132. Synthesis and NMR-Spectroscopic Structure Determination of Novel 7,7'-Diphenyl-7,7'-diapocarotenoids

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Wittig reaction of crocetindial (**1**) and benzylidenetriphenylphosphorane (**2**) gave (7E,7'Z)-7,7'-diphenyl-7-7'-diapocarotene (**3**), instead of the previously reported (7E,7'E)-isomer. Similar reaction of 8,9-didehydrocrocetindial (**4**) with **2** yielded the three acetylenic isomers **5a–c** which differ in the configuration of the terminal double bonds. Structures were established by 1D- and 2D-NMR studies. Illustrative spectra and their interpretation are presented. Most chemical shifts of corresponding protons in **3** and **5** are nearly identical, but ^{13}C shifts differ considerably.

Introduction. – Carotenoids are known to be essential for the survival of photosynthetic organisms [1]. Numerous studies [2] have shown that photoprotection involves the transfer of the chlorophyll triplet-state energy to the carotenoid forming a carotenoid triplet state. If the chlorophyll triplet state reacts with oxygen, singlet-state oxygen, a major oxidizing agent of chlorophyll, is formed. Fortunately, carotenoids can also scavenge singlet oxygen. Recent studies examined the structure of the carotenoids that best serve the photoprotect role and found that more efficient triplet-energy transfer occurs when the carotenoids contain polar functional group [3]. The carotenoid molecule must assume the proper geometry in the reaction center so that effcent triplet-energy transfer can take place [3]. It is also known that carotenoids isomerize upon binding to the reaction center, but the relationship between the tendency to isomerize and the polar or nonpolar substituents is not known. Thus, further fundamental studies of the role of substituents are desirable.

A major effort in this laboratory has been to evaluate the substituent effect on the structural [4], optical [5], electrochemical [6], and photochemical [7] properties of naturally occurring and synthetic carotenoids. In order to compare the behavior of highly polar carotenoids, *e.g.*, 7,7'-dicyano-7'-apo-β-carotene [8] [9], with less polar carotenoids, a variety of terminal substituted and non-substituted phenyl analogues was prepared. We report here the synthesis and NMR structure determination of 7,7'-diphenyl-7,7'-diapocarotene (**3**) and of the acetylenic 15,15'-didehydro derivatives **5**. ^1H- and ^{13}C-NMR chemical shifts are compared to those of the mono-phenyl compounds, (7'E)- and (7'Z)-7'-phenyl-7'-apo-β-carotene ((E)-**6** and (Z)-**6**, respectively).

Results and Discussion. – *Syntheses*. The phenyl-substituted 7,7'-diapocarotenoids were synthesized by *Wittig* reaction of the appropriate aldehyde with the phosphorus ylide **2**, which was generated *in situ* by treating benzyltriphenylphosphonium chloride with BuLi (*Scheme*). Treatment of the products from crocetindial (= 8,8'-diapocaroten-

Scheme

3 *(7E,7'Z)*

5a *(7E,7'Z)*

5b[a])   5c[a])

(E)-6[a])   *(Z)*-6[a])
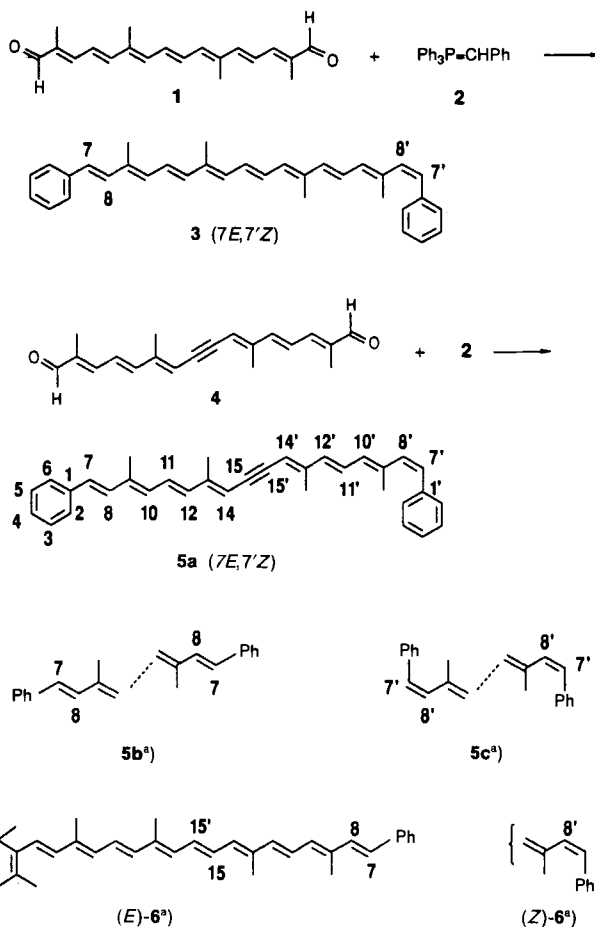
[a])   Arbitrary numbering: atoms near a Ph-substituted terminal double bond are indicated by primed numbers, if
     the configuration is *(Z)* and non-primed numbers, if it is *(E)*.

8,8'-dial; 1) with MeOH gave *(7E,7'Z)*-7,7'-diphenyl-7,7'-diapocarotene (3) as an insoluble solid. Several isomers of compound 3 have been previously prepared [10] [11]. Curiously, the *(7E,7'E)*-diphenyl derivative (m.p. 230 – 31°) was obtained by the *Wittig* reaction [11] under conditions similar to ours (PhLi, Et_2O/CH_2Cl_2, 24 h rather than BuLi, THF/CH_2Cl_2, 1 h). It seems likely that the *(7E,7'Z)*-compound 3 was initially formed but that it isomerized during the subsequent crystallizations (from C_6H_6 and $CHCl_3/EtOH$) [11].

The UV/VIS absorption maxima of compound 3 (*Fig. 1*, dashed line) are the same, within experimental error (± 1 nm), as those of the monophenyl-apo-β-carotene *(E)*-6. This suggests that one of the Ph-substituted double bonds in 3 has the *(E)*-configuration,
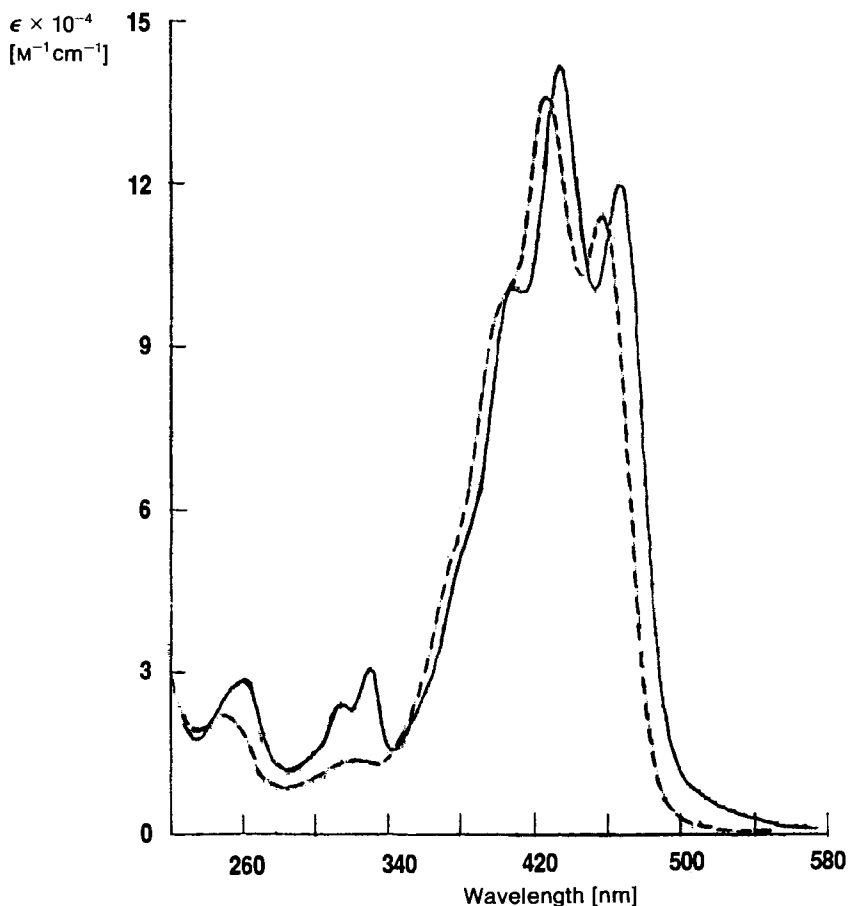
Fig. 1. *UV/VIS Spectra of* **3** *in CCl₄: pure* (– – –) *and after addition of a trace of* I_2 (——)

as it does in (*E*)-**6**, but that the other has the (*Z*)-configuration in which the Ph-substituent is twisted out of the plane of the polyene chain by steric interaction with Me–C(9′). Further, compound **3** shows the optical characteristics (*Fig. 1*) typical of (*Z/E*)-interconversions that occur when solutions of carotenoids are treated with catalytic amounts of I_2 [12]. Equilibrium mixtures are formed, in which, however, the (all-*E*)-isomer generally greatly predominates; (*E*)-isomers absorb at longer wavelength and have somewhat larger extinction coefficients than (*Z*)-isomers. The product(s) obtained by I_2 treatment of **3** show this behavior (*Fig. 1*, solid line); they also give rise to two maxima near 320 nm, which may be due to one or more isomers that have the (*Z*)-configuration at a position other than C(7′). (*Z*)-Isomers containing 10 or 11 double bonds generally show a so-called '*cis*' peak whose maximum occurs *ca.* 140 nm below the longest-wavelength maximum of the corresponding (all-*E*)-compound [12] (the effect of a Ph group is equivalent to that of 1.5 double bonds [10]). The reported absorption spectrum of the (*E,E*)-isomer (in benzene) [10] [11] is nearly identical to that of our isomerized material (in CCl₄).

Condensation of the acetylenic dialdehyde **4** with ylide **2** and purification by column chromatography of the MeOH-insoluble materials afforded a mixture of the three isomers **5a/b/c** (*ca.* 10:4:5). The mono-phenyl derivatives (*E*)-**6** and (*Z*)-**6** were similarly prepared from 8'-apo-*β*-caroten-8'-al and **2** (see [13]).

The structures of **3** and **5a–c** in the mixture were determined by NMR spectroscopy and are in accord with elemental analyses.

NMR Spectral Analyses. The ^{1}H- and ^{13}C-NMR chemical shifts depend on the configuration of the terminal chain double bonds. To simplify comparisons, atoms near a Ph-substituted double bond are given primed numbers if the configuration is (*Z*) and non-primed numbers if it is (*E*), so that all atoms in the symmetrical compound **5b** are non-primed, and those in **5c** are primed. For the mono-phenyl compound (*E*)-**6** this numbering differs from what is customarily used for carotenoids, but (*Z*)-**6** has the usual numbering (see *Scheme*).

Since the ^{1}H-NMR spectrum of **3** displays four separate CH_3 signals of equal intensity, this compound must have an unsymmetrical structure. The chemical shift of one of these signals (1.75 ppm) is similar to that of CH_3–C(9') (1.70 ppm in (*Z*)-**6** (shielding by the *cis*-oriented Ph substituent) and another (2.04 ppm) is the same as that of CH_3–C(9) (2.05 ppm) in (*E*)-**6** (for numbering, see *Scheme*). Assignment of these signals to CH_3–C(9') and CH_3–C(9) is confirmed by the results of nuclear *Overhauser* enhancement (NOE) difference spectra (*Table 1*). As shown in *Fig. 2a*, irradiation at 2.04 ppm enhances a *d* (H–C(7)) and a *dd* (H–C(11)). Since irradiation at 1.98 ppm (*Fig. 2b*) enhances the same *dd*, as well as another (overlapping) *m* (H–C(15)), this signal must be due to CH_3–C(13) (the low-intensity enhancement of the H–C(11') *dd* in *Fig. 2b* is due to partial co-saturation of CH_3–C(13') at 1.96 ppm). Other assignments shown in *Table 1* are similarly derived. Chemical shifts of H–C(8'), H–C(10'), H–C(12), H–C(14), and H–C(14') are obtained from non-overlapping cross-peaks in a COSY [14]
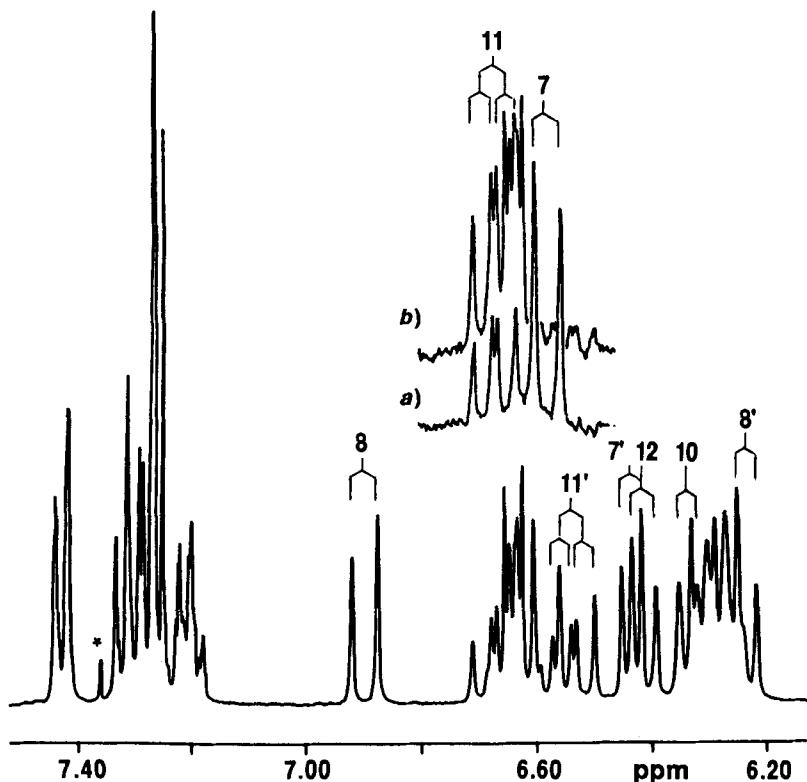
Fig. 2. *Aromatic and olefinic region of ^{1}H-NMR spectrum* (360 MHz) *of* **3** (18 mg/ml CDCl₃) *and NOE difference spectra, irradiating at* a) *2.04 and* b) *1.98 ppm* (the asterisk identifies the C₆H₆ contaminant)

Table 1. *Nuclear Overhauser Enhancements for (7E,7′Z)-7,7′-Diphenyl-7,7′-diapocarotene* (**3**)[a]

Irradiation δ [ppm]	Proton(s)	Enhancement [%] δ [ppm]		Proton(s)
2.04	Me–C(9)	6.67 (*dd*)	8.0	H–C(11)
		6.58 (*d*)	10.4	H–C(7)
1.98	Me–C(13)	6.67 (*dd*)	9.5	H–C(11)
		6.64 (*dd*)	5.7	H–C(15)
1.96	Me–C(13′)	6.54 (*dd*)	7.7	H–C(11′)
		6.63 (*dd*)	4.7	H–C(15′)
1.75	Me–C(9′)	6.54 (*dd*)	8.0	H–C(11′)
		7.26 (*s*)	1.5	H–C(2′), H–C(6′)
6.89	H–C(8)	6.33 (*d*)	2.3	H–C(10)
		7.43 (*d*)	3.2	H–C(2), H–C(6)
7.26	H–C(2′), H–C(6′)	6.44 (*d*)	2.0	H–C(7′)

[a]   360 MHz, 18 mg/1 ml CDCl$_3$. For numbering, see *Scheme*.

spectrum, which shows three-bond (H–C(7′)/H–C(8′), H–C(11)/H–C(12)) and four-bond (H–C(10′)/ CH_3–C(9′), H–C(14)/CH_3–C(13), H–C(14′)/CH_3–C(13′) couplings. H–C(10), already assigned, also shows the four-bond allylic coupling with CH_3–C(9); four-bond coupling was not detected for atoms joined by two C–C bonds, *e.g.*, H–C(8)/CH_3–C(9). Assignment of the remaining chemical shift (H–C(12′)) is made by elimination.

Chemical shifts of H–C(7) to H–C(15) ((*E*)-end) in **3** are the same as those of the corresponding protons in the mono-phenyl compound (*E*)-**6** (*Table 2*); that is, any effects of the different substituents at the other end of the polyene chain are not transmitted beyond the middle of the molecule. On the assumption that the same

Table 2. *¹H-NMR Chemical Shifts* [ppm] *of Phenyl-Substituted Carotenoids in CDCl$_3$*[a]

	3	(*E*)-**6**[b])[c]	(*Z*)-**6**[c]	**5a**	**5b**[b])[d]	**5c**[b])[d]
H–C(7)	6.58	6.57	(6.20)	6.61	6.61	–
H–C(8)	6.89	6.90	(6.14)	6.89	6.89	–
H–C(10)	6.33	6.33	(6.16)	6.31	6.31	–
H–C(11)	6.67	6.67		6.73	6.74	–
H–C(12)	6.42	6.42	(6.37)	6.41	6.42	–
H–C(14)	6.28	6.27		5.75	5.77	–
H–C(15)	6.64	6.63[e])		–	–	–
H–C(15′)	6.63	(6.63)[e])		–	–	–
H–C(14′)	6.25	(6.26)		5.73		5.71
H–C(12′)	6.32	(6.36)	6.32	6.29[e])	–	6.29[e])
H–C(11′)	6.54	(6.66)	6.53	6.59	–	6.58
H–C(10′)	6.28	(6.16)		6.25[e])	–	6.25[e])
H–C(8′)	6.24	(6.14)	6.23	6.23	–	6.23
H–C(7′)	6.44	(6.20)	6.43	6.46	–	6.46
Me–C(9)	2.04	2.05	(1.97)[f])	2.06	2.06	–
Me–C(13)	1.98	1.97[f])	(1.97)[f])	2.12	2.13	–
Me–C(13′)	1.96	(1.98)[f])	1.95[f])	2.10	–	2.09
Me–C(9′)	1.74	(1.97)[f])	1.70	1.76	–	1.7

[a]   At 360 MHz: **3** and (*E*)-**6**, 18 mg/ml; (*Z*)-**6**, 7 mg/ml. At 500 MHz: **5a**–**c**, 10 mg/ml.
[b]   Arbitrary numbering for (*E*)-**6**, **5b**, and **5c** (see *Scheme*).
[c]   Values in parentheses are for protons near the trimethylcyclohexene end group.
[d]   Since **5b** and **5c** are symmetrical molecules, each pair of non-primed and primed protons has the same chemical shift.
[e]   Approximate center of overlapping signals derived from a COSY spectrum.
[f]   Values may be interchanged.

is true for protons near the (Z)-end, some of the chemical shifts of the other mono-phenyl derivative, (Z)-6, are assigned by their similarity to those of the corresponding protons in the diphenyl derivative 3. Since the remaining signals show extensive overlap, they can not be identified. However, protons at primed C-atoms are expected to have the same δ values as in 3, and chemical shifts of protons at non-primed C-atoms of (Z)-6 should be the same as those of protons at primed C-atoms of (E)-6 (shown in parentheses, Table 2). The upfield shifts of the protons on the (Z)-double bond (H–C(7') and H–C(8')) compared to those on the (E)-double bond (H–C(7) and H–C(8)) of 3 parallel the behavior observed in other carotenoids [15] [16]. As expected, the coupling constant of the cis-protons H–C(7') and H–C(8') (J = 12.5 Hz) is smaller than that of the trans-protons H–C(7) and H–C(8) (J = 16 Hz).

A ^{1}H,^{13}C-correlation (HETCOR) [17] spectrum yields all ^{13}C chemical shifts (Table 3), except those due to quaternary C-atoms. These are obtained from a hetero-multiple bond correlation (HMBC) spectrum, using a pulse sequence which maximizes signals arising from 9-Hz (primarily three-bond) coupling [18]. The pertinent region is shown in Fig. 3, in which ^{13}C-signals are identified and cross-peaks are labeled with the protons to which these are

Table 3. ^{13}C-NMR Chemical Shifts of Phenyl-Substituted Carotenoids in CDCl$_3$[a])

	3[b])	(E)-6[c])	(Z)-6[c])[d])	5a–c[e])
C(7)	127.42	127.35	(126.72)	128.12
C(7')	128.77	(126.74)	128.69	129.37
C(8)	133.64	133.65	(137.75)	133.41
C(8')	134.61	(137.75)	134.61	134.37
C(9)	135.52	135.42	(136.11)	136.98, 136.96
C(9')	135.17	(136.14)	135.04	136.71, 136.68
C(10)	133.19	133.22	(130.81)	132.44
C(10')	133.24	(130.82)	133.25	132.44
C(11)	124.98	124.85	(125.16)	126.97, 127.00
C(11')	124.73	(125.20)	124.56	126.73, 126.70
C(12)	138.26	138.30	(137.18)	135.88
C(12')	137.96	(137.18)	137.99	135.58
C(13)	136.56	136.32	(136.70)	146.63, 146.61
C(13')	136.56	(136.77)	136.25	146.59, 146.58
C(14)	133.06	133.14	(132.33)	111.13
C(14')	132.93	(132.36)	132.98	111.02
C(15)	130.22	129.90	(130.30)	98.34, 98.27
C(15')	130.28	(130.40)	129.86	98.15, 98.03
C(1)	137.81	137.82		137.62
C(1')	138.54		138.54	138.35
C(2), C(6)	126.32	126.30		126.39
C(2'), C(6')	129.04		129.03	128.99
C(3), C(5)	128.64	128.63		128.64
C(3'), C(5')	127.82		127.80	127.85
C(4)	127.16	127.13		127.33
C(4')	126.72		126.72	126.82
Me–C(9)	12.90	12.89[f])	12.82[f])	12.92
Me–C(9')	16.71	12.83[f])	16.69	16.72
Me–C(13)	12.80	12.80[f])	12.76[f])	15.24, 15.25[f])
Me–C(13')	12.80	12.77[f])	12.76[f])	15.27[f])

[a]) At 90 MHz: 3 and (E)-6, 18 mg/ml; (Z)-6, 7 mg/ml; 5a–c, ca. 15 mg/ml. For numbering, see Scheme.
[b]) Assignments based on HETCOR, DEPT, and HMBC spectra.
[c]) For the mono-phenyl compounds 6, values in parentheses are for C-atoms near the trimethylcyclohexene end group.
[d]) Tentative assignments made by analogy to chemical shifts of the C-atoms near the terminal (Z)-double bond in 3.
[e]) Values of each set of quaternary C-atoms may be interchanged.
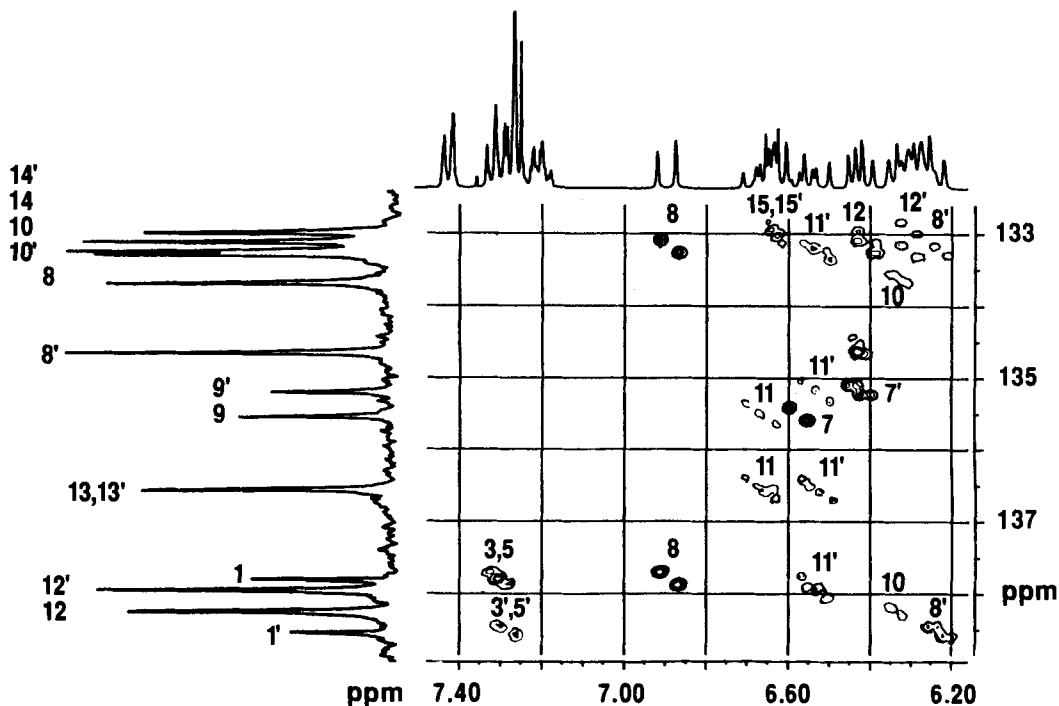[f]) Values may be interchanged.

Fig. 3. *Selected portion of HMBC spectrum of 3.* Projections along axes are 1D spectra, 360 MHz for ^{1}H, 90 MHz for ^{13}C; numbers near cross-peaks identify proton(s) coupled to indicated C-atoms.

coupled; *e.g.*, C(9′) shows long-range coupling to both H−C(7′) and H−C(11′). Other cross-peaks in the HMBC spectrum confirm the assignments made on the basis of the NOE, COSY, and HETCOR experiments.

Although the stereoisomers **5a–c** were not separated, their structures could be established by a combination of 1D- and 2D-NMR studies (^{1}H, decoupling, NOE, COSY, ^{13}C, and HETCOR). The olefinic and Me regions of a ^{1}H-NMR spectrum (500 MHz) are shown in *Figs. 4* and *5*, respectively. The aromatic region is essentially the same as that of compound **3** (*Fig. 2*). The following analysis demonstrates that, of the numerous possible (*Z/E*)-isomers, only the three compounds **5a–c** differing in the configuration of the two terminal double bonds are present.

The total areas of the aromatic, olefinic, and Me proton signals are in the required ratio of 10:12:12, but the individual CH_3 signals, for example, have non-integral areas. Two of these (*Fig. 5*, peaks II and III) have the same area and show long-range coupling ($J = 0.6$ Hz) which is absent when H−C(14) and H−C(14′) (δ near 5.75 ppm) are irradiated; they are, therefore, due to CH_3−C(13) and CH_3−C(13′) of the unsymmetrical isomer **5a**. Assignment of the lower-field peak II to CH_3−C(13) ((*E*)-end) is based on the fact that CH_3−C(13) of the symmetrical (*E,E*)-isomer **5b** is deshielded as compared to CH_3−C(13′) of the (*Z,Z*)-isomer **5c** (see below). Since two other signals (V and VI) have larger areas, show more complex multiplicities, and have chemical shifts similar to CH_3−C(9) and CH_3−C(9′) in the (*7E,7′Z*)-polyene **3** (*Table 2*), these signals are in part due to isomer **5a**. The excess area of the high-field signal (1.76 ppm) is attributed to the two CH_3−C(9′) in the symmetrical (*Z,Z*)-isomer **5c** and equals the area of peak IV, which, therefore, is due to CH_3−C(13′) in the same isomer. Similarly, the excess area of peak V equals the area of peak I, so that these can be assigned to CH_3−C(9) and CH_3−C(13), respectively, of the symmetrical (*E,E*)-isomer **5b**.

Signals due to H−C(7), H−C(11), and H−C(11′) are identified by NOE studies. Irradiation of the Me−C(9′) protons (1.76 ppm) enhances two overlapping *dd* (6.58 and 6.59 ppm), which are, therefore, attributable to H−C(11′) of **5a** and **5c**. Since somewhat more than twice as much of **5a** is present than of **5c** (which contains two equivalent H−C(11′)), the slightly more intense *dd* must be due to H−C(11′) of **5a**. Irradiation of the Me−C(9)
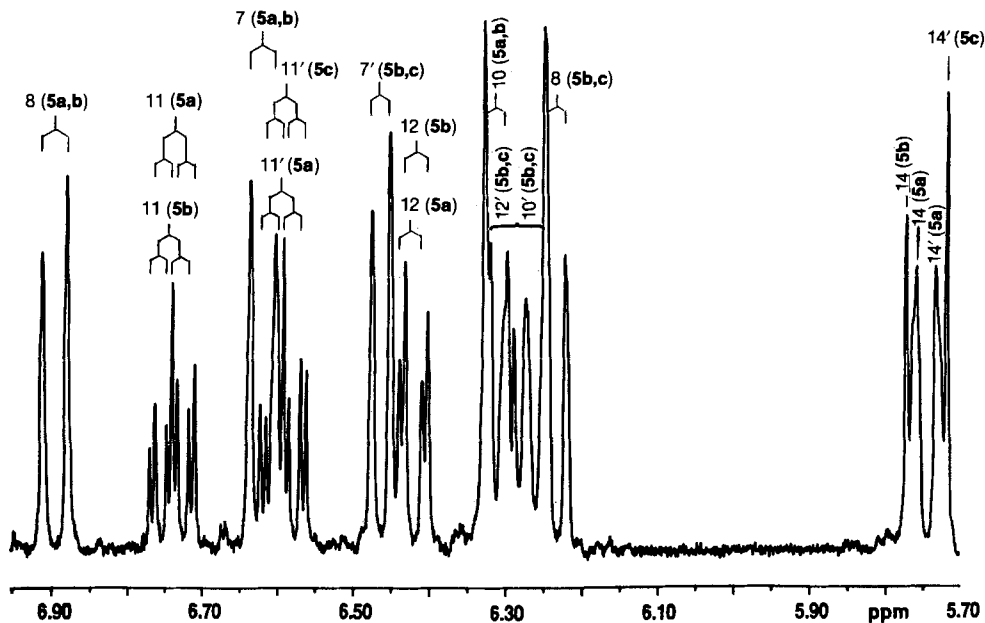
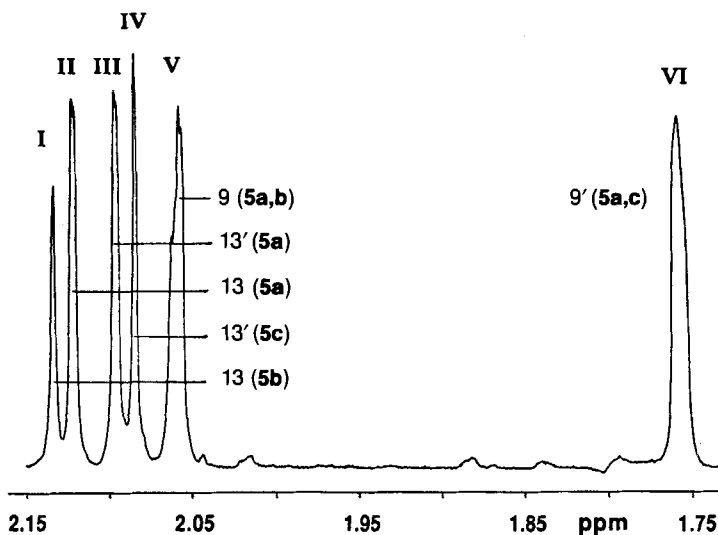Fig. 4. *Olefinic ^{1}H-NMR region* (500 MHz) *of isomer mixture* **5a–c** (10 mg/ml CDCl₃)

Fig. 5. *Methyl region of the ^{1}H-NMR spectrum* (500 MHz) *of* **5a** (*E,Z*), **5b** (*E,E*), *and* **5c** (*Z,Z*). Arabic numerals indicate atoms to which Me groups are attached. For I–VI, see text.

protons (2.06 ppm) enhances signals near 6.74 ppm (H–C(11) of **5a** and **5b**) as well as a *d* (6.62 ppm), which is therefore, due to H–C(7) of **5a** and **5b**. Irradiation at other Me-proton frequencies gives rise to enhanced overlapping *dd*'s (H–C(11) and H–C(11′)). The multiplicities of the enhanced signals are in accord with structures **5a–c** and preclude the presence of other (*Z*)-isomers; *e.g.*, in a (13*Z*)-isomer, irradiation of the Me–C(13) protons could lead to enhancement of a *d* (H–C(12)), but not to the observed *dd*.

From the product ratios, the sharp s's near 5.75 ppm can then be assigned to H−C(14) of **5b** and H−C(14') of **5c**; the lower-field of the two central broad signals is attributed to H−C(14) ((*E*)-end) in **5a** by analogy to the lower-field resonance of the H−C(14)'s in (*E*)-**6**, **3** and **5b** as compared to the H−C(14')'s ((*Z*)-end). The remaining assignments were deduced from a COSY [14] spectrum.

^{13}C-NMR chemical shifts (*Table 3*) are obtained from a HETCOR spectrum, except that those of quaternary C-atoms are assigned by their general range. The acetylenic C-atoms C(15) and C(15') are readily identified by their high-field shift as compared to the olefinic C-atoms; the phenyl C-atoms (C(1) and C(1')) and C(9) and C(9') have shifts similar to those of compounds **3**, (*E*)-**6**, and (*Z*)-**6**; and the remaining signals must be due to C(13) and C(13'), which are β to the triple bond and should, therefore, be deshielded, as is observed. Deshielding of similar magnitude has been reported for other acetylenic carotenoids, *e.g.*, alloxanthin [19]. On the other hand, C(14) and C(14'), α to the triple bond, are shielded as is observed for alloxanthin.

Conclusions. – ^{1}H-NMR Spectra of 7'-phenyl-substituted (7'*Z*)-carotenoids are characterized by large upfield shifts of H−C(8') (−0.65 ppm) and CH_3−C(9') (−0.30 ppm). Upfield shifts of protons on (*Z*)-double bonds at other positions in other carotenoids are generally smaller (up to −0.46 ppm) [15] [16]. Although signals of other protons are also at higher field in the (7'*Z*)- than in the (7'*E*)-isomers (H−C(11'), −0.13; H−C(12'), −0.10 ppm), this does not indicate the presence of another (*Z*)-double bond. The triple bond has little effect on ^{1}H chemical shifts, except those for H−C(14) and H−C(14'), but ^{13}C chemical shifts differ considerably in the doubly- and triply-bonded compounds. Except for the acetylenic C-atoms, odd-numbered C-atoms of **5** are deshielded compared to those of **3**; the effect decreases the further an atom is removed from the central triple bond. Approximate shift differences are: for C(13) 10, for C(11) 2, for C(9) 1.5, and for C(7) 0.7 ppm. In contrast, even-numbered C-atoms of **5** are shielded: for C(14) −22, for C(12) −2, for C(10) −0.8, and for C(8) −0.2 ppm. Such alternating shielding and deshielding has been described for the chain C-atoms of β-carotenals [20] and correlated with π-electron-density changes [21].

Experimental Part

General. Chemicals: **1** (20% suspension in oil) from *Roche Vitamins and Fine Chemicals*; **4** from *Hoffmann-La Roche*; silica gel *60* (70–230 mesh) for column chromatography (LC) and TLC plates ('Kieselgel' *50 F$_{254}$*, 0.2 mm) from *EM Science*; chromatography solvents (HPLC grade) from *Fisher*; N$_2$ (prepurified) from *Matheson*; CCl$_4$ (spectrometric grade) and all other chemicals from *Aldrich*. N$_2$ was passed through a column of *Drierite* (2 × 6") and 3-Å *Linde* sieves (2 × 1"). THF was freshly distilled from sodium benzophenone ketyl (N$_2$). All manipulations were carried out as rapidly as possible in near-darkness, and solvents were evaporated at < 35°/20–50 Torr. Compound **1** was isolated by extraction of the oil with hexanes. Compounds **1–5** were stored in the dark at 4° over *Drierite* or in ampoules, sealed *in vacuo*, at −20°. M.p.: *Thomas-Hoover-Uni-Melt* capillary apparatus, uncorrected. UV/VIS Spectra: *Varian-DMS100* spectrophotometer. NMR Spectra: *Bruker-AM360* (^{1}H, 360.13 MHz; ^{13}C, 90.56 MHz, 5 mm ^{1}H/^{13}C dual probe) or *AM500* (500.13 MHz) instruments at 300 K; Me$_4$Si as internal standard (δ = 0 ppm). Mass spectra: *VG-Autospec-E* spectrometer. Microanalyses were performed by *Atlantic Microlab, Inc.*, Norcross, Georgia, USA.

(7E,7'Z)-7,7'-Diphenyl-7,7'-diapocarotene (**3**). A mixture of benzyltriphenylphosphonium chloride (1.47 g, 3.79 mmol), THF (30 ml), 2.5M BuLi in hexanes (2.2 ml) was stirred under N$_2$ for 20 min and then treated with CH$_2$Cl$_2$ (15 ml). After 5 min, a soln. of **1** (0.38 g, 1.26 mmol) in CH$_2$Cl$_2$ (15 ml) was added dropwise during 5 min. TLC analysis (CHCl$_3$) showed the absence of **1** (R_f *ca.* 0.4) after 20 min. The solvent was evaporated and the residue

treated with MeOH (50 ml). The mixture was kept at 4° overnight under N_2, allowed to reach r.t., and filtered. After rinsing with MeOH (4 × 5 ml), the brick-red powder (0.45 g) was dissolved in CH_2Cl_2, deposited on silica gel (5 g), and purified by LC (silica gel (50 g), C_6H_6/hexanes 1:1): **3** (0.19 g, 34%). Glistening, copper-colored solid. M.p. 221–222°. TLC (C_6H_6/hexanes 1:1): R_f *ca.* 0.75. ¹H-NMR: H_2O-containing sample. Anal. calc. for $C_{34}H_{36}$ + 0.6 H_2O (455.5): C 89.66, H 8.23; found: C 89.76 and 89.66, H 8.03 and 8.05.

15,15′-Didehydro-7,7′-diphenyl-7,7′-diapocarotenes (**5a–c**). Prepared as above, but from **4** (0.19 g, 0.63 mmol; R_f (C_6H_6) *ca.* 0.1), the crude product was triturated with MeOH and at once subjected to LC (silica gel (25 g), C_6H_6/hexanes 1:1): **5a–c** (0.19 g, 39%). Bright orange solid. M.p. *ca.* 150° (part), resolidified by *ca.* 165°, then melt 202–208°. TLC (C_6H_6/hexanes 1:1): R_f *ca.* 0.70 and 0.75. HR-MS (EI, 70 eV): 442.270 ($C_{34}H_{34}$, calc. 442.266). Anal. calc. for $C_{34}H_{34}$ + 0.45 H_2O (450.8): C 90.60, H 7.80; found: C 90.57 and 90.49, H 7.64 and 7.69.

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