

## Factors Affecting the Intensity Ratio of the M-92/M-106 Ions in the Mass Spectra of Carotenoids

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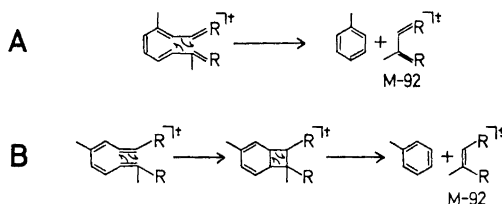
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The intensity ratio ( $R$ ) of the M-92/M-106 ions in the mass spectra of a number of aromatic carotenoids and synthetic carotenoid models is examined. It is shown that electronic effects cause variation in the ratio ( $R$ ) in these compounds. Previously published data are used to show that similar effects occur where conjugated carbonyl functions are present in the molecule. Consideration of these results and some steric effects is used to infer a modified mechanism for formation of the M-92 and M-106 ions.

In the first study of carotenoid mass spectra undertaken, Schwieter *et al.*<sup>1</sup> found the presence of M-92 and M-106 ions in the spectra of all the carotenes examined. Further work<sup>2</sup> revealed that these ions were indeed typical of carotenoids and showed that a third member of this series occurred at M-158.<sup>3</sup> When a triple bond is substituted for the double bond normally present at the central position in the carotenoid chain an M-90 ion replaces that observed at M-92.<sup>4,5</sup> In carotenoids where one of the in-chain methyl groups is substituted some part of the ions observed result from eliminations including this substituent.<sup>6,7</sup>

The above work is all in agreement with the original hypothesis<sup>1</sup> that the M-92 and M-106 ions, and by analogy the M-158 ion, are derived by extrusion of suitable fragments from the conjugated chain. The mechanism originally suggested<sup>1</sup> for the formation of the first two ions assumed rearrangement of single bonds to allow removal of six successive carbon atoms, and the methyl groups attached there-to, from the chain. This mechanism (Scheme 1A) is depicted below for the M-92 ion and while the M-106 ion may be derived similarly it is necessary to envisage the elimination of a ring containing ten carbon atoms to account for the M-158 ion.

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*Scheme 1.* Mechanisms previously suggested by Schwieter *et al.*<sup>8</sup> to account for the observation of M-92 and M-106 ions in the mass spectra of carotenoids. The mechanisms involve rearrangements of either (A) single bonds or (B) double bonds.

In a detailed study of the origin of these ions Schwieter *et al.*<sup>8</sup> found that most of the intensity was due to thermal decomposition prior to ionisation. It was therefore that he proposed that the mechanism for thermal decomposition in carotenoids<sup>9</sup> be adopted to explain the formation of these ions irrespective of whether they were formed by prior decomposition or by direct ionisation of the intact molecule. Further support for the adoption of this mechanism (Scheme 1B) which involves rearrangement of double rather than single bonds was obtained from studies on deuterated carotenes which showed that in some cases at least double bonds were rearranged.

Having looked briefly at the origin of the M-92 and M-106 ions it is interesting to consider how the intensity of these ions vary with respect to each other as structural features of the molecule are changed. At a relatively early stage it was realised<sup>2</sup> that as the number of double bonds in the acyclic chromophore (*DB*) increased there was a drop in the intensity ratio (*R*) of the M-92/M-106 ions. Certain stipulations were made as to the type of compounds which could be treated in this way. Compounds having multiple oxygen functions in one of the end groups gave values for the ratio (*R*) considerably different from those obtained in the absence of these functions. The values found in the so-called normal cases are given in Table 1A, together with examples of the structural types involved. Although the values reported were not claimed to be absolute it has appeared that little variation does in fact occur as a result of alterations in running conditions or with different machines.<sup>2,10,11</sup> Schwieter *et al.*<sup>8</sup> found that the intensities of the M-92 and M-106 ions varied with time in agreement with their partially thermal origin, but their published results indicate that even under these circumstances the ratio (*R*) is relatively invariant.

A number of 6-keto-carotenoids have been examined<sup>12</sup> and in this case also the values of (*R*) were found to be grouped. Each 6-keto function produced an effect similar to that expected on an increase of the chromophore by two double bonds (see Table 1B). An interesting facet of this observation was that a similar effect is seen in the visible absorption spectra of these compounds.

The above observations lead to speculation as to whether the variations in the intensity ratio (*R*) might be related to electronic distribution within the molecule. It has been known for some time that aromatic carotenoids produce interesting, but hitherto unexplained,<sup>13,14</sup> variations in the intensity ratio (*R*). It was therefore that it was decided to examine some natural carotenoids

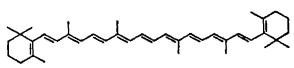
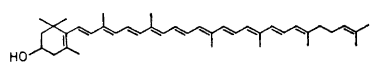
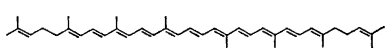
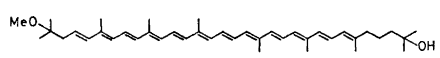
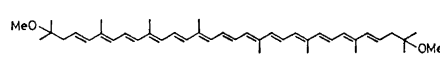
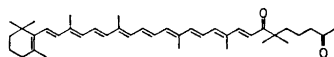
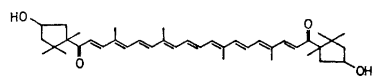
	R	DB	EXAMPLE	NAME
A	1.59 - 10	9		$\beta$ -CAROTENE <u>1</u>
	0.44-1.0	10		RUBIXANTHIN <u>2</u>
	0.26 - 0.36	11		LYCOPENE <u>3</u>
	0.057 - 0.068	12		RHODOVIBRIN <u>4</u>
	0.018 - 0.029	13		SPIRILLOXANTHIN <u>5</u>
B	0.086-0.224	9 K		SEMI- $\beta$ -CAROTENONE <u>6</u>
	0.026-0.039	9 KK		CAPSORUBIN <u>7</u>

Table 1. The intensity ratio ( $R$ ) of the  $M-92/M-106$  ions in the mass spectra of (A) carotenoids lacking fully conjugated functions<sup>3</sup> and (B) carotenoids with a 6-keto function<sup>12</sup> ( $K$ ) conjugated to the acyclic chromophore ( $DB$ ). A typical example is shown for each structural type.

and synthetic carotenoid-like models with aromatic end groups to see if any electronic effects could be seen to be operative in the intensity ratio ( $R$ ). Details of the syntheses of the latter compounds together with full physical data will be published elsewhere.<sup>15</sup>

## RESULTS AND DISCUSSION

The compounds now examined fall mostly under one heading, *i.e.* they have the same carotenoid chain as found in the bicyclic nonaenes and have aromatic end groups attached to the ends of the chain in the same way as in the parent compounds. Where this group of compounds differ from the natural compounds, they do so in the nature of the end group itself. Apart from two of the natural compounds (8 and 9) examined, about the same degree of steric interaction would be expected between the conjugated chain and the end groups in each case.

Inspection of the values found for ( $R$ ) in these di-aromatic nonaenes (see Table 2) shows that the compounds 10, 11, and 12 form a single group, having values for ( $R$ ) similar to those found normally in undecaenes. That this change in the ratio, favouring the  $M-106$  ion, has an electronic rather than a steric

basis is indicated by the fact that the compounds *13*, *14*, and *15* form a second group with somewhat lower values of (*R*). The two groups of compounds must be very alike as regards steric interaction with the conjugated chain and the variation in (*R*) would appear to be due solely to electronic differences arising from alteration of the end group. In the compound *8* the aromatic end groups are known<sup>16</sup> to be twisted out of the plane of the chromophore from their lack of contribution in the electronic spectrum and hence it is not surprising that in this compound, lacking electronic interaction of the end groups with the chain, the ratio (*R*) is as in the normal cases. Further confirmation of this argument is found in the value of (*R*) for the compound *9* which lies between the normal value and that found in *10*, *11*, and *12*. In this case one end group is conjugated with the chain and the observed value of (*R*) is similar to that found in compounds with ten conjugated double bonds.

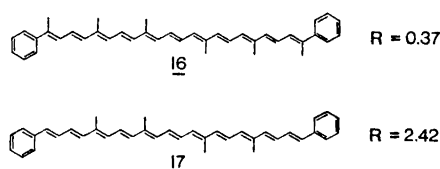
	A	B	R		A	B	R
<u>8</u>			3.4				
<u>9</u>			0.95	<u>13</u>			0.071
<u>10</u>			0.33	<u>14</u>			0.071
<u>11</u>			0.23	<u>15</u>			0.074
<u>12</u>			0.40				

Table 2. The intensity ratio (*R*) of the M-92/M-106 ions in the mass spectra of some diaromatic nonaenes.

Although the above results indicate that electronic factors influence the ratio (*R*) in the case of compounds with aromatic end groups the nature of the effect is unclear. Two main possibilities exist: either that the electronic distribution within the carotenoid chain is grossly altered, or that the effect is purely local in that a particular bond is activated. In order to look more closely at this point the compounds *16* and *17* were synthesised. Were a specific bond activation present this would now favour production of an M-92 rather than an M-106 ion as before. However, were a general effect in operation one would expect to see the same tendency as in the compounds *10-15*, *i.e.* decrease in the ratio (*R*).

In the case of *16* the value of (*R*) found was within the range normally expected for compounds with an acyclic undecaene chromophore, while compound *17* had a value for (*R*) much increased. These figures strongly suggest that a general electronic distortion is not taking place and that a specific bond activation is in fact the cause of the variation in (*R*) in the presence of

conjugated aromatic end groups. The compounds *16* and *17* each have the same possible modes of formation for the  $M-92$  and  $M-106$  ions, since it is known<sup>10,17</sup> that the 6,7-bond is not rearranged in compounds *1*, *8*, or *10*. The cause of the difference in ratio between *16* and *17* must therefore lie in the presence of the extra methyl group in *16*, *i.e.* at C-5 using the normal carotenoid numbering. It would thus seem that aromatic end groups conjugated to the chain lead to electronic enhancement of a particular mode of rearrangement in all cases, but that steric effects may minimise this effect in some cases. Presumably the enhanced mode involves the double bond  $\alpha, \beta$  to the aromatic substituent since this would be expected to be most readily affected by the methyl substituent present in compound *16*.



*Diagram.*

The above results lead to further speculation as to whether a similar explanation might be possible in the case of compounds with other conjugated end groups and which show values of ( $R$ ) divergent from the normal ones.<sup>3</sup> An obvious documented case was that of the 6-keto-carotenoids previously mentioned (Table 1B) and the trend found in these does in fact agree with that apparent in the aromatic compounds *9-15*. The change produced in the value of ( $R$ ) is, however, rather more dramatic in the case of the 6-keto compounds than in the aromatic ones.

Since  $\alpha, \beta$ -bond activation would provide an explanation for the somewhat limited case of the 6-keto-carotenoids a more general survey, based on published spectra,<sup>3</sup> was undertaken to see whether the same concept might be applied to variations in ( $R$ ) in other carotenoids with conjugated carbonyl groups. The compounds *18-23* all have structures which would be expected to lead to electronic enhancement of modes leading to  $M-106$  ions and hence lower values of ( $R$ ) than in compounds lacking fully conjugated end groups. In fact all of these compounds show the expected trend (see Table 3) but the influence of the carbonyl group at other positions is obviously less than that found in the 6-keto compounds.

Table 4 shows some conjugated carbonyl compounds which would be expected to lead to higher values of the ratio ( $R$ ) were  $\alpha, \beta$ -bond activation operative. The observed variations in ( $R$ ) are rather mixed but compounds *14*, *25*, *27*, *28*, and *29* would appear to accord with expectation. The compounds *26* and *30* show small changes towards lower values of the ratio ( $R$ ) and hence an increase in the intensity of  $M-106$  rather than in  $M-92$ . However, the last two compounds both have aromatic end groups and there is some doubt as to what value of ( $R$ ) one would expect. The relatively minor enhancement

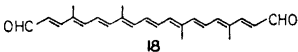
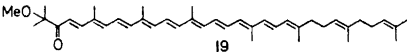
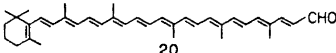
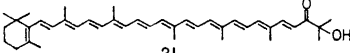
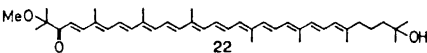
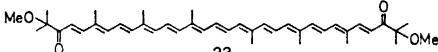
COMPOUND	DB	NORM	R
	9	1.59-10	M-106 only
	10	0.44-1.0	0.13
	11	0.26-0.36	0.13
	11	0.26-0.36	0.12
	12	0.057-0.068	0.054
	13	0.018-0.029	0.007

Table 3. The intensity ratio ( $R$ ) of the  $M-92/M-106$  ions in the mass spectra <sup>2</sup> of a number of carotenoids with carbonyl functions directly conjugated to the acyclic chromophore ( $DB$ ). In all cases  $\alpha, \beta$ -bond activation would be expected to lead to decreases in the value of ( $R$ ) as compared with the values found <sup>3</sup> in the normal cases ( $NORM$ ).

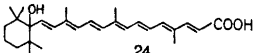
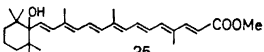
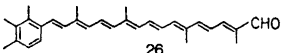
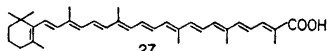
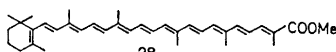
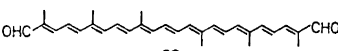
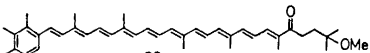
COMPOUND	DB	NORM	R
	7	?	M-92 only
	7	?	M-92 only
	9	1.59-10	0.55
	10	0.44-1.0	1.72
	10	0.44-1.0	1.25
	11	0.26-0.36	0.50
	11	0.26-0.36	0.15

Table 4. The intensity ratio ( $R$ ) of the  $M-92/M-106$  ions in the mass spectra <sup>2</sup> of a number of carotenoids with carbonyl functions directly conjugated to the acyclic chromophore ( $DB$ ). In all cases  $\alpha, \beta$ -bond activation would be expected to lead to increases in the value of ( $R$ ) as compared with the values found <sup>3</sup> in the normal cases ( $NORM$ ). In compounds 26 and 30  $DB$  has been increased by 1 to allow for the effect of the aromatic end group.

of the M-92 ion found seems to suggest that the methyl group on the  $\alpha$  C-atom results in steric hindrance which offsets the enhanced mode as in compound 16.

The nature of the electronic enhancement involved is not clear but the results show beyond doubt that substituents conjugated to the acyclic chromophore result in distortion of the ratio ( $R$ ) in a fairly regular fashion. In particular, it appears that the  $\alpha,\beta$  double bond with respect to the conjugated function is activated for rearrangement processes, either thermal or mass spectrometric, leading to the observation of M-92 or M-106 ions in the mass spectrometer. Where a methyl group is present on the  $\alpha$  C-atom this effect is offset by the extra steric hindrance provided by this substituent; normally this last factor will result in some loss of enhancement of intensity of the M-92 ion. The exact effect resulting from the various substituents can not be defined due to lack of data, but the general order of the effects seems to follow the extent of conjugation of the particular function as measured by visible light absorption spectrometry. The results provide additional circumstantial evidence that it is double bonds rather than single bonds which are rearranged in the formation of the M-92 and M-106 ions in carotenoids.

Since the above hypothesis provides both a qualitative and to a lesser extent a quantitative idea of how variations in the ratio ( $R$ ) arise in the case of compounds with conjugated substituents it is worth looking more closely at variations of the ratio ( $R$ ) in the so-called normal cases. The values found for ( $R$ ) in these cases are given in Table 1A and the suggested mechanisms<sup>1,8</sup> for the formation of the M-92 and M-106 ions in Scheme 1. Scheme 2 shows the possible modes of elimination for 92 and 106 ions diagrammatically and the ratios calculated on the basis of statistical distribution among the possible modes. It is at once apparent that the values of ( $R$ ) calculated from either the single bond or double bond rearrangement mechanisms separately do not agree with those actually observed. Further, combinations of the mechanisms in various ways do not lead to marked improvements in agreement. Some weighting factors are thus involved in the formation of the M-92 and M-106 ions.

Enzell and Liaaen-Jensen<sup>18</sup> have suggested that the variations observed in ( $R$ ) on increasing  $DB$  from 9 to 10 and 11 can be explained in terms of steric interaction between cyclic end groups and the conjugated chain. Such factors are assumed to make attainment of the necessary transition states for elimination of 92 and 106 mass units more difficult close to the cyclic end group. Experimental support for this contention may occur in that C-7 is not lost<sup>10,17</sup> in 92 mass unit fragment where the near end of the molecule is cyclised. Those authors<sup>18</sup> explained the further decrease in ( $R$ ) on going to compounds with  $DB$  equal to 12 and 13 as being due to the additional modes of formation of the M-106 ion then allowed.

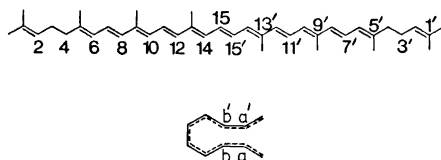
These arguments rationalise<sup>18</sup> the direction of change in the ratio ( $R$ ), but they offer no explanation as to why the ratio achieves values as low as 0.018 when  $DB$  equals 13. In fact it would appear that only by assuming in-built energetic preference for formation of M-106 rather than M-92 species can such values be explained.

Examination of the mechanisms A and B shows that each demands the

DB	92	106	R	DB	92	106	R
9	2	3	0.66	9	4	2	2.0
10	3	3	1.00	10	5	2	2.5
11	4	3	1.33	11	6	2	3.0
12	4	4	1.00	12	6	3	2.0
13	4	5	0.80	13	6	4	1.5

*Scheme 2.* Possible modes of elimination of 92 and 106 mass units from carotenoids with various acyclic chromophores (*DB*) and the ratio (*R*) expected on the basis of statistical distribution amongst the possibilities in each case. (A) refers to rearrangements of single bonds and (B) to rearrangements of double bonds.

simultaneous approach of four chain C-atoms to give a suitable geometry for elimination to proceed. These atoms, numbered *a*, *b*, *a'* and *b'* in Scheme 3, will normally carry one methyl group between them. If the mode involved leads to the loss of 92 mass units this methyl group will be at *a* or *a'*, while the substituent will be at *b* or *b'* when a 106 mass unit fragment is eliminated. Two exceptions to this general statement occur. Firstly, were the fragment to be eliminated carotenoid C-atoms 13–13' both *b* and *b'* would carry methyl groups. In fact, labelling studies showed that this mode does not occur<sup>8</sup> in practice. The second exception is where the fragment containing C-atoms 11–15' is concerned. In this case no substituents are present on the atoms *a*, *b*, *a'*, and *b'*. The labelling studies<sup>8,10,17</sup> showed that in lycopene no particular preference occurred as to the mode of elimination of the 92 mass unit fragment and this suggests that this exception is not important either. Neither of these modes will be further discussed, but it should be noted that both involve rearrangement of single bonds.



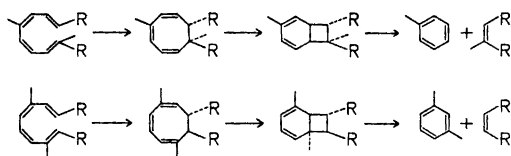
*Scheme 3.* Normal carotenoid numbering is shown for the case of lycopene together with a diagrammatic representation of the steric conformation of the carotenoid chain required for elimination of 92 or 106 mass unit fragments.

The elimination of 92 or 106 mass unit fragments would be expected to involve about the same amount of steric conflict in any mechanism involving simultaneous approach of the atoms *a*, *a'*, *b*, and *b'*. However, a real difference



in steric factors would be present if the rate determining step in the elimination involves approach of either  $a$  and  $a'$ , or  $b$  and  $b'$ . Were approach of  $a$  and  $a'$  critical loss of the 106 mass fragment would be favoured since in this case no methyl group is present at  $a$  or  $a'$ ; were  $b$  and  $b'$  critical then loss of 92 would be preferred. The observed preference for the loss of 106 mass units thus demands that the approach of  $a$  and  $a'$  is determining.

The thermal cyclisation of octatetraene to cyclooctatriene has been examined in detail by Huisgen *et al.*<sup>19</sup> and Marvell and Seubert.<sup>20</sup> Woodward and Hoffmann<sup>21a</sup> have used these results and those of Meister<sup>22</sup> to infer the intermediacy of cyclooctatriene in the thermal conversion of octatetraene to bicyclo(4,2,0)octa-2,4-diene. The extension of this mechanism to the thermal elimination of toluene and xylene from carotenoids seems plausible. The thermal elimination of these would then be written as in Scheme 4, the steps being an 8-electron conrotatory electrocyclic reaction, a 6-electron disrotatory reaction and finally the concerted scission of the cyclobutane ring which is a ( $\sigma^2s + \sigma^2a$ ) reaction.<sup>21b</sup> This would lead to a product with the stereochemistry shown while if the last step went by a radical mechanism the product would be either *cis* or *trans*. An analogous reaction can be envisaged for the loss of dimethylcyclodecapentaene.



Scheme 4. Suggested mechanism for the thermal elimination of toluene and xylene from the carotenoid chain.

It is possible to imagine that a similar sequence might apply to the mass spectrometric excision reactions in carotenoids although in this case the stereochemical configurations will be ignored. Accepting that in both thermal and electron bombardment processes the initial formation of the cyclooctatriene is the critical step a rationalisation of the very low values of ( $R$ ) found in carotenoids with  $DB$  greater than 11 may be made. In the formation of the cyclooctatriene leading to toluene elimination one of the reaction termini  $a$  or  $a'$  carries a methyl group, while for that leading to xylene elimination no such group is present. Thus the stereochemical repulsion to be overcome is greater in processes leading to excision of toluene. This explanation would lead to the expectation that for very long acyclic chromophores a stable value of ( $R$ ) would eventually be reached. Partial confirmation of this is found in the spectra of decapreno- $\beta$ -carotene ( $R = ca. 0.2$ ;  $DB = 13$ ) and dodecapreno- $\beta$ -carotene ( $R = ca. 0.1$ ;  $DB = 17$ ) published by Schwieter *et al.*<sup>8</sup> This would suggest that elimination of xylene is favoured over that of toluene by about one order of magnitude. This sort of order would explain the fact that in compounds with functions conjugated to the chromophore enhancement is much greater when the mode involved leads to loss of 106 mass units than when it leads to loss of 92 mass units.

## CONCLUSIONS

Variation in ( $R$ ) can be correlated to a number of interacting factors. These are:

(1) Loss of 106 mass units is favoured over loss of 92 mass units by about an order of magnitude as a result of steric repulsion in achieving the geometrical configuration leading to formation of the latter.

(2) Steric interaction between cyclic end groups and the conjugated chain interferes with elimination of fragments involving rearrangement of the double bond next to the cyclic end group.

(3) Functions conjugated to the acyclic chromophore enhance modes involving rearrangement of the  $\alpha, \beta$ -bond with respect to the conjugated function.

It is apparent that these factors are not independent and that considerable care is required in interpretation of the ratio ( $R$ ). In particular it seems likely that all end groups will have a certain effect on the ratio and this will probably be especially true of those that are either bulky or contain functionalities with non-bonded electrons. However, the ratio ( $R$ ) can already be used experimentally to make inferences about the nature of the polyene system in many natural carotenoids<sup>2</sup> and when the structure of a particular compound is known, it should be possible to rationalise the value of ( $R$ ) in all cases.

The evidence considered here provides further support for the proposal of Schwieter *et al.*<sup>8</sup> that the ions resulting from loss of 92 and 106 mass unit fragments are due to the rearrangement of double rather than of single bonds. The mechanism now proposed for these reactions, whether thermal or resulting directly from electronic bombardment, differs from that of Schwieter *et al.*<sup>8</sup> only in that the intermediacy of a substituted cyclooctatriene is proposed (see Scheme 4).

## EXPERIMENTAL

The mass spectra of the compounds 8-17 were obtained on an AEI MS 902 mass spectrometer using the direct inlet system, an ion source temperature of 200° and an electron bombardment energy of 70 eV.

*Note added in proof.* The amended mechanism here suggested has been proposed independently by Vetter, W., Englert, G., Rigassi, N. and Schwieter, U. in Isler, O. *Carotenoids*, Birkhäuser, Basel 1971.

*Acknowledgement.* The author wishes to thank the *University of Trondheim* for financial support during the period of this work.

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Received July 26, 1971.