double bonds give rise to significant M - 92 and M - 106 ions. These ions may thus now be regarded as characteristic of carotenoids. Since in many cases they are

Table 1. Intensity ratios of the (M-92)/(M-106) peaks (R) in the mass spectra of carotenoids with a varying number of conjugated carbon-carbon double bonds in the acyclic polyene chain (DB).

Polyene	R	DB
Zeaxanthin	10.0	9
Echinenone	4.46	9
3-Hydroxy-3'-keto- $\alpha$ -carotene	3.19	9
3-Hydroxy-3'-methoxy- $\alpha$ -carotene	2.73	9
Bicyclic		
Canthaxanthin	2.56	9
Iso-zeaxanthin	2.17	9
Lutein diacetate	1.73	9
Lutein	1.59	9
Chlorobactene	1.00	10
Mono-cyclic		
Rubixanthin	0.70	10
Rhodoxanthin*	0.55	10
Rubixanthin acetate	0.44	10
Acyclic		
Lycophyll	0.36	11
Lycopen-16-al	0.34	11
Lycopene	0.34	11
Lycoxanthin	0.34	11
1,2,1',2'-Tetrahydro-1,1'-dihydroxy-lycopene	0.34	11
Rhodopin	0.27	11
3,4,3',4'-Tetrahydro-spirilloxanthin	0.26	11
Anhydro-rhodovibrin	0.068	12
Rhodovibrin	0.057	12
OH-Spirilloxanthin	0.029	13
Spirilloxanthin	0.018	13

\* Rhodoxanthin is a bicyclic retro-compound, whereas the other compounds having 10 double bonds are monocyclic.

more abundant than the molecular ion, they can be useful indicators of the

molecular weight, when this is difficult to determine directly.

The intensities of the  $M - 92$  and  $M - 106$  peaks show considerable variations with respect to each other and this cannot be accounted for by the mechanism previously proposed<sup>1</sup> for this fragmentation without taking other factors into consideration. As shown by the data given in Table 1, these variations are related to the number of double bonds in the acyclic conjugated chain, the  $(M - 92)/(M - 106)$  ratio decreasing as the number of double bonds increases from 9 to 13. This relationship holds well for all  $C_{40}$ -carotenoids containing no more than one oxygen substituent in each end group. The compounds having two oxygen atoms in one of the end groups or one end of the molecule shortened do not fit the simple pattern, but when these are grouped according to the oxygen function present the same trend is observed within each set. The compounds examined having both ends shortened, bis-apo-carotenals, do not normally show the  $M - 92$  and  $M - 106$  peaks.

The values in Table 1 show a definite grouping according to the number of double bonds present, but further data are required to define the limits for each group. Present evidence suggests that the intensity ratio is independent of the geometry of the instrument and the state of the ion source. On our instrument the values have been found to be reproducible over several months and the values calculated from the carotene spectra published by Schwietter *et al.*<sup>1</sup> (Table 2) accord with the present findings. Direct comparison with published spectra is only possible for lycopene<sup>1</sup> and rhodoxanthin.<sup>5</sup> The value calculated from the previously reported spectrum of lycopene is in good agreement with our result (0.30 and 0.34), and that for rhodoxanthin agrees satisfactorily (0.74 and 0.55).

In agreement with previous work on carotenes,<sup>1</sup> most of the compounds gave metastable ions corresponding to the loss of 92 mass units, but none corresponding to the loss of 106 mass units. This may indicate that different mechanisms are involved in the two cases. Any detailed

Table 2. Intensity ratios  $(M - 92)/(M - 106)$  for various carotenes from Ref. 1.

	Carotene	R	DB
Bicyclic	$\beta$ -Carotene	12.9	9
	$\alpha$ -Carotene	7.5	9
	$\epsilon$ -Carotene	3.1	9
Monocyclic	$\gamma$ -Carotene	0.85	10
	$\delta$ -Carotene	0.43	10
Acyclic	Lycopene	0.30	11

mechanism explaining the formation of the  $M - 92$  and  $M - 106$  ions and the observed relationship between intensity ratio and acyclic polyene chain length must await labelling studies.

The mass spectra were obtained on an LKB 9000 instrument at 70 eV using the direct inlet system and an ion source temperature of 290°–310°. The probe temperature was kept to a minimum (100–200°). The structures of the compounds discussed in this communication are given in reference works.<sup>6,7</sup>

*Acknowledgement.* We are indebted to Dr. O. Isler, Hoffmann-La Roche, Basel, for gifts of several synthetic carotenoids.

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Received March 11, 1968.