Mass Spectrometric Studies of Carotenoids

4.* In-chain Elimination Reactions

H. KJØSEN and S. LIAAEN-JENSEN

Organic Chemistry Laboratories, Norwegian Institute of Technology, University of Trondheim, Trondheim, Norway

C. R. ENZELL

Chemical Research Department, Swedish Tobacco Co., S-104 62 Stockholm, Sweden

In-chain elimination reactions leading to the formation of $M-92$, $M-106$, and $M-158$ ions, which give rise to significant peaks in most carotenoid spectra, have been studied with the aid of acyclic and bicyclic carotenoids labelled with deuterium in the 7,7'-positions. The origin of the toluene, xylene, and dimethylcyclododecapentaene species eliminated is discussed. The results are compatible with the mechanism presented by Edmunds and Johnstone for the corresponding thermal reactions.

Initial mass spectrometric studies by Schwieter *et al.*[1] of carotenes have shown that these compounds give rise to prominent $M-92$ and $M-106$ ions, which were assigned to the loss of toluene and xylene from the central chain of the molecule. The mechanism first suggested for these eliminations involved cleavage of single bonds.[1] It has been demonstrated in earlier papers of this series [2,3] that these reactions are characteristic of carotenoids and also that $M-158$ ions, associated with the loss of $C_{10}H_8(CH_3)_2$ from the central chain of the molecular ion, are frequently encountered. Moreover, the intensity ratio of the $M-92$ *versus* the $M-106$ peaks has been correlated with the number of conjugated double bonds in the central chain.[2]

In view of the above findings it was of interest to study these reactions in further detail, and the present paper deals with the examination of acyclic and bicyclic carotenoids, labelled with deuterium in the 7,7'-positions. A preliminary account of some of these results has been given elsewhere.[4] Coincidently with these studies Schwieter *et al.*[5] investigated the in-chain elimination reactions by means of carotenes labelled with deuterium in the 15,15'-positions.

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SYNTHESIS AND PROPERTIES OF LABELLED COMPOUNDS

The bicyclic aryl carotenes $7,7'-d_2$-renierapurpurin (7) and $7,7'-d_2$-iso-renieratene (13) were synthesized according to Scheme 1. The 2,3,4-trimethyl-benzoic acid (1), obtained from the corresponding benzyl alcohol [6,7] by chromic acid oxidation,[8] was reduced to the alcohol 2 with lithium aluminium deuteride. The labelled alcohol (2) was converted to the bromide (3) by means of phos-phorus tribromide, and subsequent treatment with triphenylphosphine gave the corresponding Wittig salt (4). The phosphorane (5) obtained on treatment of 4 with butyl lithium was condensed with crocetindial (6) to $7,7'-d_2$-reniera-purpurin (7). The 2,3,6-trimethylbenzoic acid (8), prepared from 1-bromo-2,3,6-trimethylbenzene via the Grignard reagent,[9] was subjected to the same sequence of reactions to give $7,7'-d_2$-isorenieratene (13).
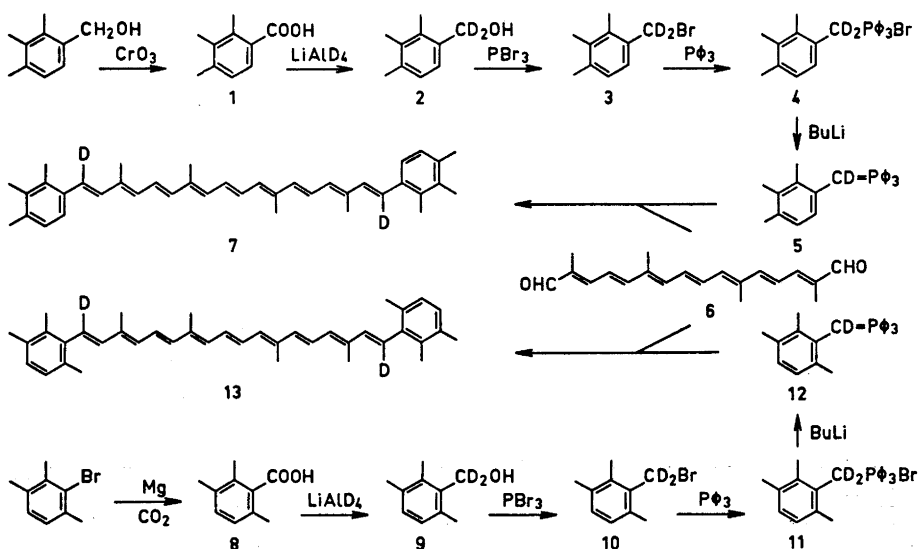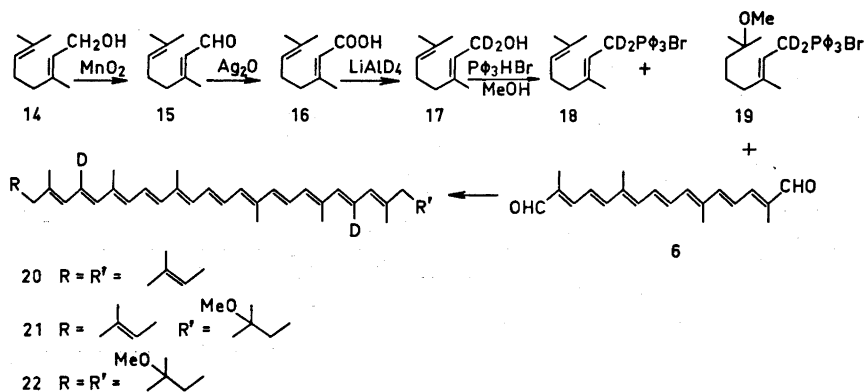

Scheme 1

The total synthesis of unlabelled isorenieratene has previously been effected via three different routes by Yamaguchi,[10] Khosla and Karrer,[11] and Cooper et al.[7] Unlabelled renierapurpurin has been synthesized by Yamaguchi[12] and Cooper et al.,[7] and our synthesis followed in principle that of the latter authors.

The deuterium incorporation into the benzylic alcohols 4 and 9 and the bromides 5 and 10 was quantitative. However, the incorporation in the final products (7 and 13) was lower and decreased during the isolation and chro-matographic purification, suggesting that the benzylic hydrogens can undergo exchange.

The synthesis of the acyclic compounds $7,7'-d_2$-lycopene (20), 1-methoxy-1,2-dihydro-$7,7'-d_2$-lycopene (21), and $7,7'-d_2$-3,4,3',4'-tetrahydrospirilloxanthin

Scheme 2

(22) was accomplished as depicted in Scheme 2. 1,1-d_2-Geraniol (17) was produced from geraniol (14) by stepwise oxidation with manganese dioxide and silver oxide via citral (15) to geranic acid (16), followed by reduction with lithium aluminium deuteride. The latter alcohol (17), when reacted with triphenyl phosphonium bromide in methanol, gave the corresponding Wittig salts (18 and 19) in about equal amounts.[13] The mixed phosphoranes, obtained on treatment with butyl lithium, were condensed with crocetin dial (6), and furnished a mixture of the products 20, 21, and 22, which were separated by chromatography.

The total synthesis of unlabelled lycopene has previously been performed by several alternative routes.[14] Two total syntheses of 3,4,3',4'-tetrahydrospirilloxanthin have also been published,[15,16] whereas the synthesis of 1-methoxy-1,2-dihydrolycopene is not yet reported. The deuterium incorporation in these carotenoids was far more satisfactory than in the aryl carotenes. The 220 Mc/sec PMR spectra of 20, 21, and 22, compared with the spectrum of unlabelled lycopene,[5] confirmed the location of the two deuterium atoms in 7,7'-position. Thus the olefinic protons at C-6, C-6' now give rise to a sharp singlet at 4.14 τ, while in unlabelled lycopene they exhibit a characteristic doublet at τ 4.1. Only one report has previously been published on infrared spectra of deuterated carotenoids, namely by Strain et al.[17] on fully deuterated α-carotene, β-carotene, and lutein. Except for weak C−D stretching vibrations, the 7,7'-d_2-derivatives studied here deviated mainly from those of the corresponding non-deuterated carotenoids by a weak absorption at 923 cm^{-1}, tentatively ascribed to a monodeuterated trans double bond.

According to expectation, other physical properties of the d_2-derivatives, such as chromatographic properties and visible light absorption spectra, did not differ significantly from those of the non-deuterated carotenoids. The lower extinction coefficients and melting points observed were caused by a lipid impurity derived from the petroleum ether used. More marked differences in physical properties between fully deuterated and undeuterated carotenoids have been reported by Strain et al.[17]

MASS SPECTROMETRIC RESULTS AND DISCUSSION

Examination of the bicyclic aryl carotenes (7 and 13) shows that no deuterium was present in the toluene and xylene species eliminated. It follows, if the reasonable assumption is made, that both reactions involve loss of six consecutive, trigonally hybridised carbons, that toluene is derived exclusively from the $10-10'$ range, and xylene exclusively from the $8-8'$ range.

In the case of the acyclic compounds (20, 21, and 22) no deuterium was present in the xylene species eliminated, showing that elimination of xylene is restricted to the same range as in the bicyclic compounds. Of the toluene species, however, the d_1-derivative represented about 35 %, while the non-deuterated species accounted for about 65 %.

Results obtained for $15,15'$-d_2-β-carotene, $15,15'$-d_2-lycopene and the corresponding unlabelled compounds by Schwieter et al.[5] show that in the labelled bicyclic compound the loss of toluene involves partly the d_2-species (40 %) and partly the d_1-species (60 %). The xylene eliminated, however, contained no label, while the dimethylcyclodecapentaene contained both deuterium atoms. The labelled aliphatic derivative gave essentially the same results, with the exception that loss of unlabelled toluene is also observed.

It follows, when the results for the $7,7'$-d_2-derivatives are taken in conjunction with those for the $15,15'$-d_2-compounds, that the elimination of toluene and xylene is limited to the parts of the polyene chain indicated in Scheme 3. Loss of $C_{10}H_8(CH_3)_2$ seems to occur from the same parts of the polyene chain as toluene, but the corresponding peaks are less intense and the evaluation of the data is in this case less certain.
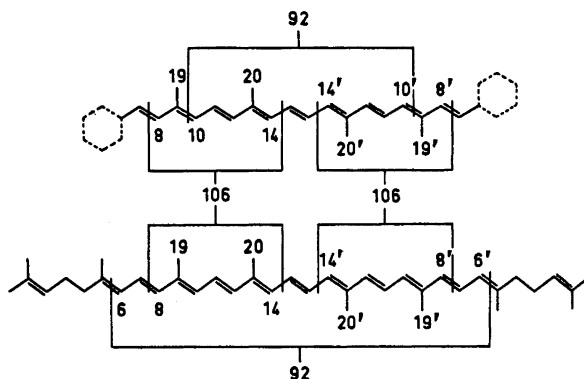
Scheme 3

On the basis of the results obtained for the $15,15'$-d_2-derivatives, Schwieter et al.[1] have suggested that the common losses of 92, 106, and 158 mass units in carotenoid mass spectra occur by the same mechanism as that previously proposed by Edmunds and Johnstone [18] for the thermal elimination of toluene and xylene from carotenoids, and that the 158 fragment is 1,6-dimethyl-

cyclodecapentaene. The present results, summarised in Table 1, are fully consistent with this mechanism, which is depicted in Scheme 4 for the case of xylene elimination from β-carotene.
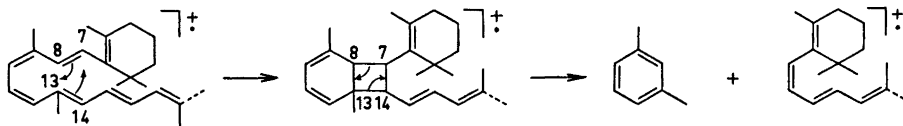
Scheme 4

Table 1. Calculated and observed ratios for deuterated and non-deuterated toluene and xylene, based on examination of ions derived from the molecular ion of $7,7'-d_2$-carotenoids by loss of these fragments.

Carotenoids	Species lost	No. of possible sites of elimination	Calculated $d_1:d_0$	Observed $d_1:d_0$
Bicyclic	Toluene	4	0:4	0:4
	Xylene	2	0:2	0:2
Acyclic (lycopene chromophore)	Toluene	6	2:4	2:4
	Xylene	2	0:2	0:2

It follows from the present findings (*cf.* Scheme 3), that it should be possible to differentiate between substitution in the 19(19') and 20(20') methyl groups in bicyclic carotenoids on the basis of the mass shifts observed for products formed in the in-chain elimination reactions, provided that these are not inhibited by the substitution. Such differentiation is obviously impossible in the acyclic series.

EXPERIMENTAL

Materials and methods. Paper chromatography was made on Schleicher and Schüll Nos. 287 (kieselgur) and 288 (aluminium oxide), and Whatman AH81 (aluminium hydroxide) papers.

In reactions, analytical grade and, for chromatography, distilled technical grade solvents were used.

Visible light absorption spectra were recorded on a Coleman Hitachi 124 spectrometer, IR spectra on a Perkin Elmer 257 spectrometer, and NMR spectra on a Varian A60-A spectrometer in $CDCl_3$, if not stated otherwise. Spectra of *20, 21,* and *22* were also recorded on a Varian HR-220 spectrometer. Mass spectra were obtained on an AEI MS902 spectrometer (70 eV, ion source temperature 230—260°), except for *13,* where an LKB 9000 spectrometer (70 eV, ion source 290—310°, probe 100—200°) was used. For the reaction intermediates, only diagnostically significant spectral properties are quoted. Melting points were determined with an Electrothermal melting point apparatus and are uncorrected.

7,7'-d_2-Renierapurpurin (7)

2,3,6-Trimethylbenzoic acid (1). 2,3,6-Trimethylbenzyl alcohol (4 g), prepared from hemimellitene as previously described,[16] was oxidized to *1* by means of Jones reagent;[8] yield 4.3 g (98 %) *1* on recrystallization from $CHCl_3$; m.p. 165° (reported [19] 167.5°); ν_{max} (KBr) 3500 − 2500 (OH, CH), 1670 (C = O); *m/e* 164 (100 %, M).

2,3,4-Trimethyl-d_2-benzyl alcohol (2). *1* (2.5 g) in dry ether was reduced with $LiAlD_4$ for 5 h at room temperature. The product was isolated in the usual manner, acidic components being removed by extraction with aqueous alkali; yield 1.56 g (68 %) *2*; m.p. 44° (reported [7] 48.5 − 49.5° for the nondeuterated derivative); ν_{max} (liq.) 3320 (OH), 2200, 2090 (CD) cm^{-1}; τ 2.95 s (2H, aromatic), 7.71 s (2 CH_3), 7.79 s (CH_3), 8.43 s (CD_2OH) and no CH_2OH resonance.

2,3,4-Trimethyl-d_2-benzyl bromide (3) was prepared from *2* (1.5 g) by the procedure of Cooper *et al.*[7] for the non-deuterated derivative; yield 1.99 g (93 %) *3*; colourless needles m.p. 28° (non-deuterated compound isolated as a crude oil [7]); ν_{max} (liq.) no OH freq. τ 2.94 d, 3.10 d ($J = 8$ cps, 2H, aromatic), 7.70 s, 7.73 s, 7.82 s (3 CH_3) and no CH_2 resonance.

2,3,4-Trimethyl-d_2-benzyltriphenylphosphonium bromide (4) was prepared from *3* (1.99 g) by the procedure of Cooper *et al.*[7]; yield 3.94 g (89 %) *4*; m.p. 215 − 220° (reported [7] 222 − 223° for the non-deuterated compound).

7,7'-d_2-renierapurpurin (7) was prepared from *4* (1.4 g) and crocetindial (*6*, 148 mg) by the procedure of Cooper *et al.*[7] The reaction mixture was partitioned between CS_2 and 90 % aqueous CH_3OH, and the CS_2 concentrate chromatographed on Spence type H alumina activity grade 2 [20] (required eluent 10 % ether in petroleum ether for 7) and rechromatographed on magnesium oxide (benzene). Crystallization from CH_2Cl_2 gave 80 mg *7*; m.p. 233.5 − 233.6° undepressed on admixture with undeuterated renierapurpurin [7] (m.p. 237 − 238°). No chromatographic separation was achieved of *trans* − *7* and undeuterated *trans*-renierapurpurin on kieselgur paper (1 % acetone in petroleum ether), aluminium oxide paper, or aluminium hydroxide paper (5 % acetone in petroleum ether), TLC on kieselgel G ($CHCl_3$ or benzene) or aluminium oxide (0.5 % acetone in petroleum ether). *7* had λ_{max} (petroleum ether) at (447), 468 [$E(1$ %, 1 cm) = 2500] and 497 nm, % III/II [21] = 26, λ_{max} (CS_2) at (477), 504 [$E(1$ %, 1 cm) = 2065] and 544 nm; ν_{max} (KBr) 3040 − 2800 (CH), 1510 (arom C = C), 1440, 1395, and 1370 (CH_3), 1245, 1070, 1025, 1009, 971 (*trans*-CH = CH −), 911 (− CH = CD − ?), 886, 838, 825 (− CH = C −) and 813 (2 adjacent aromatic H) cm^{-1}; τ (CS_2, low solubility) 7.75 s (4 aromatic CH_3), 7.82 s (2 aromatic CH_3), 7.98 s (2 in-chain CH_3), 8.03 s (2 in-chain CH_3); *m/e* 530, 529, 528 (M), 438, 437 (M − 92), 424, 423, 422 (M − 106), 396, 395 (M − 134), 134 (90 %), 133 (100 %), 119, 105, 91; d_0:d_1:d_2:d_3:d_4 = 15:44:33:5:3.

7,7'-d_2-Isorenieratene (13)

2,3,6-Trimethylbenzoic acid (8) was prepared from 1-bromo-2,3,6-trimethylbenzene [22] (19.9 g) by the method of Gilman and Parker,[9] yield 8.8 g (54 %) *8* on crystallization from $CHCl_3$-petroleum ether; m.p. 101 − 103° (reported [23] 105 − 106°); λ_{max} (CH_3OH) 276 nm; ν_{max} (KBr) 3390, 3300 − 2800 (OH, CH), 1690 (C = O), 808 (two adjacent aromatic H) cm^{-1}; τ − 0.62 (COO*H*), 2.90 d, 3.08 d ($J = 8$ cps, 2H, aromatic), 7.64 s, 7.71 s, 7.75 s (3 CH_3); *m/e* 164 (100 %, M).

2,3,6-Trimethyl-d_2-benzyl alcohol (9). *8* (5.0 g) was treated in the same manner as *1* above; yield 1.64 g (35 %) *9* from petroleum ether; m.p. 74 − 75° (reported [7] 84.5 − 85.5° for the undeuterated compound); ν_{max} (liq.) 3320 (OH), 2210, 2100 (CD) cm^{-1}; τ 3.01 s (2H, aromatic), 7.60 s, 7.66 s, 7.71 s (3 CH_3), 8.45 s (CD_2OH) and no CH_2 resonance.

2,3,6-Trimethyl-d_2-benzyl bromide (10). *9* (1.6 g) was subjected to the same procedure as *2*; yield 1.81 g (80 %) *10* (oil); τ 2.99 d, 3.12 d ($J = 8$ cps, 2H, aromatic), 7.65 s, 7.72 s, 7.78 s (3 CH_3) and no CH_2 resonance.

2,3,6-Trimethyl-d_2-benzyltriphenylphosphonium bromide (11) was prepared from *10* (1.81 g) by the same procedure as *4* above; yield 3.01 g (75 %) crude *11*; m.p. 183 − 186°C (reported [7] 243 − 245°C for the undeuterated analogue).

7,7'-d_2-Isorenieratene (13) was prepared by the same procedure as *7* from *11* (1 g) and crocetindial (*6*, 150 mg). Direct precipitation from the CS_2 extract and recrystallization from CH_2Cl_2 gave *13* (lot 1); *m/e* 530, 529, 528 (M); d_0:d_1:d_2:d_3:d_4 = 20:45:28:5:2.

The rest of the carotenoids present in the CS_2 extract (308 mg) were chromatographed on Spence type H alumina activity grade 2 (required eluent for *13* 7 % ether in petroleum ether) and rechromatographed on magnesium oxide (developer: benzene). *13* (homogeneous by TLC on Al_2O_3, 0.5 % acetone in petroleum ether) was crystallized from $CH_2Cl_2 - CH_3OH$; yield 43.2 mg *13* (lot 2); m.p. 175 – 178°, undepressed on admixture with undeuterated isorenieratene (reported [7] m.p. 191 – 192°). *13* could not be separated from the undeuterated analogue in any of the systems described for *7*: λ_{max} (petroleum ether) at (426), 448 [E(1 %, 1 cm) = 2080] and 475 nm, % $D_B/D_{II} = 9$, % III/II = 17, ν_{max} (CS_2) at (456), 479 and 507 nm; ν_{max} (KBr) 3020 – 2800 (CH), 1625, 1520 (arom. $C = C$), 1440, 1380 (CH_3), 1170, 1075, 1030, 1003, 967 (*trans*-CH = CH −), 830 (− CH = C −), and 811 (2 adjacent aromatic H) cm^{-1}; τ (CS_2, low solubility) 3.21 s (4H, aromatic), 3.4 – 4.1 (*ca.* 13 H olefinic) 7.81 s (6 aromatic CH_3), 7.89 s (2 in-chain CH_3), 8.06 s (2 in-chain CH_3); m/e 530, 529, 528 (M), 436 (M − 92), 422 (M − 106), 133 (100 %), 105, 91; d_0:d_1:d_2 = 80:18:2.

7,7'-d_2-L y c o p e n e (*20*), 1 - m e t h o x y -1,2-d i h y d r o-7,7'-d_2- l y c o p e n e (*21*), a n d 7,7'-d_2-3,4,3',4'-t e t r a h y d r o - s p i r i l l o x a n t h i n (*22*).

cis-trans-*Citral (15)* was prepared from geraniol (*14*, 50 g) by MnO_2 oxidation according to Attenburrow *et al.*;[24] yield 48 g estimated by NMR spectroscopy to contain *15* (75 %) and unreacted *14* (25 %).

cis-trans-*Geranic acid (16)*. The above mixture of *15* and *14* (27 g) was oxidized with Ag_2O by the procedure of Bernhauer and Forster.[25] The acidic products were isolated in the usual manner and distilled; yield 7 g (32 %) *16*, b.p. 150 – 154° at 16 mmHg; ν_{max} (liq.) 3300 – 2800 (OH, CH), 1685 (C = O) cm^{-1}; τ − 1.90 (COOH), 4.30 s broad (1H, olefinic), 4.91 m (1H, isopropylidene), 7.81, 7.83 (allylic CH_2 and *trans* CH_3), 8.08, 8.10 (allylic CH_2 and *cis* CH_3), 8.31 s, 8.38 s (isopropylidene CH_3).

d_2-*Geraniol (17)* was prepared from *16* by the procedure used for *2* and *9*; yield 3.04 g (66 %) *17* (oil); ν_{max} (liq.) 3320 (OH), 2200, 2190, 2090 (CD) cm^{-1}; τ 4.57 (1H, olefinic), 4.87 m (1H, isopropylidene), 7.82, 7.88, 7.94 (5H, $CD_2O H$ and 2 allylic CH_2), 8.24 and 8.26 (*cis* and *trans* CH_3), 8.31, 8.37 (2 isopropylidene CH_3) and no CH_2OH resonance.

d_2-*Geranyltriphenylphosphonium bromide (18)* and *(1,1-d_2-7-methoxy-3,7-dimethyl-oct-2-enyl)triphenylphosphonium bromide (19)* were prepared from *17* (3.0 g) by the procedure described elsewhere;[13] yield 4.89 g *18* and *19* (53 %) in a 1:1 ratio (NMR spectrum); m.p. 153 – 158°.

7,7'-d_2-Lycopene (20), 1-methoxy-1,2-dihydro-7,7'-d_2-lycopene (21) and *7,7'-d_2-3,4,3'4'-tetrahydrospirilloxanthin (22)* were prepared from *18* and *19* (1750 mg) and crocetindial *(6,* 150 mg) by the general procedure. Chromatography twice on Spence type H alumina activity grade 2 furnished *20* (75 mg) required eluent 0 – 5 %, *21* (110 mg) required eluent 5 – 7 %, and *22* (35 mg) required eluent 7.5 – 15 % ether in petroleum ether.

7,7'-d_2-Lycopene (20) yield 32.1 mg from ether-CH_3OH; m.p. 140 – 160° (reported [26] 171° for the undeuterated analogue), undepressed on admixture with undeuterated lycopene. No separation from the latter was achieved on kieselgur paper (petroleum ether or 2 % acetone in petroleum ether), aluminium oxide or aluminium hydroxide paper (2 % acetone in petroleum ether), and TLC on kieselgel G (CHCl$_3$ or benzene) or aluminium oxide (1 % acetone in petroleum ether). *20* had λ_{max} (petroleum ether) at 444, 470 [E(1 %, 1 cm) = 2480] and 502 nm, % $D_B/D_{II} = 8$, % III/II = 80; ν_{max} (KBr) 3000 – 2810 (CH), 1620 (C=C), 1458, 1377 (CH_3) 960 (*trans*-CH = CH −), 925 (*trans*-CH = CD − ?), 835 (− CH = C −), and 727 (imp.) cm^{-1}; at 220 Mc/sec τ 3.3 – 4.0 (*ca.* 12H, olefinic), 4.14 s (2H, H-6, H-6'), 4.89 m (2H, isopropylidene), 7.88 (4 allylic CH_2), 8.01 s (4 in-chain CH_3), 8.15 s (2 end-of-chain CH_3), 8.30 s, 8.38 s (4 isopropylidene CH_3), 8.73 (imp.); m/e 538, 537, 536 (M), 469 (M − 69), 459 (M − 79), 446, 445 (M − 92), 432, 431 (M − 106), 119, 106, 105, 92, 91, 69 (100 %); d_0:d_1:d_2:d_3:d_4 = 4:15:75:3:3.

1-Methoxy-1,2-dihydro-7,7'-d_2-lycopene (21). After rechromatography on a kieselgel column (benzene), crystallization from ether-CH_3OH gave 33.8 mg *21*, m.p. 143 – 148°; kieselgur paper $R_F = 0.28$ (petroleum ether) and $R_F = 0.66$ (2 % acetone in petroleum

ether), on aluminium oxide paper $R_F = 0.50$ (2 % acetone in petroleum ether), and by TLC on kieselgel G $R_F = 0.54$ (CHCl$_3$) and $R_F = 0.65$ (benzene). *21* had λ_{max} (petroleum ether) at 444, 470 [E(1 %, 1 cm) = 1965] and 502 nm, % III/II = 77; ν_{max} (KBr) 3020 — 2800 (CH), 1730, 1620 (C=C), 1460 — 1440, 1378, 1367 (CH$_3$), 1083 (OCH$_3$), 959 (*trans*-CH=CH—), 923 (*trans*-CH=CD—?), 830 (—CH=C—) and 727 (imp.) cm^{-1}; at 220 Mc/sec τ 3.3 — 4.0 (*ca.* 12H, olefinic), 4.14 s (2H, H-6,H-6'), 4.89 m (1H, isopropylidene), 6.82 s (OCH$_3$), 7.88 (3 allylic CH$_3$), 8.01 s, (4 in-chain CH$_3$), 8.15 s (2 end-of-chain CH$_3$), 8.30 s, 8.38 s (2 isopropylidene CH$_3$), 8.52 m (*ca.* 4H, 2 CH$_2$), 8.73 (imp.), 8.84 s (—C(CH$_3$)$_2$OCH$_3$); *m/e* 570, 569, 568 (M), 538 (M — 32), 478, 477 (M — 92), 464, 463 (M — 106), 412 (M — 158), 395 (M — 106 — 69), 241, 119, 106, 105, 92, 91, 73, 69 (100 %); d_0:d_1:d_2:d_3 = 4:28:65:3.

7,7′-d_2-3,4,3′,4′-Tetrahydrospirilloxanthin (22). Rechromatography on a column of kieselgel (eluent 30 % CHCl$_3$ in benzene) gave 12.4 mg *22* m.p. 140 — 160° (reported [14] 174° for the undeuterated analogue), undepressed on admixture with the undeuterated compound. No separation was achieved in the systems listed for *20*. *22* had λ_{max} (petroleum ether) at 443, 470 and 501 nm, % III/II = 75; ν_{max} (KBr) 3020 — 2800 (CH), 1632, 1622 (C=C), 1460 — 1440, 1379, 1364 (CH$_3$), 1083 (OCH$_3$), 959 (*trans*-CH=CH—), 923 (*trans*-CH=CD—?), 833 (—CH=C—), and 728 (imp.) cm^{-1}; at 220 Mc/sec τ 3.3 — 4.0 (12H, olefinic), 4.14 s (2H, H-6, H-6'), 6.82 s 2 OCH$_3$), 7.88 m (2 allylic CH$_2$), 8.01 s (4 in-chain CH$_3$), 8.15 s (2 end-of-chain CH$_3$), 8.52 m (4 CH$_2$), 8.72 (imp.), 8.83 s (2 C(CH$_3$)$_2$-OCH$_3$); *m/e* 602, 601 (M), 587 (M — 15), 570 (M — 32), 538 (M — 32 — 32), 523 (M — 79), 510, 509 (M — 92), 496, 495 (M — 106), 478 (M — 92 — 32), 464 (M — 106 — 32), 444, 443 (M — 158), 120, 119, 106, 105, 92, 91, 73 (100 %); 69; d_0:d_1:d_2 = 5:27:68.

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