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C_{50}-Carotenoids. 12.* Steric Effects on the Intensity Ratios of the (M − 92)/(M − 106) Ions in the Mass Spectra of Carotenoids

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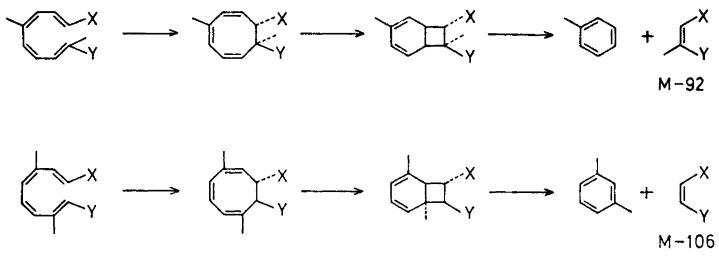
Steric factors are shown to allow rationalisation of hitherto unexplained variations of the ratio (R) of the (M − 92)/(M − 106) ions in the mass spectra of C_{50}-carotenoids. It is suggested that this ratio may be used to provide information about the position of the extra prenyl groups relative to the chromophoric system in acyclic C_{50}-carotenoids.

Characteristic ions at M − 92 and M − 106 mass units are observed in the mass spectra of virtually all carotenoids.[1-4] These ions are attributed to species where six consecutive carbon atoms of the conjugated chain and the substituents carried by these atoms have been extruded. The mechanism shown in Scheme 1 has been proposed for the formation of both M − 92 and M − 106 mass unit species and may be applied to their genesis by either direct electron bombardment or through the intermediacy of prior thermal decomposition.[5,6]

The values obtained for the intensity ratio (R) of the (M − 92)/(M − 106) ions can be related to the chromophoric system present in most cases.[2,6] In particular, in the case of C_{40}-carotenoids lacking substituents directly conjugated to the acyclic chromophore, the R-values found decrease as the number of double bonds in the acyclic chromophore (DB) increases from 9 to 13; representative examples and the observed limits for R are cited in Scheme 2.[2] The R-values found when carbonyl or aromatic functions are directly conjugated to the acyclic chromophore vary from those found in the above case, but may be rationalised in terms of the type of substitution present.[6] The ratio R may thus be used to obtain information about the chromophore of C_{40}-carotenoids.

RESULTS AND DISCUSSION

The R-values found with C_{45}- and C_{50}-carotenoids are often markedly different from those obtained with C_{40}-carotenoids having the same chromophore.[7] Consideration of work [8] on the responsibility of steric factors, particularly



Scheme 1. Proposed mechanism for the formation of M − 92 and M − 106 mass unit species found in the mass spectra of carotenoids.[5,6]

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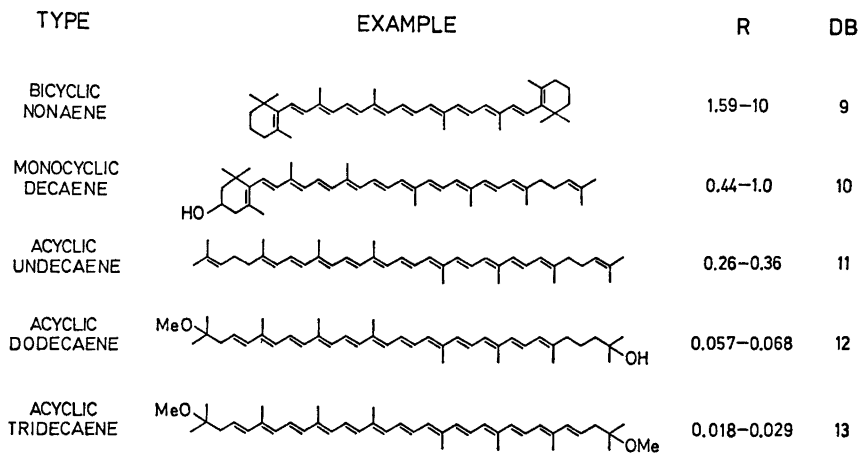
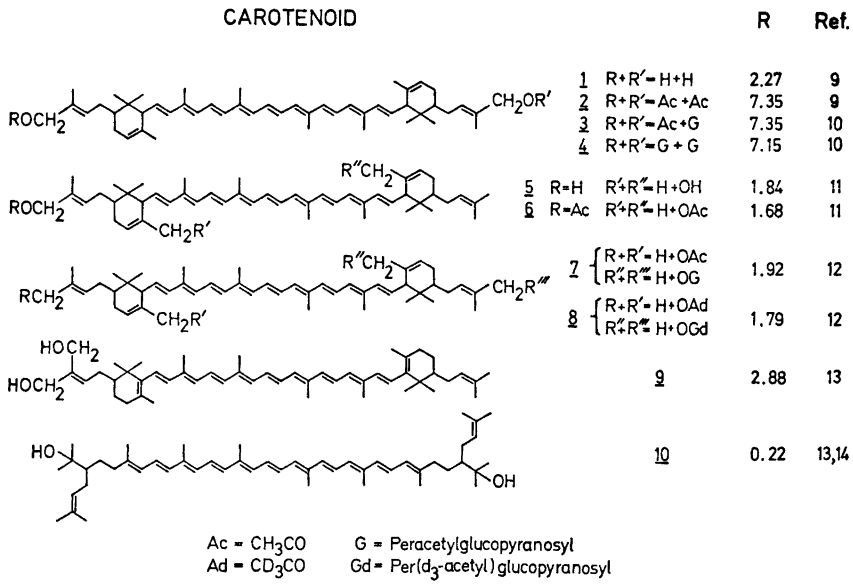


Scheme 2. Range of values for the intensity ratio (R) of the $(M-92)/(M-106)$ ions in the mass spectra of C_{40}-carotenoids having various numbers of double bonds (DB) in the acyclic chromophore. A typical example of each structural type is shown.[2]

end group bulk (see Fig. 1), for variations in this intensity ratio in the case of C_{40}-carotenoids suggested that steric effects might also be of decisive importance in the present case.

The end groups found in carotenoids with supernumerary carbon atoms may be categorised according to whether the additional prenyl unit is immediately adjacent to the acyclic chromophore or not. Those compounds (*1–10*) shown in Scheme 3 have only end



Scheme 3. Observed values for the intensity ratio (R) for C_{50}-carotenoids showing R-values similar to those found in C_{40}-carotenoids. The compounds *1–9* have nine double bonds in the acyclic chromophore ($DB=9$), while the compound *10* has $DB=11$.

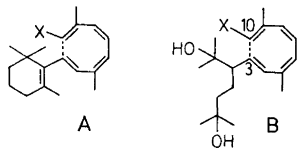
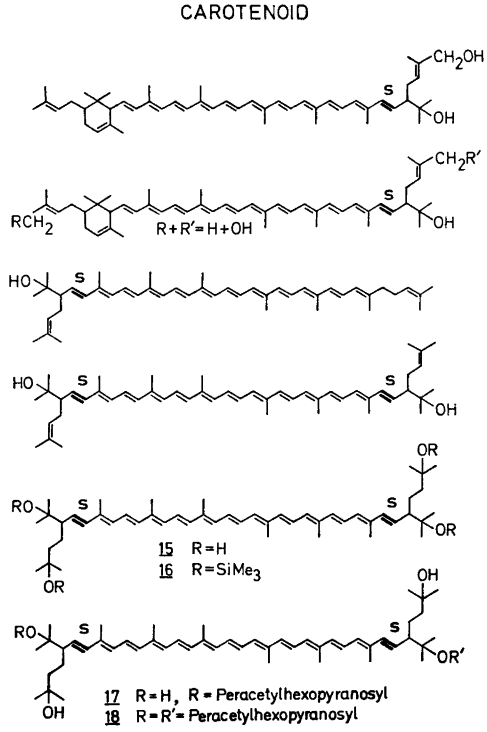


Fig. 1. Steric conflict in the cyclisation process required to provide M − 106 mass unit species by rearrangement of the terminal double bond of the acyclic chromophore in the presence of (*A*) cyclic end groups,[8] and (*B*) acyclic end groups carrying an additional prenyl group.

groups belonging to the latter category and all show values [9–14] of the ratio (*R*) close to those found with C_{40}-carotenoids having the same *DB*-values, *cf.* Scheme 2. The *R*-values are thus normal and in agreement with the structural classification of these compounds (*1 – 10*) as remotely-substituted C_{40}-carotenoids.

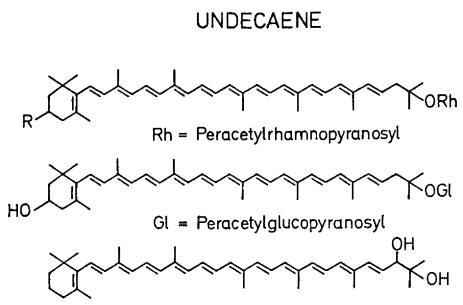
The compounds *11 – 18*, shown in Scheme 4, all contain at least one end group where the extra prenyl group is carried by the carbon atom immediately adjacent to the terminus of the conjugated chain. Before examining the observed *R*-values [7,13–15] for these compounds it should be noted that the position of the methyl groups carried by the conjugated chain is known to be critical in determining these values.[8,16] The compounds *11* and *12* [7,18] are thus not directly comparable to the usual C_{40}-carotenoid undecaenes which have symmetric chromophoric systems carrying six methyl groups, and must be compared with monocyclic undecaenes carrying five methyl groups on the aliphatic polyene chain. Available data [17,18] for monocyclic C_{40}-carotenoids with $DB = 11$ are compiled in Scheme 5 with *R*-values (0.052 – 0.081) considerably lower than for the acyclic undecaenes (0.26 – 0.36).

Examination of the *R*-values [7,13–15] for the compounds *11 – 18* reveals that in all cases the observed values are considerably higher than



CAROTENOID	DB	R	RA	RB	Ref.
11	11	0.39	0.052–0.081	0.44–1.0	7,13
12	11	0.23	0.052–0.081	0.44–1.0	7,13
13	12	0.25	0.057–0.068	0.26–0.36	7,13
14	13	0.11	0.018–0.029	0.26–0.36	7,13
15	13	0.23	0.018–0.029	0.26–0.36	14,15
16	13	0.25	0.018–0.029	0.26–0.36	7,14
17	13	0.30	0.018–0.029	0.26–0.36	15
18	13	0.26	0.018–0.029	0.26–0.36	15

Scheme 4. *R*-values for C_{45} and C_{50}-carotenoids having at least one acyclic end group with a sterically hindered double bond (*s*). *DB* indicates the length of the acyclic chromophore and *RA* the range of *R*-values found in C_{40}-carotenoids having this chromophoric system. *RB* gives the range of values expected for the ratio (*R*) in compounds lacking the sterically hindered double bond(s).



	R	Ref.
R = H	0.065	17
R = OH	0.081	17
	0.052	17
	0.057 *	18

[* Average Value]

Scheme 5. *R*-values for some monocyclic carotenoid undecaenes ($DB = 11$). The *R*-value for the diol was redetermined for this investigation.

those found for C_{40}-carotenoids with the same chromophore. Thus, the formation of the M − 106 species is less favourable than would be expected by analogy with C_{40}-carotenoids with the same chromophoric system.

The critical factor in extrusion reactions leading to M − 92 and M − 106 mass unit species is believed to be the initial new bond formation.[6] Where the C-2 carbon atom in an acyclic end group carries an extra prenyl group, as with the compounds in Scheme 4, the approach of C-3 and C-10 will be more difficult than in the absence of such substituents. The extrusion modes at more distant sites would be little affected. Thus, the only mode affected by this cause of steric hindrance is one leading to an M − 106 mass unit species and this steric factor may thus be applied to explain the observation that the *R*-values for the compounds *11* − *18* are only slightly lower than those expected for C_{40}-carotenoids lacking the 3,4-double bond. The somewhat lower values may in fact be the result of the higher temperatures needed for volatilisation of C_{45} and C_{50}-carotenoids as compared with those for the C_{40}-compounds: the contribution of thermal genesis is less for the M − 92 than for the M − 106 mass unit species.[16]

The above argument allows rationalisation of the recorded *R*-values for carotenoids with extra prenyl groups. It should thus be possible to use *R*-values for acyclic carotenoids with extra prenyl groups to indicate the position of these extra groups relative to the chromophore. The *R*-values used in this study were obtained from spectra previously published or recorded during previous work on C_{45} and C_{50}-carotenoids.[7,9–15]

EXPERIMENTAL

The spectra of the C_{45} and C_{50}-carotenoids were recorded on an AEI MS 902 mass spectrometer using the direct insertion probe. All spectra were recorded at 70 eV, 4 or 8 KV, and with the ion source at the minimum temperature required to achieve volatilisation (190 − 290 C). The time elapsing between insertion of the probe into the ion source and recording of the spectra was kept to a minimum in order to reduce thermal decomposition as much as possible.

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