36. C_{45}- and C_{50}-Carotenoids

Part 8[1])

Synthesis of (all-*E*,2*S*,2′*S*)-Bacterioruberin, (all-*E*,2*S*,2′*S*)-Monoanhydrobacterioruberin, (all-*E*,2*S*,2′*S*)-Bisanhydrobacterioruberin, (all-*E*,2*R*,2′*R*)-3,4,3′,4′-Tetrahydrobisanhydrobacterioruberin, and (all-*E*,*S*)-2-Isopentenyl-3,4-dehydrorhodopin

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Starting from (*R*)-3-hydroxybutyric acid ((*R*)-**10**) the C_{45}- and C_{50}-carotenoids (all-*E*,2*S*,2′*S*)-bacterioruberin (**1**), (all-*E*,2*S*,2′*S*)-monoanhydrobacterioruberin (**2**), (all-*E*,2*S*,2′*S*)-bisanhydrobacterioruberin (**3**), (all-*E*,2*R*,2′*R*)-3,4,3′,4′-tetrahydrobisanhydrobacterioruberin (**5**), and (all-*E*,*S*)-2-isopentenyl-3,4-dehydrorhodopin (**6**) were synthesized. By comparison of the chiroptical data of the natural and the synthetic compounds, the (2*S*)- and (2′*S*)-configuration of the natural products **1**–**3** and **6** was established.

Introduction. – The C_{40}-carotenoids, containing eight isoprenoid units, are very widespread in Nature. In contrast, the C_{45}- and C_{50}-carotenoids with one or two additional C_5-units, have been found only in bacteria and archaea. Up to now, C_{45}- and C_{50}-carotenoids with acyclic end groups have been mainly isolated from extremely halophilic bacteria as, *e.g.*, *Halobacteria* and *Halococci*. Characteristically, the additional isoprenoid unit in the C_{45}- and C_{50}-carotenoids is bound to C(2) and C(2′). Bacterioruberin (**1**) is in many bacteria the main pigment, and it was postulated that its main function is to act as membrane reinforce [2] [3]. Besides **1**, also monoanhydrobacterioruberin (**2**), bisanhydrobacterioruberin (= dianhydrobacterioruberin; **3**), trisanhydrobacterioruberin (= trianhydrobacterioruberin; **4**), 3,4,3′,4′-tetrahydrobisanhydrobacterioruberin (= 3,4,3′,4′-tetrahydrodianhydrobacterioruberin; **5**), and 2-isopentenyl-3,4-dehydrorhodopin (= 3,4-didehydro-2-(3-methylbut-2-enyl)rhodopin; **6**) have been isolated[4]).

In view of the elucidation of the configuration of the natural products, we report in the present paper the synthesis of (all-*E*,2*S*,2′*S*)-**1**, (all-*E*,2*S*,2′*S*)-**2**, (all-*E*,2*S*,2′*S*)-**3**, (all-*E*,2*R*,2′*R*)-**5**, and (all-*E*,*S*)-**6**[5]).

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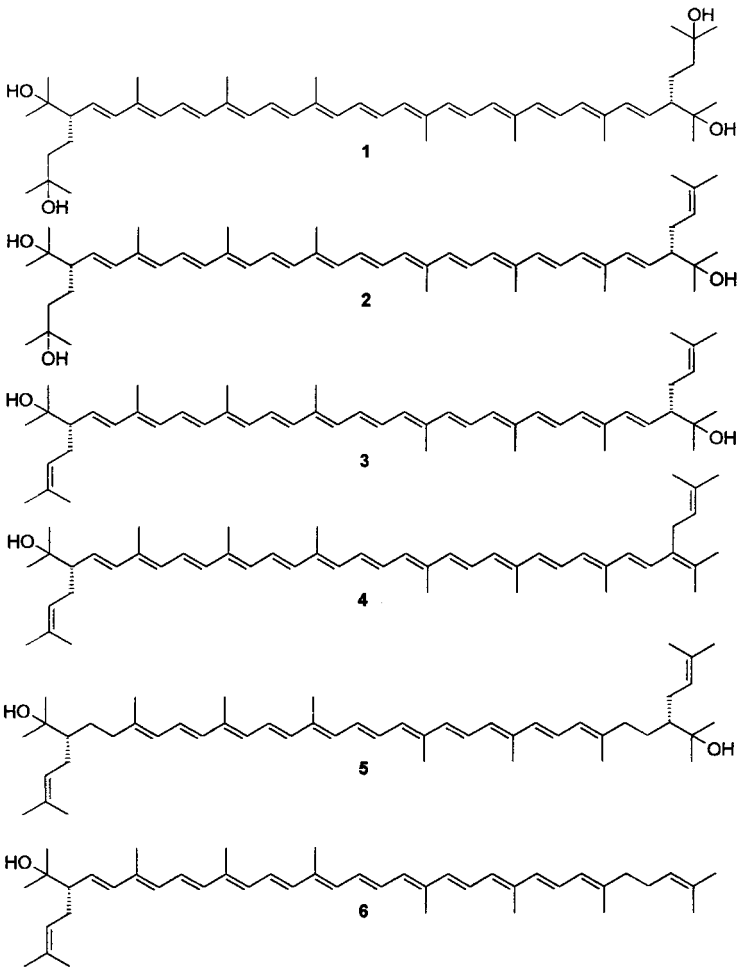
[1]) Part 7: [1].

[2]) Diploma Work of *D.S.*, Bern, 1994.

[3]) Part of the planned Ph.D. Thesis of *B.T.*

[4]) For a complete list of C_{45}- and C_{50}-carotenoids, see [4]. Recently, new compounds have been found [5].

[5]) For the synthesis of (*S*)-**4**, see [6].

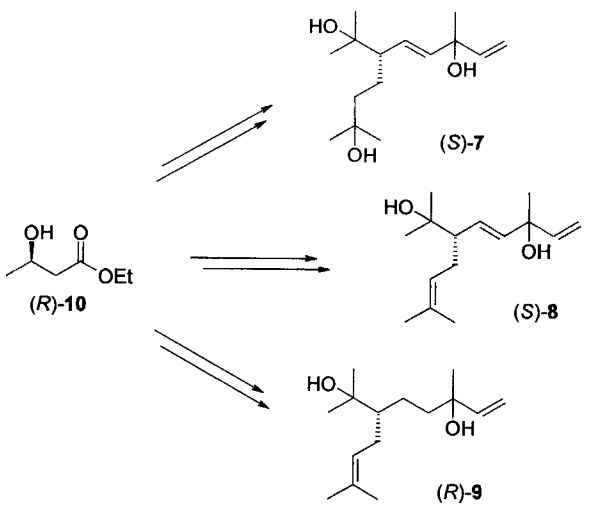


Results and Discussion. – *General.* For the synthesis of C_{40}-carotenoids, the strategy $C_{10} + C_{20} + C'_{10} = C_{40}$ is often used. In analogy, for the synthesis of the C_{50}-carotenoids, the general approach $C_{15} + C_{20} + C'_{15} = C_{50}$ was chosen. For the synthesis of **6**, the sequence $C_{15} + C_{30} = C_{45}$ was selected. The compounds **1**–**6** possess as partial structure one or two optically active end group(s). The synthesis of suitable, optically active C_{15}-building blocks (*S*)-**7**, (*S*)-**8**, and (*R*)-**9**, starting from (*R*)-3-hydroxybutyric acid ((*R*)-**10**), has been reported earlier [7] [8] (*Scheme 1*).

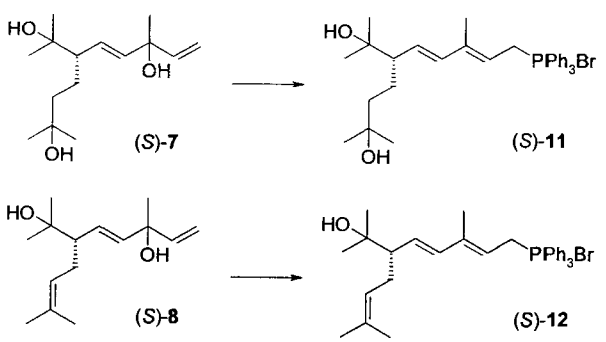
The key intermediates for the synthesis of **1**–**4** and **6** in optically active form are the compounds (*S*)-**7** and (*S*)-**8** which were converted to the corresponding phosphonium salts (*S*)-**11** (yield 65%) and (*S*)-**12** (yield 50%) by the reaction with triphenylphosphonium bromide in MeOH (*Scheme 2*).

*(all-*E,*2S,2'*S*)-Bacterioruberin* ((all-*E*,2*S*,2'*S*)-**1**). The phosphonium salt (*S*)-**11** was reacted with crocetindialdehyde (= 8,8'-diapocaroten-8,8'-dial; **13**; ratio 8:1) in butylene

Scheme 1



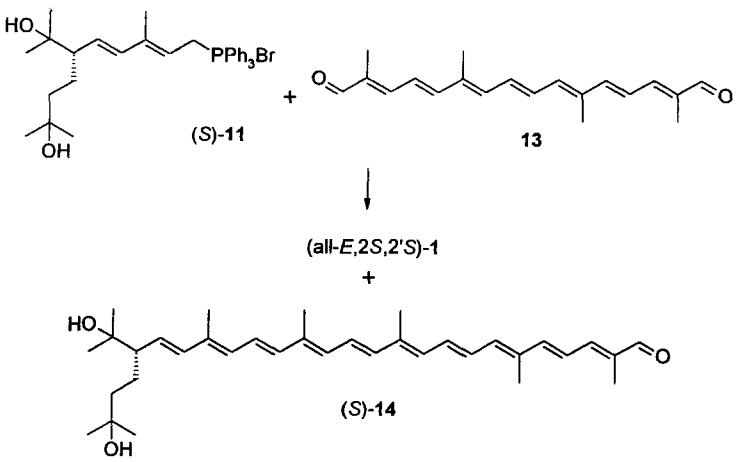
Scheme 2



oxide (= ethyloxirane) at 40° (*Scheme 3*). After flash chromatography (FC), prep. TLC, and repeated crystallization, (all-*E*,2*S*,2′*S*)-**1** was isolated (yield 0.75%). The extremely low yield is mainly due to the fact that the C_{35}-monoaldehyde **14** was the main product in the *Wittig* reaction (yield *ca.* 75%) besides unreacted dialdehyde **13**. Attempts to improve the yield by varying the reaction conditions (CH_2Cl_2, NaOEt as base) were unsuccessful. Another reason for the low yield was the loss of material during recrystallization. It is well known that **1** undergoes a rapid (*E*/*Z*)-isomerization in solution [9] [10]. Therefore, it was necessary to recrystallize several times in order to get the pure (all-*E*)-isomer.

The spectroscopical data of the compound established the structure of (all-*E*,2*S*,2′*S*)-**1**. The maxima of the UV/VIS spectrum (in acetone: 533, 499, 470, and 389 nm) and the fine structure are in agreement with the tridecaene system and the literature [9][10]. The MS shows the molecular ion at *m*/*z* 740 (M^+), and the major fragmentation can be attributed to the loss of H_2O ($[M-18]^+$), acetone ($[M-58]^+$), toluene ($[M-92]^+$), xylene ($[M-106]^+$), and combinations thereof.

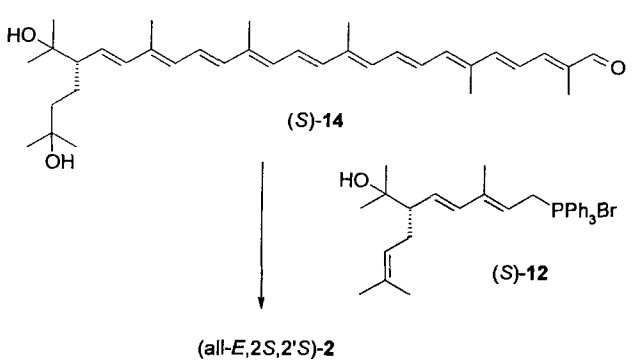
Scheme 3



The 400-MHz ^{1}H-NMR data (*Exper. Part*) are in full agreement with the structure of (all-*E*,2*S*,2′*S*)-**1** and identical to that of the natural product [11]. The CD spectra of the synthetic compound (see *Fig. 1*, below) and the natural product [11] [12] are identical, and, therefore, the (2*S*,2′*S*)-configuration of natural bacterioruberin (**1**) is established.

*(all-*E,2S,2′S*)-Monoanhydrobacterioruberin* ((all-*E*,2*S*,2′*S*)-**2**). The phosphonium salt (*S*)-**11** was reacted in a two-phase *Wittig* reaction (CH_2Cl_2/2N NaOH 1:1) with crocetindialdehyde (**13**) to the monoaldehyde (*S*)-**14**. After FC and prep. TLC, (*S*)-**14** was obtained as a mixture of (*E*/*Z*)-isomers (62% yield) which was not separated and directly used for the further synthesis. As by-product, 2% of (2*S*,2′*S*)-**1** was obtained as a mixture of (*E*/*Z*)-isomers. For the synthesis of (2*S*,2′*S*)-**2**, the C_{35}-monoaldehyde (*S*)-**14** was reacted with the phosphonium salt (*S*)-**12** (CH_2Cl_2/2N NaOH 1:1) (*Scheme 4*). Besides the mixture of the (*E*/*Z*)-isomers of the unreacted C_{35}-monoaldehyde (*S*)-**14**, a mixture of (*E*/*Z*)-isomers of the desired (2*S*,2′*S*)-**2** was obtained. The separation of this complex mixture proved to be difficult, and no TLC system which gave a satisfactory separation could be found. Therefore, after a pre-separation by TLC, the mixture was subjected to HPLC, and pure (all-*E*,2*S*,2′*S*)-**2** could be isolated (yield 1.5%).

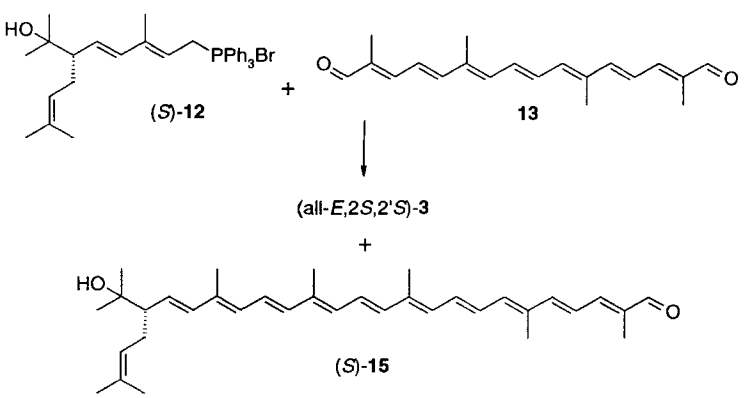
Scheme 4



The UV/VIS spectrum (acetone) of (all-*E*,2*S*,2′*S*)-**2** shows maxima at 530, 497, 469, and 389 nm and is in agreement with that of the natural product [11]. In the MS, the molecular ion can be observed at *m/z* 722 (M^+) and major fragments at 704 ($[M - H_2O]^+$), 686 ($[M - 2\,H_2O]^+$), and 644 ($[M$ – acetone$]^+$). As monoanhydrobacterioruberin (**2**) contains half of the molecule of **1** and **3**, respectively, the ^{1}H-NMR spectrum of (all-*E*,2*S*,2′*S*)-**2** is as expected a superposition of the spectra of (all-*E*,2*S*,2′*S*)-**1** and (all-*E*,2*S*,2′*S*)-**3**. The CD spectrum of the synthetic compound (see *Fig. 2*, below) is identical to that of the natural product [11], and therefore, the (2*S*,2′*S*)-configuration of natural monoanhydrobacterioruberin (**2**) is established.

*(all-*E,2S,2′S*)-Bisanhydrobacterioruberin* ((all-*E*,2*S*,2′*S*)-**3**). The phosphonium salt (*S*)-**12** was reacted with crocetindialdehyde (**13**; ratio 4:1) in CH_2Cl_2/EtOH with NaOEt as base (*Scheme 5*). After twofold prep. TLC and crystallization, (all-*E*,2*S*,2′*S*)-bisanhydrobacterioruberin ((all-*E*,2*S*,2′*S*)-**3**) was obtained in 17.2% yield. As side products, a (*Z*)-isomer of **3** (yield 7%) and the unnatural C_{35}-monoaldehyde (*S*)-**15** were isolated.

Scheme 5

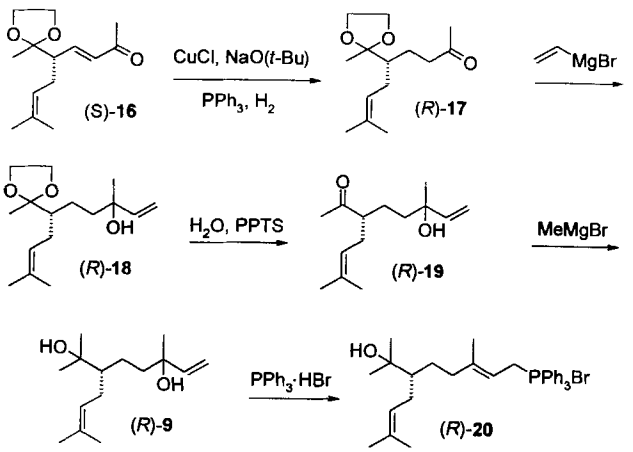


The spectroscopical data of the main product are in agreement with the structure of (all-*E*,2*S*,2′*S*)-**3**. The UV/VIS spectrum (hexane) shows maxima at 526, 493, 464, 386, and 368 nm and a pronounced fine structure and is in accordance with the spectrum of natural **3** [10] [13]. The MS exhibits the molecular ion at *m/z* 704 (M^+) and characteristic fragments at 686 ($[M - H_2O]^+$), 668 ($[M - 2\,H_2O]^+$), 646 ($[M$ – acetone$]^+$), 612 ($[M$ – toluene$]^+$), and 598 ($[M$ – xylene$]^+$). The 400-MHz ^{1}H-NMR data (*Exper. Part*) are in agreement with the date published previously [14]. The CD spectrum (see *Fig. 3*, below) is identical to that of the natural product [11] and the configuration of natural bisanhydrobacterioruberin (**3**) is established as (2*S*,2′*S*).

The UV/VIS spectrum (EtOH) of the monoaldehyde (*S*)-**15** shows a maximum at 478 nm. After the reduction of (*S*)-**15** with $NaBH_4$, a fine structure can be observed in the UV/VIS spectrum (in EtOH: 483, 452, 427, 346, 331, and 280 nm). The MS exhibits the molecular ion at *m/z* 500 (M^+) and characteristic fragments at 482 ($[M - H_2O]^+$), 442 ($[M$ – acetone$]^+$), and 394 ($[M$ – xylene$]^+$). The CD spectrum (Et_2O/isopentane/EtOH 5:5:2, + 20°; see *Fig. 4*, below) shows the following maxima: 360 (pos. max.), 346 (pos. max.), 291 (pos. max.), 282 (sh), 250 (neg. max.), 222 (pos. max.), and 204 (pos. max.).

(2R,2'R)-3,4,3',4'-Tetrahydrobisanhydrobacterioruberin End Group: Phosphonium Salt (R)-**20**. The preparation of the building block (*R*)-**9** according to [8] resulted in a dramatic decrease of the optical purity to 30% ee. This partial racemization occurred during the reduction of the α,β-unsaturated ketone (*S*)-**16** to the ketone (*R*)-**17** with tris(triphenylphosphine)rhodium(I) chloride and triethylsilane. A regioselective reduction of (*S*)-**16** with complete retention of the configuration at C(5) was achieved by the use of (triphenylphosphine)copper(I)-hydride hexamer as reducing agent (*Scheme 6*). When the copper hydride complex was prepared *in situ*, the best yields were obtained, and no enantiomeric (*S*)-**17** was detected by GC [15]. The optically pure (*R*)-**17** was converted *via* (*R*)-**18** and (*R*)-**19** according to [8], with slight modifications, into the C_{15}-diol (*R*)-**9**. The phosphonium salt (*R*)-**20** was then prepared (yield 81%) by the reaction of (*R*)-**9** with triphenylphosphonium bromide in $MeOH/CHCl_3$ 1:1.

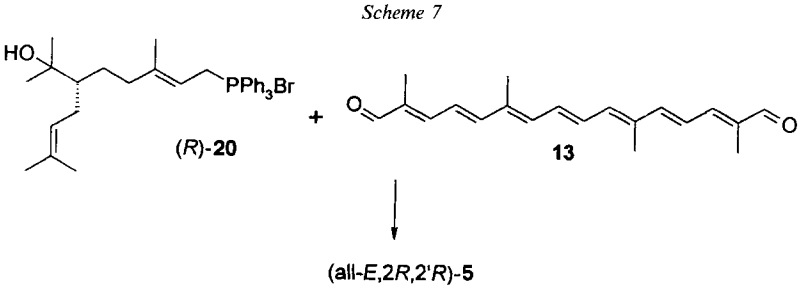
Scheme 6



*(all-*E,2R,2'R*)-3,4,3',4'-Tetrahydrobisanhydrobacterioruberin* ((all-*E*,2*R*,2'*R*)-**5**). The phosphonium salt (*R*)-**20** was refluxed with crocetindialdehyde (**13**; ratio 7:1) in butylene oxide (*Scheme 7*). The (all-*E*)-isomer of **5** was separated from its (*Z*)-isomers and the C_{35}-monoaldehyde by flash chromatography.

The spectroscopical data of (all-*E*,2*R*,2'*R*)-**5**, especially the 400-MHz ^{1}H-NMR data (*Exper. Part*), are in agreement with the proposed structure, which was postulated by

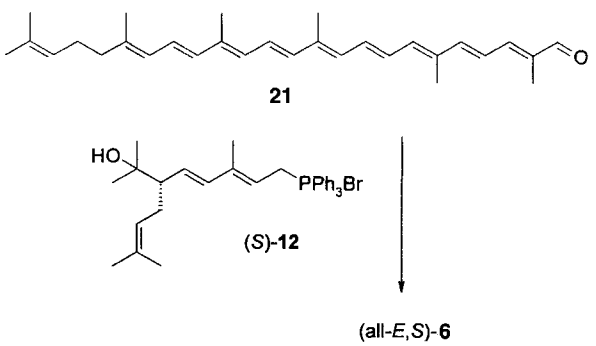
Scheme 7



Norgard et al. [13] based on biochemical considerations and UV/VIS and mass spectroscopy. The UV/VIS spectrum (acetone) shows maxima at 503, 473, 448, 362, and 346 nm and is identical with that of the natural product [13]. As no CD spectrum of the natural compound is available, only a reisolation of the natural product will give information on its configuration.

*(all-*E,S*)-2-Isopentenyl-3,4-dehydrorhodopin* ((all-*E,S*)-**6**). For the synthesis of (all-*E,S*)-**6**, the phosphonium salt (*S*)-**12** was reacted in CH_2Cl_2/EtOH, with NaOEt as base, with 8′-apo-ψ-caroten-8′-al[6]) (**21**; ratio 3:1; *Scheme 8*). After separation by FC, twofold prep. TLC, and crystallization, pure (all-*E,S*)-**6** was obtained in 30% yield. Furthermore, a (*Z*)-isomer (10%) was isolated which was not further investigated.

Scheme 8



The UV/VIS spectrum (hexane) of (all-*E,S*)-**6** shows maxima at 518, 484, 456, and 375 nm and is in agreement with that of the natural product [11]. The MS exhibits the molecular ion at *m/z* 620 (M^+) and, with low intensities, signals at 602 ($[M - H_2O]^+$), 562 ($[M$ – acetone$]^+$), and 514 ($[M$ – xylene$]^+$). In the ^{1}H-NMR spectrum, the signals of the 'bacterioruberin-end group' as well as those of the ψ-end group of lycopene (ψ,ψ-carotene) [17] can be observed. The CD spectra of the synthetic and natural (all-*E,S*)-**6** are in agreement, establishing the (*S*)-configuration for natural **6** [11] [18] (see *Fig. 6*, below).

CD Spectra. Figs. 1–3 and *6* show the CD spectra of the synthetic compounds **1**–**3** and **6**. They are identical in their maxima and the shape of the curves with the natural compounds [11]. Due to the small amounts of the synthesized carotenoids, the zero line may be partly slightly shifted, and no quantitative intensities ($\Delta\varepsilon$ values) can be given, since the exact concentrations of the solutions were not known. As the identity is given by the synthesis, chromatography, and the NMR spectra, the CD spectra prove the identical chirality of the natural compounds and the synthetic products.

The CD spectra are only approximately of the 'conservative type', in which the integral of all the peaks are equal to zero, and in which the signs of the maxima change regularly [19]. Such spectra have been observed for carotenoids in which at one or both ends of the coplanar conjugated polyene chain, the double bond of the ring is deviated

[6]) For the synthesis of **21**, see [16].

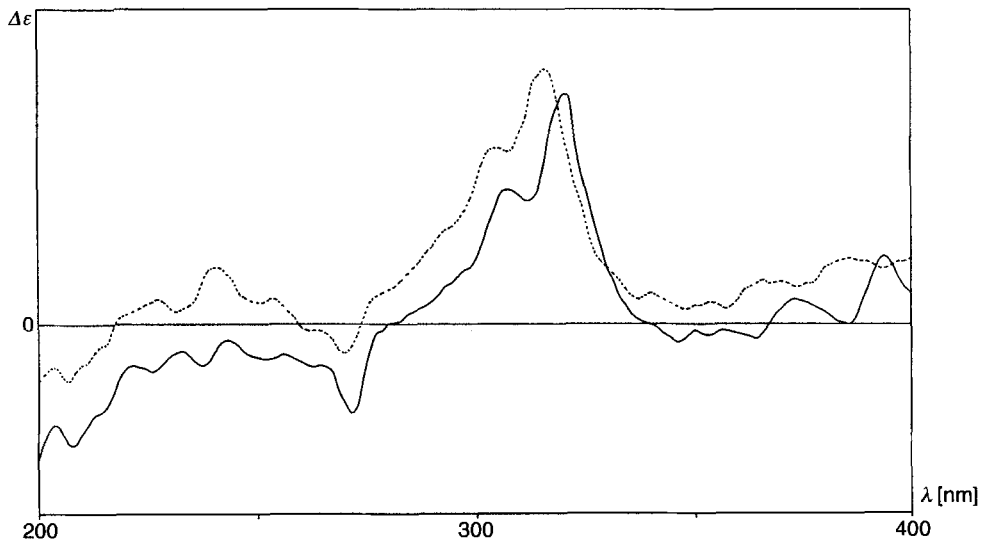


Fig. 1. *CD Spectra of (all*-E,2S,2'S)-**1** (—— −180°, ---- +20°)

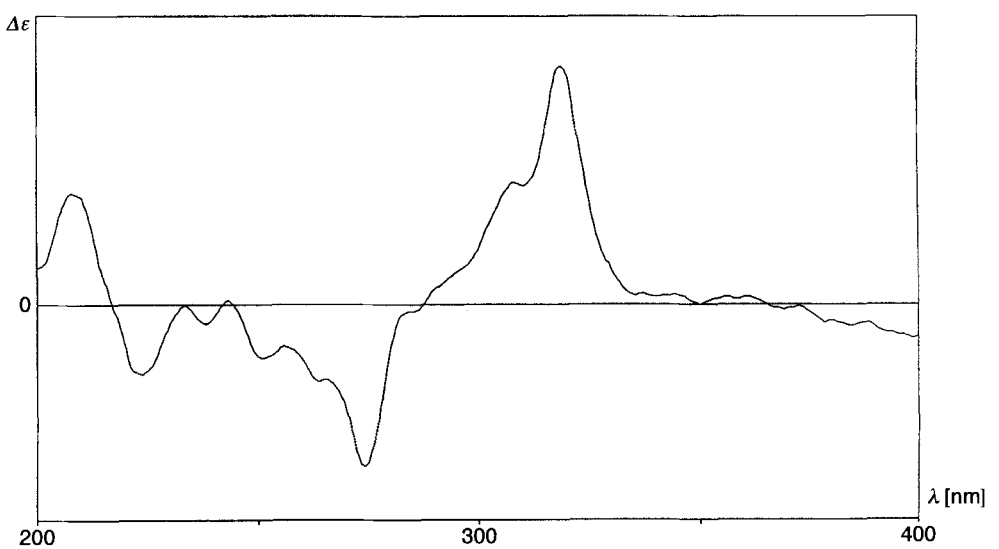


Fig. 2. *CD Spectrum of (all*-E,2S,2'S)-**2** *at* + 20°

from the plane of the chain (*e.g.* zeaxanthin) [20] [10]. The CD spectra of **1**–**3** and **6** are more complex, and, most important, a strong CD effect with very distinct vibrational fine structure in the area of the main absorbance occurs. On cooling, a large increase of the CD is observed in the region of the VIS absorption. This is because of a shift of the temperature-dependant conformational equilibrium. In addition to this, the CD maxima as well as the absorption maxima are shifted towards longer wavelengths. This is espe-

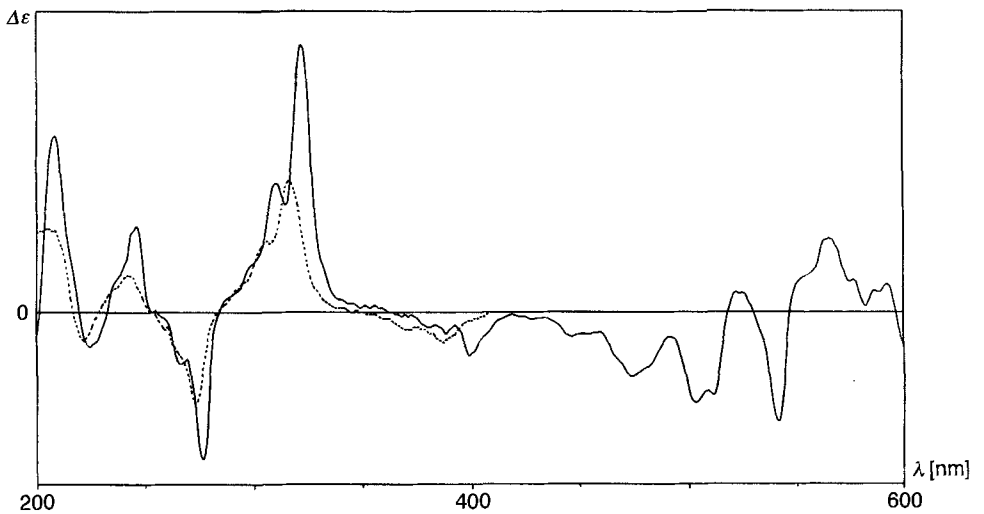


Fig. 3. *CD Spectra of (all-*E,2S,2'S*)-***3** (—— −180°, ---- +20°)

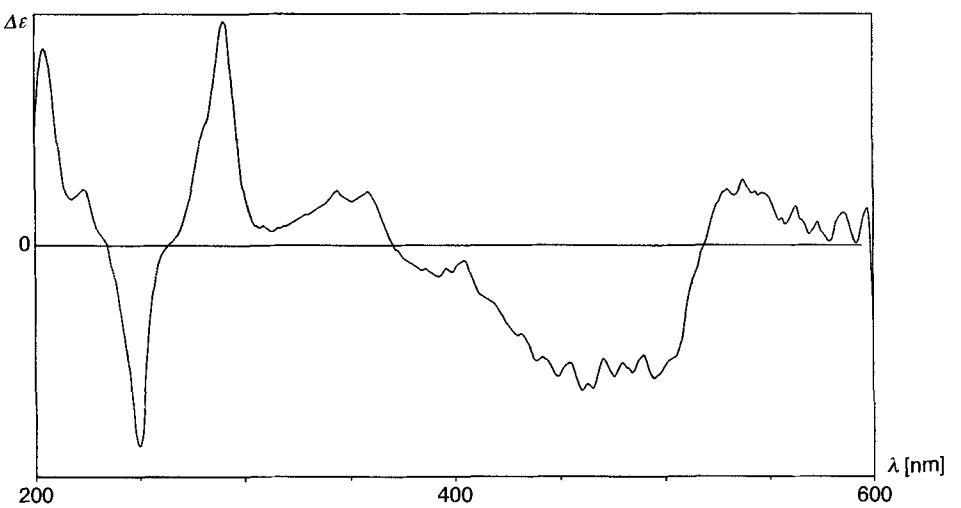


Fig. 4. *CD Spectrum of (all-*E,2S,2'S*)-***15** *at* + 25°

cially pronounced in the principal absorption band of the VIS region. The approximate shift there is 20 nm, whereas in the UV region, the shift is *ca.* 5 nm. This red shift may be a result of an improved degree of conjugation at lower temperatures. Moreover, the position of the maxima is, as expected, dependant on the number of conjugated double bonds, *i.e.*, larger number results in a bathochromic shift. The observable positive maximum in the region of 300 nm is at 292 nm for **15** (*Fig. 4*) (10 conjugated C=C and one C=O bonds), at 304 nm for **6** (12 conjugated C=C bonds), and at 315 and 317 nm for **1** and **2**, respectively (both 13 conjugated C=C bonds).

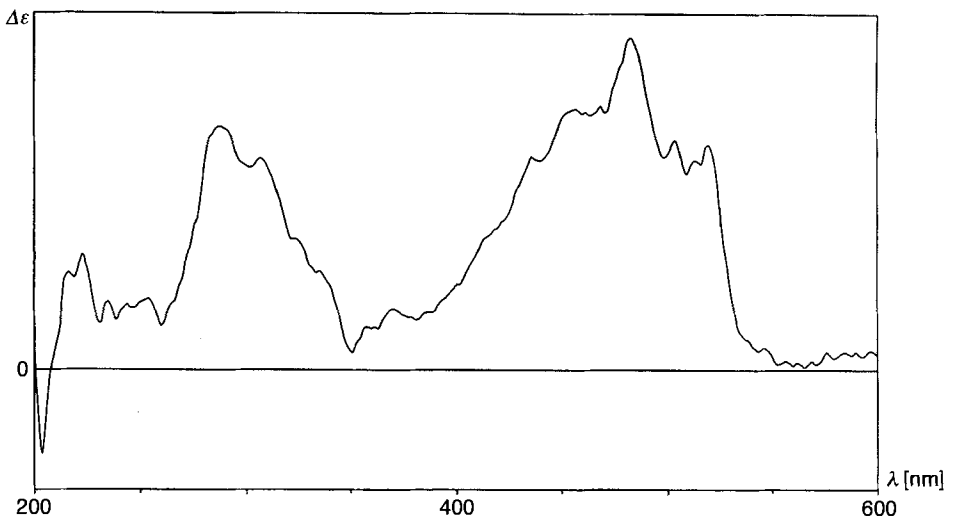


Fig. 5. *CD Spectrum of (all-*E,2R,2'R*)-***5** *at* $-180°$

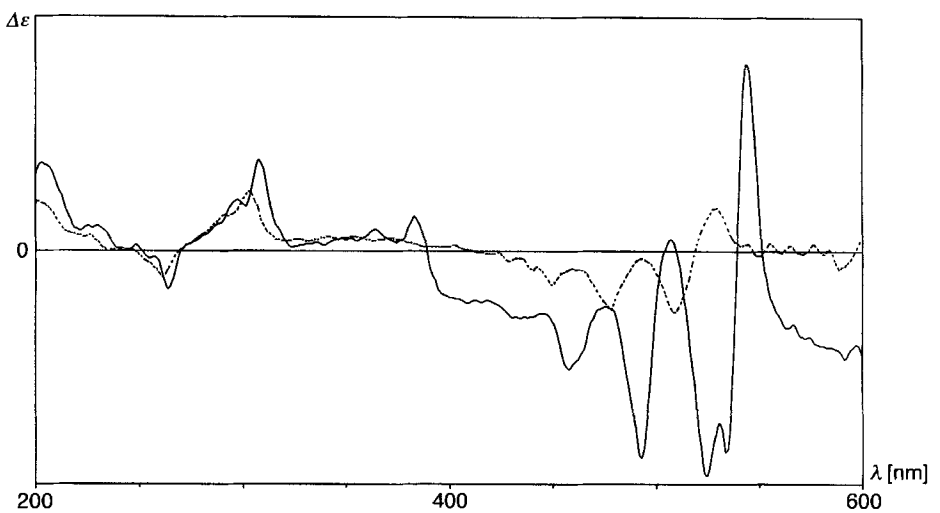


Fig. 6. *CD Spectra of (all-*E,2S*)-***6** (—— $-180°$, ---- $+20°$)

The strongly pronounced vibrational fine structure of the CD in the principle absorption region, which is especially observable at low temperature, together with a split of the individual vibrational bonds in a positive and a negative component, is based upon a perturbation in the transitions of different symmetries [20–22].

The CD spectrum of **5** (*Fig. 5*) shows only very weak absorptions. As the chiral center is in γ-position to the chromophore, only a small influence of the chiral center can be expected. The spectrum itself is cleary of a non-conservative type, and cooling to $-180°$ is necessary to obtain significant signals.

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Experimental Part

1. *General.* The reagents were purchased from *Fluka AG*, *E. Merck*, or *Aldrich*. The solvents were purified according to [23]. Flash chromatography (FC): *J. T. Baker* and *E. Merck*, silica gel *60*, 0.040–0.063 mm. TLC: *E. Merck*, 'DC-Fertigplatten', silica gel *60* F_{254}. HPLC: LC pump *T414* (*Kontron*), *Waters-991-PDA* detector; t_R in min. M.p.: *Tottoli* apparatus, open capillary; corrected. UV/VIS Spectra: spectrophotometer *Perkin-Elmer 554*; λ_{max} in nm. CD Spectra: *Dichrograph II* (modified) (*Jobin-Yvon*); λ in nm (neg. or pos. maxima); EPA = Et_2O/isopentane/EtOH 5:5:2; no quantitative intensity values ($\Delta\varepsilon$) are given, because the concentrations were unknown due to the small amounts of sample material available. IR Spectra: *Perkin-Elmer 399 B*; $\tilde{\nu}$ in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker-Spectrospin AM 400* and *WM 400* (^1H, 400 MHz), *Varian XL-300* (^1H, 300 MHz), *Bruker-Spectrospin WM 400* (^{13}C, 100.6 MHz), and *Varian XL-100* (^{13}C, 25.2 MHz); chemical shifts δ in ppm rel. to Me_4Si as internal reference, J in Hz. MS: *Varian-MAT-CH-7A* spectrometer with direct sample inlet (70 eV); *m/z* (rel. %).

2. *(5S,E)-5-(1-Hydroxy-1-methylethyl)-2,8-dimethyldeca-6,9-diene-2,8-diol* ((*S*)-**7**). According to [8].

3. *(3S,E)-2,6-Dimethyl-3-(3-methylbut-2-enyl)octa-4,7-diene-2,6-diol* ((*S*)-**8**). According to [8].

4. *[(6S,2E,4E)-9-Hydroxy-6-(1-hydroxy-1-methylethyl)-3,9-dimethyldeca-2,4-dienyl]triphenylphosphonium Bromide* ((*S*)-**11**). A soln. of (*S*)-**7** (0.50 g, 1.95 mmol) in abs. MeOH (10 ml) was added dropwise within 2 h to a stirred soln. of triphenylphosphonium bromide (0.67 g, 1.95 mmol) in abs. MeOH (10 ml). After 17 h stirring at r.t., the mixture was evaporated. The residue was dissolved in a small amount of CH_2Cl_2, and afterwards Et_2O was added until a precipitate was observed. Upon vigorous shaking, this precipitate was sticking at the wall of the round bottom flask. The soln. was removed with a pipette and discarded. This process was repeated 4 times, until the product was colorless. Drying under h.v. gave 0.72 g (63.5%) of (*S*)-**11** as almost white solid (m.p. 49–50°) which was directly used for the further synthesis.

5. *[(6S,2E,4E)-6-(1-Hydroxy-1-methylethyl)-3,9-dimethyldeca-2,4,8-trienyl]triphenylphosphonium Bromide* ((*S*)-**12**). A soln. of triphenylphosphonium bromide (0.79 g, 2.3 mmol) in abs. MeOH (10 ml) was added dropwise within 2 h to a stirred soln. of (*S*)-**8** (0.546 g, 2.3 mmol) in abs. MeOH (10 ml). After 44 h stirring at r.t., the mixture was evaporated and the residue dissolved in CH_2Cl_2 (2 ml). Upon addition of Et_2O (50 ml), a white precipitate was observed. The solvent was discarded and the precipitate washed twice with Et_2O and then dried under h.v.: 845 mg (65%) of slightly yellow solid (m.p. 198°) which was directly used for the next step.

6. *(all-E,2S,2'S)-Bacterioruberin* (= *3,4,3',4'-Tetradeyhdro-1,2,1',2'-tetrahydro-2,2'-bis(3-hydroxy-3-methylbutyl)-ψ,ψ-carotene-1,1'-diol*; (all-*E*,2*S*,2'*S*)-**1**). A soln. of (*S*)-**11** (217.5 mg, 0.375 mmol) and crocetindialdehyde (**13**; 27.6 mg, 0.09 mmol) in ethyloxirane (butylene oxide; 5 ml) was stirred for 6 h at 40° under Ar in the dark. Then the mixture was evaporated and the residue separated by FC (AcOEt + 0.1% *N*-ethyldiisopropylamine). Besides a fraction which contained *ca.* 37 mg of C_{35}-monoaldehyde (*S*)-**14**, another fraction was isolated (*ca.* 5 mg) with a complex mixture of (*E*/*Z*)-isomers of **1**. This mixture was subject to prep. TLC (AcOEt + 0.1% *N*-ethyldiisopropylamin), whereby an enrichment of the (all-*E*)-isomer was achieved. After a fourfold crystallization (acetone/petroleum ether), 0.75 mg (0.18% rel.to **13**) of pure (all-*E*,2*S*,2'*S*)-**1** was isolated. Dark, metallically shining crystals. UV/VIS (acetone): 532, 498, 470, 390; $D_C/D_\beta = 0.11$; $\alpha/\beta = 0.59$. UV/VIS (MeOH): 529, 495, 408, 389; $D_C/D_\beta = 0.11$; $\alpha/\beta = 0.56$; $\varepsilon = 197000 \pm 12000\ mol^{-1}\,cm^{-1}$. CD (EPA, + 20°): 386 (pos. max.), 374 (pos. min.), 367 (pos. max.), 356 (pos. min.), 340 (pos. max.), 315 (pos. max.), 305 (pos. max.), 293 (sh), 278 (sh), 270 (neg. max.), 265 (sh), 253 (sh), 241 (pos. max.), 233 (pos. min.), 226 (pos. max.), 203 (neg. max). CD (EPA, −180°): 395 (pos. max.), 385 (neg. min.), 378 (pos. max.), 320 (pos. max.), 308 (pos. max.), 282 (sh), 272 (neg. max), 204 (neg. max.). IR ($CHCl_3$): 3600*w*, 3200–3600*w*, 2965*s*, 2940*s*, 2480*m*, 1710*s*, 1670*s*, 1460*m*, 1370*s*, 1260*s*, 1095*s*, 1020*s*, 970*m*, 915*m*, 870*w*. ^1H-NMR (400 MHz, $CDCl_3$): 1.171 (*s*, Me(16,16')); 1.203 (*s*, Me(4'',4''') Me–C(3'',3'''); 1.210 (*s*, Me(17,17')); 1.24–1.33 (*m*, CH_2(2'',2''')); 1.42–1.48, 1.73–1.81 (2*m*, CH_2(1'',1''')); 1.919 (*s*, Me(18,18')); 1.967 (*s*, Me(19,19')); 1.977 (*s*, Me(20,20')); 1.98–2.04 (*m*, H–C(2,2')); 5.447 (*dd*, J = 15.5, 11, H–C(3,3')); 6.137 (*d*, J = 11, H–C(6,6')); 6.186 (*d*, J = 15.5, H–C(4,4')); 6.236 (*d*, J = 12.5, H–C(10,10')); 6.28 (*m*, H–C(14,14')); 6.366 (*d*, J = 15, H–C(8,8')); 6.381 (*d*, J = 15, H–C(12,12')); 6.587 (*dd*, J = 15, 11, H–C(7,7')); 6.637 (*dd*, J = 15, 12.5, H–C(11,11')); 6.60–6.68 (*m*, H–C(15,15')). MS: 740 (0.3, M^+), 722 (0.9), 704 (0.9), 686 (0.3), 682 (0.3), 664 (0.7), 646 (0.4), 634 (0.4), 630 (0.3), 616 (1), 598 (0.8), 590 (0.4), 580 (0.4), 576 (0.6), 558 (0.7), 503 (2), 429 (9), 355 (19), 281 (51), 207 (28), 152 (47), 109 (53), 97 (100), 81 (41), 69 (47), 59 (89), 43 (91).

7. *(all-*E,2S,2'S*)-Monoanhydrobacterioruberin* (= *3,4,3',4'-Tetradehydro-1,2,1',2'-tetrahydro-2-(3-hydroxy-3-methylbutyl)-2'-(3-methylbut-2-enyl)-ψ,ψ-carotene-1,1-diol*; (all-*E*,2*S*,2'*S*)-**2**). To a two-phase system of CH_2Cl_2 (2 ml) and 2N NaOH (2 ml) containing **13** (50 mg, 0.169 mmol), a soln. of (*S*)-**11** (50 mg, 0.086 mmol) in CH_2Cl_2 (0.5 ml) was added dropwise with vigorous stirring at r.t. under Ar. After 1 h stirring, the mixture was distributed between Et_2O/phosphate buffer (pH 7.00), and the aq. phase was extracted with Et_2O (3 ×). The combined org. phases were dried ($MgSO_4$) and evaporated. With FC (Et_2O), the unreacted **13** was removed, and crude (*S*)-**14** and a small amount of **1** were eluted with EtOH. Prep. TLC (toluene/petroleum ether/EtOH 50:50:8 + 1% Et_3N) and crystallization (toluene/petroleum ether) gave 27.6 mg (62%) of (*S*)-**14** as mixture of (*E*/*Z*)-isomers which was directly used for the further synthesis. Besides (*S*)-**14**, also (2*S*,2'*S*)-**1** (2.9 mg) was isolated.

A soln. of (*S*)-**12** (200 mg, 0.354 mmol) in CH_2Cl_2 (3 ml) was added through a septum by syringe to a two-phase system of CH_2Cl_2 (3 ml) and 2N NaOH (3 ml) containing (*S*)-**14** (92 mg, 0.178 mmol; mixture of (*E*/*Z*)-isomers). After stirring 24 h in the dark under Ar the mixture was worked up as for (*S*)-**14**. Prep. TLC (toluene/petroleum ether/EtOH 50:50:8 + 1% Et_3N) removed by-products. Pure (all-*E*,2*S*,2'*S*)-**2** (1.9 mg, 1.7%) was obtained by HPLC (*Nucelosil 5* C_{18} (*Macherey Nagel*), 250 × 10 mm i.d.; mobile phase *A*/*B* 45:55, with *A* = MeOH/H_2O 9:1 + 1% Et_3N and *B* = MeOH/AcOEt 8:2 + 1% Et_3N (flow rate 3.5 ml/min; t_R for (all-*E*,2*S*,2'*S*)-**2** 11.99, for (*Z*)-isomers 13.42, 13.60, 14.42, 16.23, and 16.86). UV/VIS (acetone): 530, 497, 469, 389. CD (EPA, + 20°): 316(pos. max.), 306(sh), 292(sh), 271(neg. max.), 262(sh), 248(neg. max.), 222(neg. max.), 207(pos. max.). ^{1}H-NMR (400 MHz, $CDCl_3$): within the exper. error, the NMR data are a superposition of the data of **1** and **3**. MS: 722 (56, M^+), 704 (7), 686 (3), 664 (16), 616 (66), 630 (8), 616 (67), 157 (84), 145 (100), 133 (61), 119 (88), 91 (84), 69 (75), 43 (19).

8. *(all-*E,2S,2'S*)-Dianhydrobacterioruberin* (= *3,4,3',4'-Tetradehydro-1,2,1',2'-tetrahydro-2,2'-bis(3-methylbut-2-enyl)-ψ,ψ-carotene-1,1'-diol*; (all-*E*,2*S*,2'*S*)-**3**). To a soln. of (*S*)-**12** (300 mg, 0.53 mmol) and crocetindialdehyde (**13**; 40 mg, 0.13 mmol) in CH_2Cl_2 (6 ml) was added dropwise within 1 h under Ar in the dark freshly prepared 0.16M NaOEt in EtOH (5 ml, 0.79 mmol). After stirring for 7 h at r.t., H_2O (30 ml) was added and the mixture extracted 3 times with CH_2Cl_2 (50 ml). The combined org. phases were washed twice with H_2O (60 ml), dried (Na_2SO_4), and evaporated. Prep. TLC (toluene/petroleum ether/EtOH 50:50:6) gave 34.7 mg of crude **3**. After crystallization (toluene/petroleum ether), 16 mg (17.2% rel. to **12**) of pure (all-*E*,2*S*,2'*S*)-**3** was obtained. M.p. 171°. UV/VIS (acetone): 532, 498, 470, 390; $D_C/D_\beta = 0.11$; $\alpha/\beta = 0.59$. UV/VIS (MeOH): 529, 495, 468, 389; $D_C/D_\beta = 0.11$; $\alpha/\beta = 0.56$. CD (EPA, + 20°): 526(neg. max.), 493(neg. max.), 476(neg. max.), 467(neg. max.), 317(pos. max.), 306(sh), 273(neg. max.), 264(sh), 243(pos. max.), 222(neg. max.), 205(pos. max.). CD (EPA, − 80°): 543(neg. max.), 525(pos. max.), 510(neg. max.), 505(neg. max.), 476(neg. max.), 400(neg. max.), 323(pos. max.), 310(pos. max.), 275(neg. max.), 268(sh), 255(sh), 244(pos. max.), 207(pos. max.). IR ($CHCl_3$): 3610*w*, 3800–3300*w*, 2960*s*, 2925*s*, 2860*m*, 1730*s*, 1600*w*, 1580*w*, 1460*m*, 1381*m*, 1290*s*, 1280*s*, 1125*m*, 1070*m*, 1000*w*, 970*s*. ^{1}H-NMR (400 MHz, $CDCl_3$); 1.181 (*s*, Me(16,16')); 1.220 (*s*, Me(17,17')); 1.604 (*s*, Me–C(3'',3''')); 1.664 (*s*, Me(4'',4''')); 1.918 (*s*, Me(18,18')); 1.975 (*s*, Me(19,19')); 1.984 (*s*, Me(20,20')); 1.95–2.05, 2.30–2.40 (2*m*, CH_2(1'',1''')); 2.05–2.15 (*td*, *J* = 9, 3, H–C(2,2')); 5.058 (*m*, H–C(2'',2''')); 5.501 (*dd*, *J* = 16, 9, H–C(3,3')); 6.134 (*d*, *J* = 12, H–C(6,6')); 6.168 (*d*, *J* = 16, H–C(4,4')); 6.238 (*d*, *J* = 12, H–C(10,10')); 6.276 (*m*, H–C(14,14')); 6.36 (*d*, *J* = 15, H–C(8,8')); 6.383 (*d*, *J* = 15, H–C(12,12')); 6.600 (*dd*, *J* = 15, 12, H–C(7,7')); 6.640 (*m*, H–C(15,15')); 6.644 (*dd*, *J* = 15, 12, H–C(11,11')). MS: 704(2, M^+), 686 (1), 628 (1), 612 (1), 598 (3), 588 (1), 368 (1), 315 (1), 290 (2), 273 (3), 261 (4), 253 (2), 251 (4), 209 (15), 197 (15), 183 (16), 163 (18), 157 (31), 145 (41), 119 (48), 105 (53), 91 (16), 81 (50), 69 (100), 59 (56), 43 (61).

9. *(2S)-3,4-Didehydro-1,2-dihydro-1-hydroxy-2-(3-methylbut-2-enyl)-8'-apo-ψ-caroten-8'-al* ((*S*)-**15**). Crystallization from toluene/petroleum ether. Red crystals. M.p. 142°. UV/VIS (EtOH): 478. UV/VIS (EtOH + $NaBH_4$): 483, 452, 427, 346, 331, 280. CD (EPA, + 25°): 360(pos. max.), 346(pos. max.), 291(pos. max.), 250(neg. max.), 222(pos. max.), 204(pos. max.). IR ($CHCl_3$): 3605*w*, 2930*m*, 2860*m*, 1665*s*, 1610*w*, 1555*m*, 1520*w*, 1405*w*, 1385*w*, 1360*w*, 1315*w*, 1280*w*, 1000*m*, 970*s*, 930*m*. ^{1}H-NMR (400 MHz, $CDCl_3$): 1.18, 1.22 (2*s*, Me(16), Me(17)); 1.60 (*s*, Me–C(3''), *cis* to C(1'')); 1.66 (*s*, Me(4''), *trans* to C(1'')); 1.60–1.63 (*s*, HO–C(1)); 1.90 (*s*, Me(19')); 1.92 (*s*, Me(18)); 1.99 (*s*, Me(19), Me(20,20')); 2.06–2.13 (*m*, H–C(2)); 1.95–2.05, 2.30–2.40 (2*m*, CH_2(1'')); 5.06 (*m*, H–C(2'')); 5.51 (*dd*, *J* = 16, 9, H–C(3)); 6.13 (*d*, *J* = 11, H–C(6)); 6.16 (*d*, *J* = 16, H–C(4)); 6.23 (*d*, *J* = 11.5, H–C(10)); 6.28 (*d*, *J* = 12, H–C(14)); 6.36 (*d*, *J* = 15, H–C(7)); 6.62 (*dd*, *J* = 15, 11, H–C(15')); 6.66 (*dd*, *J* = 15, 11, H–C(11')); 6.69 (*dd*, *J* = 15, 11, H–C(11)); 6.76 (*d*, *J* = 15, H–C(12')); 6.76 (*dd*, *J* = 15, 11, H–C(15)); 6.93 (*dd*, *J* = 11, 11, H–C(10')); 9.44 (*s*, H–C(8')). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 9.61 (C(19)); 12.67, 12.86, 13.02 (C(18), C(19), C(20, 20')); 17.92 (*Me*–C(2''), *cis* to C(1'')); 25.70 (C(4''), *trans* to C(1'')); 26.96 (C(17)); 27.57 (C(16)); 28.71 (C(1'')); 55.60 (C(2)); 72.45 (C(1)); 122.73 (C(11')); 123.01 (C(2'')); 124.97 (C(7)); 126.15 (C(11)); 129.43 (C(15')); 129.78 (C(3)); 131.04 (C(6)); 132.47 (C(14)); 132.53 (C(10)); 132.94 (C(15)); 134.97, 135.06 (C(9'), C(13')); 136.46, 136.59 (C(9), C(13)); 137.50 (C(14')); 137.64 (C(8), C(12)); 138.05

(C(4)); 138.28 (C(5)); 145.63 (C(12')); 148.93 (C(10')); 194.01 (C(8')). MS: 500 (38, M^+), 482 (2), 442 (11), 432 (2), 413 (1), 394 (2), 386 (2), 373 (2), 372 (2), 355 (3), 336 (2), 223 (8), 209 (13), 197 (13), 183 (13), 171 (15), 157 (30), 145 (42), 131 (25), 119 (45), 105 (50), 91 (49), 81 (34), 69 (94), 59 (100), 55 (45), 43 (66), 41 (72).

10. *(5*R*)-8-Methyl-5-(2'-methyl-1',3'-dioxolan-2'-yl)non-7-en-2-one* ((*R*)-**17**). A mixture of CuCl (750 mg, 7.6 mmol), NaO(*t*-Bu) (750 mg, 7.8 mmol), and triphenylphosphine (5.0 g, 19.1 mmol) was flushed with N_2, connected to a hydrogenation apparatus, and twice alternatively evacuated and filled with H_2. Benzene (50 ml) was added and the mixture stirred for 2 h under H_2 (→ deep red soln.). The atmosphere was replaced through N_2, and a soln. of (*S*)-**16** (500 mg, 2.1 mmol) in benzene (40 ml) was added dropwise. The mixture was stirred under N_2 for 14 h, the flask opened, and the mixture stirred for another 60 min. Filtration over *Celite* and FC (silica gel, hexane/AcOEt) gave 300 mg (60%) of (*R*)-**17**. Colorless oil. GC (200°, 30% *Acetoxygamma in OV-1701*, 10 m): t_R 55.4; enantiomeric excess > 99%. $[\alpha]_D^{22} = -0.53$ ($c = 0.17$, $CHCl_3$). ^{1}H-NMR (300 MHz, $CDCl_3$): 1.25 (*s*, Me–C(2')); 1.60 (*s*, Me–C(8)); 1.67 (*s*, Me(9)); 1.52–1.96 (*m*, 2 H–C(4), H–C(5), H–C(6)); 2.11 (*s*, Me(1)); 2.23 (br. *d*, $J = 10.7$, H–C(6)); 2.53 (*dd*, $J = 6.6, 1.0$, 2 H–C(3)); 3.90 (*m*, CH_2(4'), CH_2(5')); 5.12 (*tq*, $J = 7.1, 1.5$, H–C(7)). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 17.79 (*Me*–C(8)); 23.59 (*Me*–C(2')); 25.77 (C(9)); 28.99 (C(6)); 29.80 (C(1)); 42.44 (C(3)); 45.94 (C(5)); 64.28, 64.41 (C(4'), C(5')); 112.32 (C(2')); 123.41 (C(7)); 132.09 (C(8)); 209.26 (C(2)): IR and MS: see [8].

11. *(6*R*)-3,9-Dimethyl-6-(2'-methyl-1',3'-dioxolan-2'-yl)deca-1,8-dien-3-ol* ((*R*)-**18**). A soln. of (*R*)-**17** (2.16 g, 8.99 mmol) in abs. THF (20 ml) was added dropwise to a soln. of vinylmagnesium bromide (1M in THF; 36 ml, 36 mmol) in abs. THF (40 ml) at 0°. The mixture was stirred for 2 h at 0°, hydrolyzed with sat. NH_4Cl soln. (200 ml), partitioned between Et_2O and H_2O, dried (Na_2SO_4), and evaporated. FC (silica gel, hexane/Et_2O 1:5) gave 2.38 g (98%) of (*R*)-**18**. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.25 (*s*, Me–C(3), Me–C(2')); 1.60 (*s*, Me–C(9)); 1.43–1.64 (*m*, CH_2(4), CH_2(5), H–C(6)); 1.68 (Me(10)); 1.7–2.0 (br. *s*, HO–C(3)); 1.92 (*m* H–C(7)); 2.23 (*m*, H–C(7)); 3.91 (*m*, CH_2(4'), CH_2(5')); 5.02 (*dt*, $J = 10.6, 1.5$, H–C(1)); 5.14 (*m*, H–C(8)); 5.18 (*dd*, $J = 17.3, 1.5$, H–C(1)); 5.87 (*dd*, $J = 10.6, 17.3$, H–C(2)). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 17.81 (*Me*–C(9)); 20.89 (*Me*–C(2')); 24.17 (C(5)); 25.78 (C(10)); 27.75 (*Me*–C(3)); 29.06 (C(7)); 40.89 (C(4)); 47.11 (C(6)); 64.38, 64.39 (C(4'), C(5')); 73.55 (C(3)); 111.52 (C(1)); 112.60 (C(2')); 123.69 (C(8)); 131.63 (C(9)); 145.26 (C(2)). IR and MS: see [8].

12. *(3*R*)-6-Hydroxy-6-methyl-3-(3'-methylbut-2'-enyl)oct-7-en-2-one* ((*R*)-**19**). A soln. of (*R*)-**18** (5.45 g, 20.3 mmol) and pyridinium toluene-4-sulfonate (PPTS; 630 mg, 2.5 mmol) in 90% aq. acetone (200 ml) was refluxed for 2 h and cooled to r.t. H_2O (50 ml) was added, the acetone evaporated, and the aq. phase extracted with AcOEt. Drying ($MgSO_4$) and FC (silica gel, hexane/AcOEt) afforded 4.12 g (91%) of (*R*)-**19**. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.26 (*s*, Me–C(6)); 1.40–1.72 (*m*, CH_2(4), CH_2(5)); 1.61 (*s*, Me–C(3')); 1.68 (*s*, Me(4')); 2.10 (*s*, Me(1)); 2.13 (*q*, $J = 7.3$, H–C(1')); 2.25 (*q*, $J = 7.3$, H–C(1')); 2.45 (*m*, H–C(3)); 5.01 (*tq*, $J = 7.3, 1.5$, H–C(2')); 5.05 (*d*, $J = 9.9$, H–C(8)); 5.19 (*d*, $J = 16.5$, H–C(8)); 5.86 (*dd*, $J = 16.5, 9.9$, H–C(7)). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 14.11 (*Me*–C(6)); 17.70 (*Me*–C(3')); 25.25 (C(4)); 25.65 (C(4')); 27.85 (C(1)); 30.32 (C(1')); 39.49 (C(5)); 53.24 (C(3)); 72.85 (C(6)); 111.83 (C(8)); 121.04 (C(2')); 133.55 (C(3')); 144.69 (C(7)); 212.58 (C(2)). IR and MS: see [8].

13. *(3*R*)-2,6-Dimethyl-3-(3'-methylbut-2'-enyl)oct-7-ene-2,6-diol* ((*R*)-**9**). A soln. of 3M MeMgBr in Et_2O (23 ml, 69 mmol) was diluted in *t*-BuOMe (120 ml; → white precipitation). A soln. of (*R*)-**19** (4.02 g, 18 mmol) in *t*-BuOMe (20 ml) was added under N_2 so that the temp. did not exceed 30°. The mixture was refluxed for 3 h, cooled to 0°, hydrolyzed with half-sat. NH_4Cl soln. (20 ml) and partitioned between *t*-BuOMe and H_2O. The org. layer was dried ($MgSO_4$) and evaporated. FC (silica gel, hexane/AcOEt 7:3) gave 3.98 g (92%) of (*R*)-**9**. Colorless oil. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.16 (*s*, Me–C(6)); 1.71 (*s*, Me(1)); 1.24 (*m*, H–C(5)); 1.25 (*s*, Me–C(2)); 1.34 (*m*, H–C(6)); 1.58 (*m*, CH_2(4), H–C(5)); 1.61 (*s*, Me–C(3')); 1.68 (*s*, Me(4')); 1.96 (*m*, H–C(1')); 2.14 (*m*, H–C(1')); 2.33 (br. *s*, HO–C(2), HO–C(6)); 5.03 (*dd*, $J = 8.1, 1.5$, H–C(8)); 5.16 (*tq*, $J = 6.5, 1.5$, H–C(2')); 5.18 (*dd*, $J = 17.3, 1.5$, H–C(8)); 5.86 (*dd*, $J = 17.3, 8.1$, H–C(7)): ^{13}C-NMR (75.5 MHz, $CDCl_3$): 17.86 (*Me*–C(3')); 24.37 (C(4)); 25.78 (C(4')); 27.04 (*Me*–C(6)); 27.52 (C(1)); 28.10 (*Me*–C(2)); 29.50 (C(1')); 41.80 (C(5)); 50.12 (C(3)); 73.29 (C(6)); 74.19 (C(2)); 111.64 (C(8)); 124.33 (C(2)); 131.69 (C(3')); 145.41 (C(7)). IR and MS: see [8].

14. *[(6*R*,4*E*)-6-(1'-Hydroxy-1'-methylethyl)-3,9-dimethyldeca-2,8-dien-1-yl]triphenylphosphonium Bromide* ((*R*)-**20**). A soln. of (*R*)-**9** (1.00 g, 4.2 mmol) in $CHCl_3$/MeOH 1:1 (20 ml) was added to a soln. of triphenylphosphonium bromide (1.54 g, 4.5 mmol) in $CHCl_3$/MeOH 1:1 (20 ml). The mixture was stirred under N_2 and exclusion of light for 3 d and evaporated and the residue dissolved in little CH_2Cl_2. The soln. was precipitated in ice-cold hexane/*t*-BuOMe 1:5, washed twice with *t*-BuOMe, and dried under h.v. to give 1.91 g (81%) of (*R*)-**20** as a white powder (m.p. 67°) which was directly used for the next step.

15. *(all-*E*,2*R*,2'*R*)-3,4,3',4'-Tetrahydrodianhydrobacterioruberin* (= *1,2,1',2'-Tetrahydro-2,2'-bis(3-methylbut-2-enyl)-ψ,ψ-carotene-1,1'-diol*; (all-*E*,2*R*,2'*R*)-**5**). A soln. of 10% KOH in MeOH (1 ml) was added to a soln.

of (*R*)-**20** (650 mg, 1.15 mmol) and crocetindialdehyde (**13**); (50 mg, 0.16 mmol) in CH_2Cl_2 (10 ml) and refluxed under N_2 and exclusion of light for 24 h. The mixture was extracted with CH_2Cl_2 (3 ×) and the org. layer dried (Na_2SO_4) and evaporated. FC (silica gel, hexane/AcOEt 20:1 + 0.5% Et_3N) gave 14.3 mg (13%) of (all-*E*,2*R*,2′*R*)-**5** and 36.8 mg (32%) of (*Z*)-isomers of **5**. Red powder. M.p. 130°. UV/VIS (acetone): 503, 473, 448, 362, 346; $D_C/D_\beta = 0.16$; $\alpha/\beta = 0.83$; %III/II = 50.4. CD (EPA, −180°): 223(pos. max.); 260(neg. max.); 289(pos. max.); 306(sh); 322(sh); 350(neg. max.); 369(pos. max.); 380(neg. max); 434(sh); 454(sh), 484(pos. max.); 498(neg. max.); 504(pos. max); 510(neg. max); 521(pos. max.). ^{1}H-NMR (400 MHz, $CDCl_3$): 1.36 (*s*, Me(16,16′), Me(17,17′)); 1.675 (*s*, Me−C(3″,3‴)); 1.71 (*s*, Me(4″,4‴)); 1.88 (*m*, CH_2(3,3′)); 1.91 (*s*, Me(18,18′)); 1.99 (*s*, Me(19,19′), Me(20,20′)); 2.04 (*m*, H−C(2,2′)); 2.14 (*m*, CH_2(4,4′)); 2.17 (*m*, H−C(1″,1‴)); 2.80 (*m*, H−C(1″,1‴)); 5.05 (*m*, H−C(2″,2‴)); 5.97 (*d*, *J* = 11.2, H−C(6,6′)); 6.20 (*d*, *J* = 11.2, H−C(10,10′)); 6.26 (part of *AA′XX′*, H−C(14,14′)); 6.27 (*d*, *J* = 14.9, H−C(8,8′)); 6.37 (*d*, *J* = 14.7, H−C(12,12′)); 6.50 (*dd*, *J* = 14.9, 11.2, H−C(7,7′)); 6.65 (part of *AA′XX′*, H−C(15,15′)); 6.66 (*dd*, *J* = 14.7, H−C(11,11′)). ^{13}C-NMR (100.6 MHz, $CDCl_3$): 12.84 (C(19,19′), C(20,20′)); 16.95 (C(18,18′)); 17.77 (C(5″,5‴)); 24.14 (C(3,3′)); 25.79 (C(4″,4‴)); 29.48 (C(16,16′), C(17,17′)); 31.33 (C(1″,1‴)); 40.17 (C(4,4′)); 47.15 (C(2,2′)); 77.14 (C(1,1′)); 122.96 (C(2″,2‴)); 124.60 (C(7,7′)); 125.01 (C(11,11′)); 125.42 (C(6,6′)); 129.94 (C(15,15′)); 131.38 (C(10,10′)); 132.41 (C(14,14′)); 132.66 (C(3″,3‴)); 135.28 (C(8,8′)); 136.17 (C(9,9′)); 136.55 (C(13,13′)); 137.13 (C(12,12′)); 140.15 (C(5,5′)). MS: 619(1), 223(6), 188 (56), 160 (51), 121 (29), 105 (28), 95 (44), 92 (46), 69 (85), 41 (100).

16. *(all-*E*,2*S*)-3,4-Didehydro-2-(3-methylbut-2-enyl)orhodopin* (= *3,4-Didehydro-1,2-dihydro-2-(3-methylbut-2-enyl)-ψ,ψ-caroten-1-ol;* (*S*)-**6**). To a soln. of (*S*)-**12** (204 mg, 0.50 mmol) and 8′-apo-ψ-caroten-8′-al (**21**, 60 mg, 0.14 mmol) in CH_2Cl_2 (6 ml), freshly prepared 0.15M NaOEt in EtOH (5 ml, 0.75 mmol) was added dropwise within 1 h. After 3.5 h (*S*)-**12** (80 mg, 0.142 mmol) and 0.15M NaOEt (1 ml, 0.15 mmol) was added. After additional 1.25 h, H_2O (30 ml) was added and the aq. phase extracted 3 times with CH_2Cl_2 (50 ml). The combined org. phases were twice washed with H_2O (60 ml), dried (Na_2SO_4), and evaporated. After FC (hexane/AcOEt 8:3), the crude product was submitted to prep. TLC (toluene/petroleum ether/EtOH 50:50:8) to give 21.1 mg (30%) of pure (all-*E*,*S*)-**6**. M.p. 152–153°. UV/VIS (hexane): 518, 484, 456, 375. CD (EPA, + 20°): 528(pos. max.), 509(neg. max.), 477(neg. max.), 450(neg. max.), 373(pos. max.), 304(pos. max.), 294(sh), 262(neg. max.), 230(sh), 204(pos. max.). CD (EPA, −180°): 543(pos. max.), 533(neg. max.), 525(neg. max.), 506(pos. max.), 493(neg. max.), 458(neg. max.), 383(pos. max.), 364(pos. max.), 350(pos. max.), 309(pos. max.), 298(pos. max.), 265(neg. max.), 228(pos. max.), 205(pos. max.), 194(neg. max.). IR ($CHCl_3$): 3610*w*, 3640–3300*w*, 2970*w*, 2920*w*, 1710*s*, 1595*w*, 1360*m*, 1330*w*, 965*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.176 (*s*, Me(16)); 1.219 (*s*, Me(17)); 1.596 (*s*, Me−C(3″)); 1.605 (*s*, Me(17′)); 1.653 (*s*, Me(4″)); 1.677 (*s*, Me(16′)); 1.824 (*s*, Me(18)); 1.972 (*s*, Me(19,19′), Me(20′)); 1.985 (*s*, Me(20)); 1.87–2.01, 2.30–2.41 (2*m*, CH_2(1″)); 2.05–2.13 (*m*, H−C(2)); 2.11 (*m*, CH_2(3′), CH_2(4′)); 5.058 (*m*, H−C(2″)); 5.106 (*m*, H−C(2′)); 5.496 (*dd*, *J* = 16, 9, H−C(3)); 5.954 (*d*, *J* = 11, H−C(6′)); 6.128 (*d*, *J* = 11, H−C(6)); 6.175 (*d*, *J* = 16, H−C(4)); 6.19 (*d*, *J* = 11, H−C(10′)); 6.24 (*d*, *J* = 11, H−C(10)), 6.25 (*d*, *J* = 15, H−C(8′)); 6.20–6.30 (*m*, H−C(14,14′)); 6.36 (*d*, *J* = 14, H−C(12′)); 6.37 (*d*, *J* = 15, H−C(8)); 6.38 (*d*, *J* = 14, H−C(12)); 6.49 (*dd*, *J* = 15, 11, H−C(7′)); 6.60 (*dd*, *J* = 15, 11, H−C(7)); 6.63 (*dd*, *J* = 16, 12, H−C(11,11′)); 6.64 (*m*, H−C(15,15′)). MS: 620 (3, M^+), 601 (1), 562 (1), 514 (1), 359 (1), 333 (1), 321 (1), 301 (1), 223(3), 209(7), 197(9), 183 (7), 171(10), 157(16), 145 (21), 133 (14), 113 (27), 105 (34), 91(38), 81(32), 69 (100), 55 (24), 41 (72).

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