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Mass Spectrometry of Carotenoids— In-chain Fragmentations of Deuterium Labelled Carotenoids

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In-chain fragmentations of specifically labelled 7,7′-D_2- (*1*—*3*), 11,11′-D_2- (*4*—*6*) and 19,19′-D_6- (*7*) carotenoids have been studied.

The data support the modified Edmunds-Johnstone mechanism for in-chain eliminations of toluene, xylene, and dimethylcyclodecapentaene, and the previously given ranges for the sites of these eliminations.

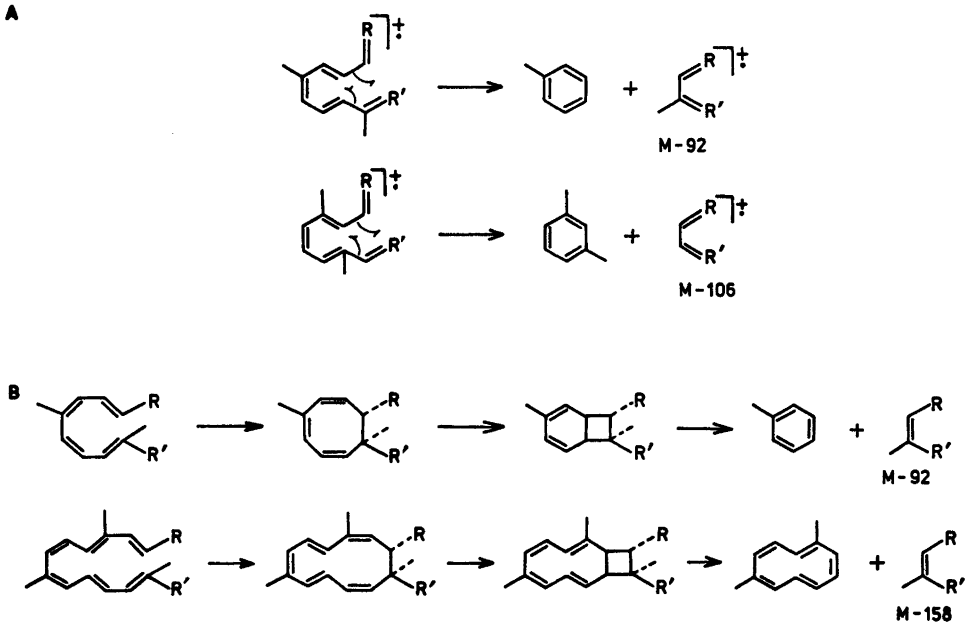
In bicyclic carotenoids the expulsion of dimethylcyclodecapentaene is restricted to the C(10)—C(10′) range.

Rationalization by others of a common M − 79 ion as elimination of a cyclopentadienyl radical from the polyene chain seems valid and appears to be restricted to the C(11)—C(11′) range for bicyclic carotenoids.

Formal loss of methylbenzyne instead of toluene may be general for bicyclic 15,15′-didehydro carotenoids.

Evidence for some in-chain cleavages with hydrogen transfer was also obtained.

Fragmentations leading to losses of 92 (toluene), 106 (xylene), and 158 (dimethylcyclodecapentaene) from the polyene chain due to electron impact induced and thermal processes are con-



Scheme 1.

sidered characteristic of carotenoid mass spectra.[1,2] A comprehensive review on carotenoid mass spectrometry was recently published.[3] Further systematic studies have since appeared.[4–9]

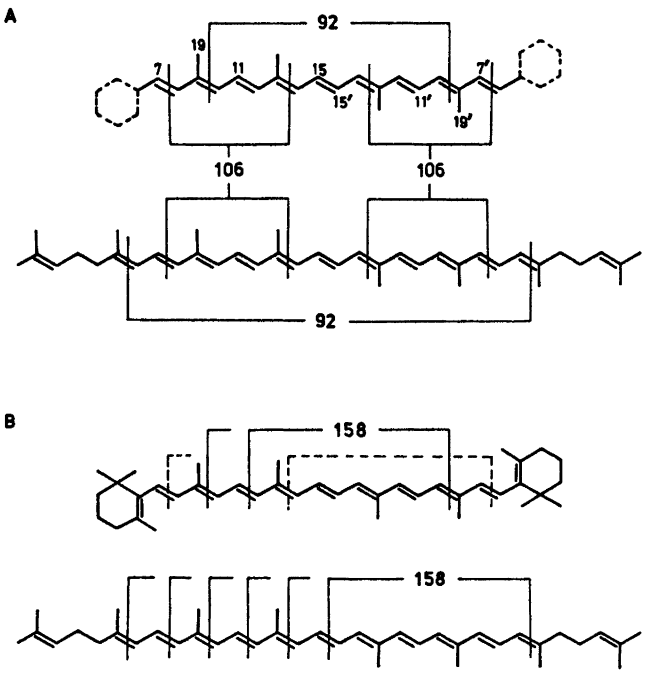
For the eliminations from the polyene chain the alternative mechanisms A[1] and B[4] have been considered. Mechanism A, exemplified in Scheme 1A for the loss of toluene and xylene involves rupture of single bonds, whereas mechanism B implies cleavage of double bonds in the original carotenoid. Mechanism B, as recently indepently modified by Vetter *et al.*[3] and Francis [6] according to the principle of conservation of orbital symmetry,[10] is illustrated for the expulsion of toluene in Scheme 1B. As dicussed by others [6,7] this modification involves an eight-electron conrotatory electrocyclic reaction followed by a disrotatory six-electron electrocyclic reaction and scission of the four-membered transition state. The formation of toluene and dimethylcyclodecapentaene may be envisaged by analogous reactions; transitions through twelve- and ten-electron electrocyclic reactions [3,6,7] being involved in the latter case as illustrated in Scheme 1B.

From consideration of the fragmentation pattern of 15,15′-D_2- and 7,7′-D_2-carotenes mechanism B has been favoured, and the origin of toluene, xylene, and dimethylcyclodecapentaene from acyclic and bicyclic carotenoids has been proposed.[11,12] Scheme 2A, B gives the presumed range for these eliminations. Several modes of elimination are considered involved [4,11,13] as illustrated for the M − 158 elimination in Scheme 2B.

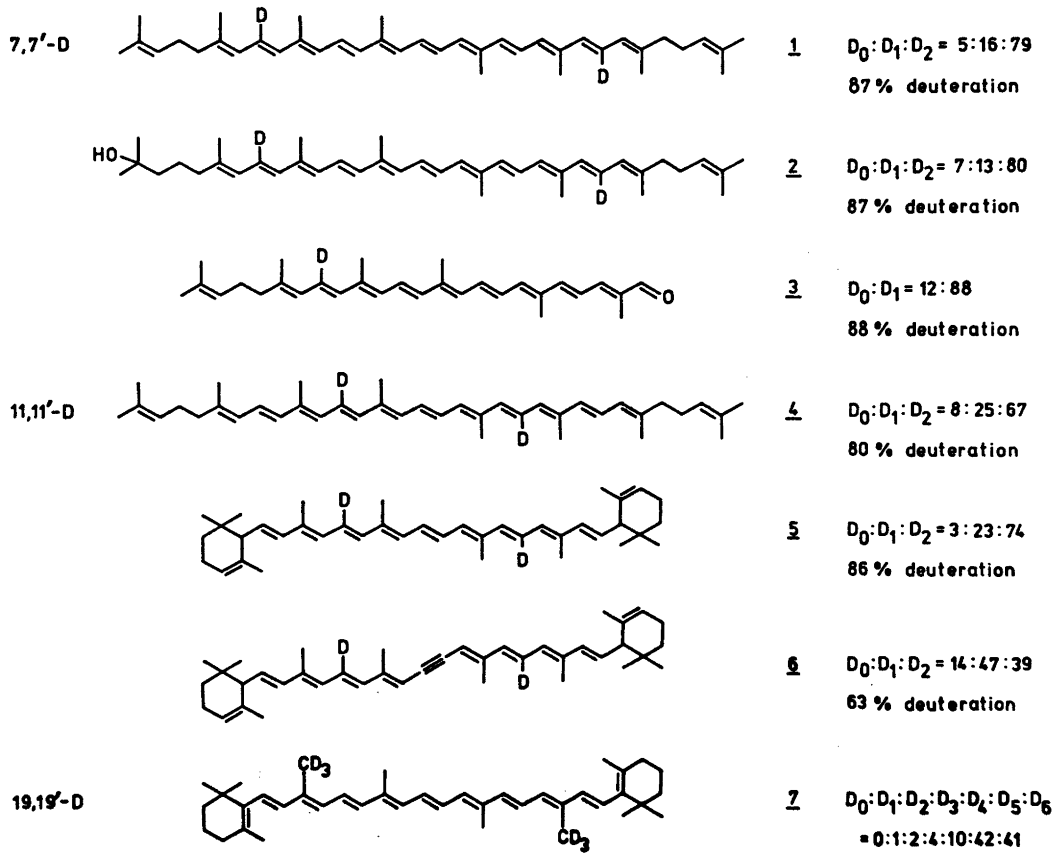
RESULTS AND DISCUSSION

In order to obtain further evidence for these in-chain eliminations 7,7′-D_2-[13], 11,11′-D_2-[14] and 19,19′-D_6-carotenoids [15a] have been synthesized. The carotenoids here studied and their degree of deuteration estimated by mass spectrometry are given in Scheme 3. The ratio of deuterated species has been calculated taking into account ^{13}C isotope contributions, *cf.* Ref. 15b. Percentage deuteration reflects average number of deuterium atoms incorporated relative to the theoretically possible incorporation.

In the following considerations are made as to



Scheme 2.



Scheme 3.

the preferred mechanism (A or B) and sites of in-chain eliminations. The ratio of eliminated, labelled, and unlabelled species, calculated theoretically on the basis of a valid mechanism, should within experimental error agree with values calculated from observed spectra. Conclusions provide that the rate of elimination be the same from all parts of the aliphatic polyene chain. Also hydrogen-deuterium scrambling through sigmatropic shifts in the mass spectrometer should not take place. This has been considered and rejected.[7,11]

Steric conflicts in the intermediate are considered responsible [1,6,12] for the reduction of the theoretically possible modes of elimination of toluene [11] and dimethylcyclodecapentaene [5] in bicyclic carotenoids. Such limits become obvious when figures obtained for a given compound do not fit a generally preferred mechanism.

Mechanism and range for elimination of toluene, xylene and dimethylcyclodecapentaene. Taking into consideration all possible modes of elimination of toluene, xylene, and dimethylcyclodecapentaene by mechanisms A and B the calculated and observed ratios of deuterium incorporation in the expelled fragments from *1*, *2*, *4*, *5*, and *7* are given in Table 1.

For the 7,7'-D_2-compounds *1* and *2* the results for toluene and xylene formation is consistent with those previously obtained for acyclic 7,7'-D_2-carotenoids [11] in favour of mechanism B. The deuterium incorporation in the expelled toluene and xylene from the 11,11'-D_2-carotenes *4* and *5* also shows a clear preference for

Table 1. Calculated and observed ratios for deuterated and non-deuterated toluene, xylene, and dimethylcyclodecapentaene, based on examination of ions derived from the molecular ions of carotenoids *1*, *2*, *4*, *5*, and *7* by loss of these fragments.

Carotenoid		Toluene $D_0:D_1:D_2:D_3$			Xylene $D_0:D_1:D_2:D_3$			Dimethylcyclodecapentaene $D_0:D_1:D_2:D_3$		
		Observed	Calc. mech. A	Calc. mech. B	Observed	Calc. mech. A	Calc. mech. B	Observed	Calc. mech. A	Calc. mech. B
Acyclic	7,7′-D_2-lycopene (*1*)	65:35:0:0	50:30:0:0	67:33:0:0	100:0:0:0	60:40:0:0	100:0:0:0	59:41:0:0	43:57:0:0	67:33:0:0
	7,7′-D_2-rhodopin (*2*)	70:30:0:0	50:50:0:0	67:33:0:0	100:0:0:0	60:40:0:0	100:0:0:0	—	—	—
	11,11′-D_2-lycopene (*4*)	38:62:0:0	0:100:0:0	33:67:0:0	0:100:0:0	60:40:0:0	0:100:0:0	0:100:0:0	0:86:14:0	0:100:0:0
Bicyclic	11,11′-D_2-ε-carotene (*5*)	37:63:0:0	0:100:0:0	50:50:0:0	0:100:0:0	33:67:0:0	0:100:0:0	0:100:0:0	0:80:20:0	0:100:0:0[a] 0:100:0:0[b]
	19,19′-D_2-β-carotene (*7*)	100:0:0:0	50:0:0:50	100:0:0:0	0:0:0:100	33:0:0:67	0:0:0:100	100:0:0:0	20:0:0:80	50:0:0:50[a] 100:0:0:0[b]

[a] Assuming C(8)—C(8′) range of elimination. [b] Assuming C(10)—C(10′) range of elimination.

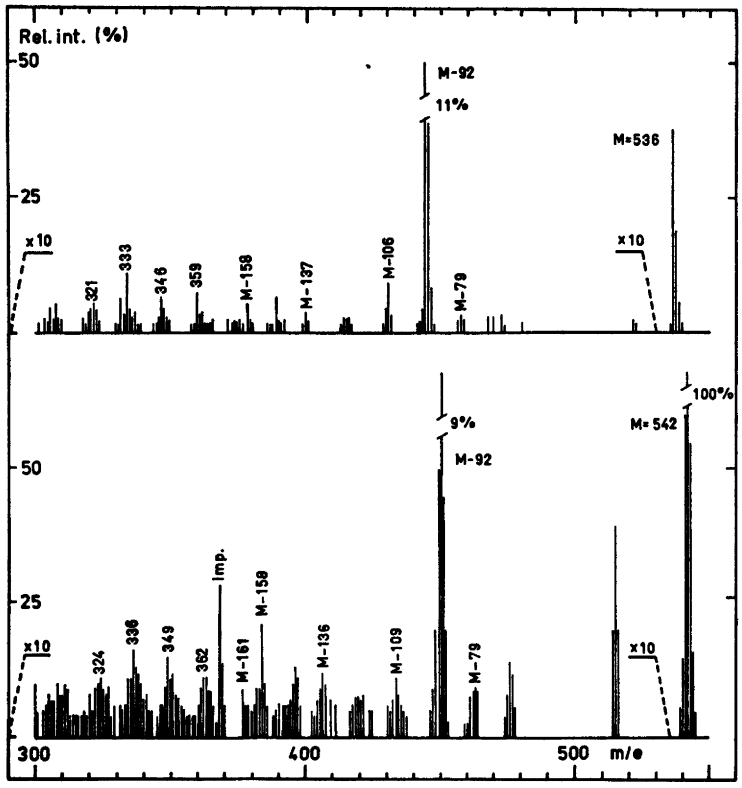


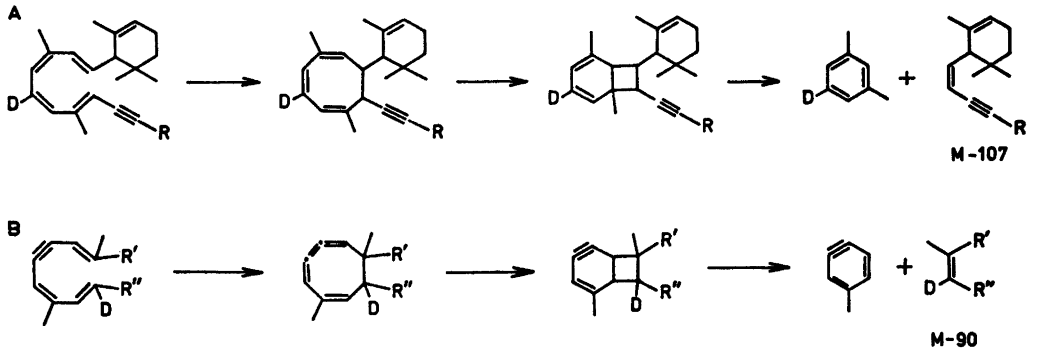
Fig. 1. Mass spectra of 19,19′-D_6-β-carotene (*7*, lower curve) and undeuterated β-carotene (upper curve).

mechanism B. The preference is still more obvious for the most heavily deuterated test compound, 19,19′-D_6-β-carotene (*7*), judged by the data for toluene and xylene in Table 1 and Fig. 1.

Considered jointly these results for toluene and xylene clearly support mechanism B, rather than A, and the previously assumed ranges for the origin of these species.

Regarding the origin of the less abundant M − 158 ion the possible modes of elimination by mechanism B are given in Scheme 2B. Satisfactory agreement is observed (Table 1) for mechanism B and the C(6) − C(6′), range for acyclic carotenoids. However, the range appears to be limited to C(10) − C(10′) in the bicyclic series, if the reasonable assumption is made that mechanism B also is valid here. Thus no loss of trideuterio-dimethylcyclodecapentaene (161 mass units) is observed from 19,19′-D_6-β-carotene (*7*). This situation was already suggested in previous work [11] and is later documented by Brzezinka [5] on the basis of results for 11,12,-11′,12′-deuterated carotenoids. The steric argument previously advanced [12] and further elaborated [3,6,7] is likely to be valid in this case, see Scheme 1B.

Eliminations from 15,15′-didehydrocarotenoids. The fragmentation pattern of the acetylenic analogue *6* of 11,11′-dideuterio-ε-carotene (*5*) was studied. It has previously been claimed that a triple bond in 15,15′-position totally inhibits the loss of toluene and xylene.[3] According to mechanism B and the ranges given in Scheme 2 for toluene and xylene eliminations, this should be true only for the toluene case (Scheme 4A). However, a small peak at M − 90, ascribed to the loss of methylbenzyne has previously been observed.[3,16,17] This loss may also be rationalized by mechanism B, although this implies a



Scheme 4.

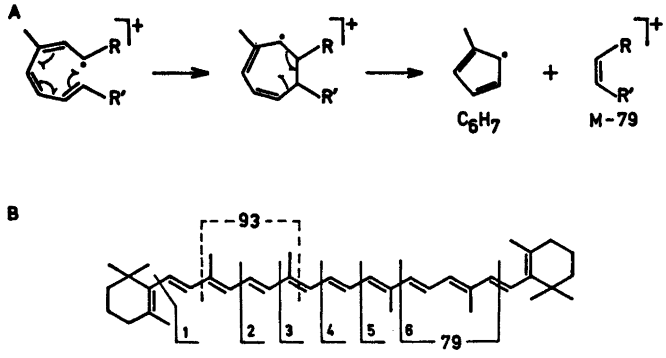
strongly deformed, energetically unfavourable transition state (Scheme 4B). The 11,11'-labelled acetylenic compound *6* should according to mechanism B and the ranges given in Scheme 2 give rise to monodeuterated xylene and undeuterated methylbenzyne. Indeed M − 107 and M − 90 ions were observed.

An M − 156 peak has previously been reported for undeuterated 15,15'-didehydro-β-carotene,[5] and the expected M − 158 peak for the 11,11'-D_2-15,15'-didehydro compound *6* was observed. It is also mentioned that the M − 15 peak, usually encoutered in the spectra of 15,15'-didehydro compounds,[5] was also observed for *6*.

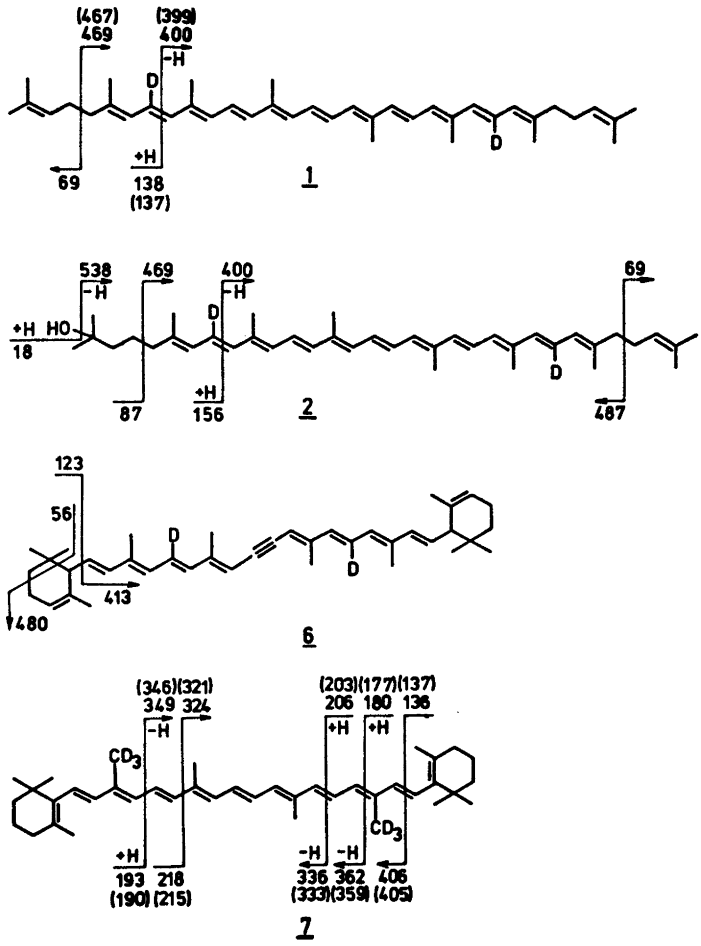
Apo-carotenoids. Apo-carotenoids, here represented by 7-D-8'-apolycopenal (*3*), Scheme 3, are known to give weak and inconsistent M − 92 and M − 106 ions.[16] Only very weak M − 92 and M − 106 ions were observed for *3*, not suitable for mechanistic considerations.

Mechanism for elimination of methylcyclopentadienyl radical. It was early recognized that in addition to M − 92, M − 106 and M − 158 ions a less abundant M − 79 ion is characteristic of carotenoid mass spectra. A methylcyclopentadienyl radical was considered the species involved.[2] Kjøsen [7] has recently rationalized the formation of this common M − 79 ion as loss of a methylcyclopentadienyl radical from the polyene chain, also explaining the formation of M − 78 and M − 80 ions from a common seven-membered transition state (*8*), here cited in Scheme 5A for the loss of 79 mass units.

Six alternative modes of eliminations by this mechanism for the bicyclic case are illustrated in Scheme 5B. Particularly modes 1 and 6 are considered less likely due to steric hindrance, leaving the C(11) − C(11') range as likely site of elimination. Only the D_6-model compound has sufficient number of labels to provide information in this case. It appears from the mass spectrum of 19,19'-D_6-β-carotene (*7*), as compared with that of undeuterated β-carotene, Fig. 1, that the fragment lost is undeuterated. This



Scheme 5.



Scheme 6.

may support the origin suggested by Kjøsen [7] of the M − 78, M − 79, and M − 80 ions, and the C(11) − C(11′) range of expulsion in the bicyclic case.

In acyclic undecaenes such as lycopene the entire C(6) − C(6′) range is expected to serve as sites for these eliminations.

In-chain cleavages. In-chain cleavages are not abundant amongst carotenoids of type *1*, *2*, *4* − *7*.[3] However, unlabelled *β*-carotene and 19,19′-D_6-*β*-carotene (*7*) showed fragment ions consistent with the in-chain cleavages given in Scheme 6, generally occurring with hydrogen transfer. Values in parenthesis refer to unlabelled compounds. Some of these cleavages have not been previously reported.[3,8] Cleavage of the 7-double bond with hydrogen transfer to the smaller, uncharged fragment was also confirmed for unlabelled and labelled lycopene (*1*) and indicated for labelled rhodopin (*2*).

EXPERIMENTAL

The syntheses of the compounds studied are described elsewhere.[13–15] 11,11′-D_2-15,15′-didehydro-*ε*-carotene (*6*) was here prepared in small scale by a procedure analogous to that used for *7*, using an acetylenic center-piece. *6* had *m/e* 536 (M), M − 15, M − 56, M − 90, M − 107 M − 123 (*cf.* Scheme 6), M − 158 and no M − 91, M − 92 or M − 93 ions.

Mass spectra were recorded on an AE1 MS 902 mass spectrometer with direct insertion probe. Spectra were recorded at 70 eV, 6 kV

and with the ion source at minimum temperature required to achieve vapourization (190 – 200°C).

The accuracy of the present intensity ratio calculations depends on absolute peak intensity and is estimated to *ca.* ± 5 % in most cases.

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