45. Synthesis of (all-*E*,2*R*,2′*R*)-Oscillol

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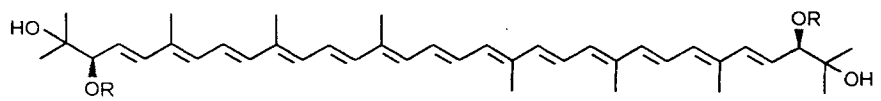
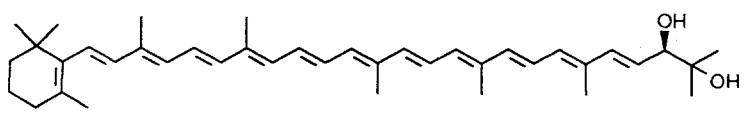
Optically active (all-*E*,2*R*,2′*R*)-oscillol (= (all-*E*,2*R*,2′*R*)-3,4,3′,4′-tetradehydro-1,2,1′,2′-tetrahydro-ψ,ψ-carotene-1,2,1′,2′-tetrol; **1**) was synthesized according to the $C_{10} + C_{20} + C_{10} = C_{40}$ strategy, applying the *Wittig* reaction to couple the synthons **4** and **6**. The chiral centre was introduced by a *Sharpless* dihydroxylation of 3-methylbut-2-enyl 4-nitrobenzoate (**8**).

1. Introduction. – The tetrahydroxycarotenoid oscillol (= 3,4,3′,4′-tetradehydro-1,2,1′,2′-tetrahydro-ψ,ψ-carotene-1,2,1′,2′-tetrol; **1**) has been identified as the aglycon of oscillaxanthin (**2**) which was isolated for the first time by *Karrer* and *Rutschmann* from the cyanobacteria *Oscillatoria rubescens* [1]. Later, **2** was isolated also from *Athrospira sp.* [2], *O. princeps* [3], *O. aghardi* [4], and *Spirulina platensis* [5]. α-L-Quinovose [6] [7] and α-L-fucose [5] have been identified as carbohydrate part of **2**. Based on UV/VIS and mass spectra, the constitution of **1** was elucidated by *Hertzberg* and *Liaaen-Jensen* [6]. Basic as well as enzymatic hydrolysis of **2** failed, and hydrolysis under acidic conditions led to decomposition of the carotenoid [8]. Based on the comparison of the CD spectra of **2** and plectaniaxanthin (**3**), the (*R*)-configuration at C(2) and C(2′) of oscillol (**1**) was postulated [8].



1 R = H: (all-*E*,2*R*,2′*R*)-oscillol

2 R = α-L-quinovose or α-L-fucose: oscillaxanthin



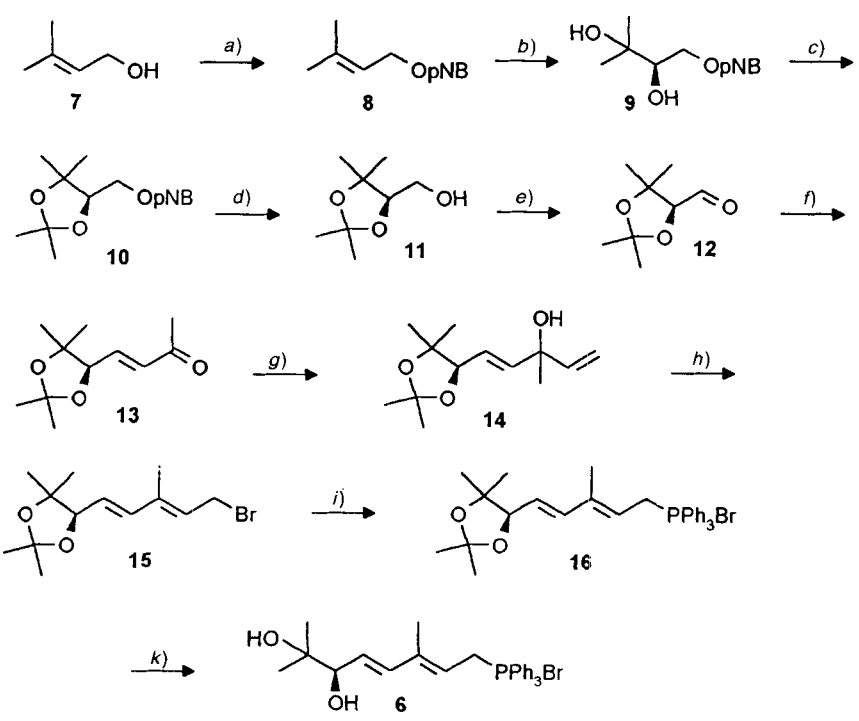
3 plectaniaxanthin

In view of the structure elucidation of oscillol (**1**) and oscillaxanthin (**2**), we report here on the total synthesis of (all-*E*,2*R*,2′*R*)-oscillol (**1**).

[1]) Diploma work and part of the Ph. D. thesis of *B. Traber*.

2. Results and Discussions. – For the total synthesis of **1**, the strategy $C_{10} + C_{20} + C_{10} = C_{40}$, which is often used for the synthesis of acyclic C_{40}-carotenoids, was selected. Having at hand crocetindialdehyde (= 8,8′-diapocarotene-8,8′-dial; **4**) and 15,15′-dide-hydrocrocetindialdehyde (**5**) as C_{20}-building blocks, the chiral C_{10}-phosphonium salt **6** was the target compound in the present synthesis. As key step for the introduction of the chirality, the *Sharpless* dihydroxylation [9], which is catalyzed by 1,4-bis(dihydro-quinidin-9-*O*-yl)phthalazine ($DHQD_2$-PHAL) and potassium osmate, was selected. The starting material 3-methylbut-2-en-1-ol (**7**) was converted with 4-nitrobenzoyl chloride to ester **8** in 88% yield after recrystallization. The *Sharpless* dihydroxylation [9] of **8** with AD-mix-β (see *Exper. Part*) gave the optically active diol **9** with the (2*R*)-configuration in 59% yield. Acetal **10** was obtained by reaction of **9** with dimethoxypropane/TsOH in 77% yield after flash chromatography. Gas chromatography exhibited an enantiomeric excess of 91.4%. By saponification of **10** in *t*-BuOH with aqueous NaOH solution, the primary alcohol **11** was obtained in 90% yield. *Swern* oxidation with oxalyl chloride/DMSO in CH_2Cl_2 gave aldehyde **12** which was converted in a *Wittig* reaction with (acetylmethylidene)triphenylphosphorane to ketone **13** ((*E*)/(*Z*) 68:32) in 76% yield for both steps. The (*E*)/(*Z*) isomers were separated by flash chromatography, and the

Scheme 1

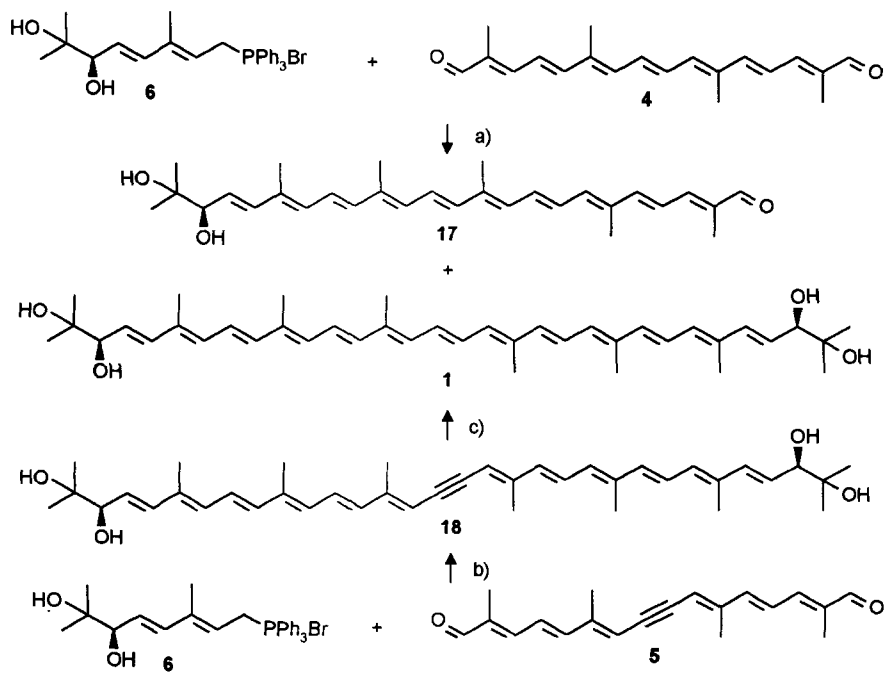


a) 4-$NO_2C_6H_4COCl$, pyridine. *b*) AD-mix β, $MeSO_2NH_2$, Na_2SO_3, *t*-BuOH/H_2O. *c*) Dimethoxy-propane, TsOH, acetone. *d*) 2N NaOH, *t*-BuOH. *e*) $(COCl)_2$, DMSO, CH_2Cl_2, −65°. *f*) $AcCHPPh_3$, CH_2Cl_2. *g*) $CH_2CHMgBr$, THF. *h*) PBr_3, petroleum ether. *i*) PPh_3, Et_2O. *k*) 10% AcOH/H_2O.

(*E*)-isomer was reacted in a *Grignard* reaction with vinylmagnesium bromide to give **14** as a mixture of diastereoisomers. The diastereoisomer mixture **14** was reacted with PBr_3 in petroleum ether to give the primary bromide **15** which was immediately converted with PPh_3 in Et_2O to the phosphonium salt **16** in 38% yield for both steps. Hydrolysis of the acetal group in 10% aqueous AcOH solution gave in almost quantitative yield the phosphonium salt **6** (*Scheme 1*).

The coupling of the phosphonium salt **6** with crocetindialdehyde (**4**) in a two-phase (2N NaOH/CH_2Cl_2) *Wittig* reaction resulted in a mixture of (*E*/*Z*)-isomeric oscillols (41%), the stereoisomeric C_{30}-monoadducts **17** (51%), and unreacted **4** (8%). The by-product Ph_3PO showed in various mixtures of solvents almost the same polarity as oscillol (**1**); its separation was finally achieved by flash chromatography on silica gel with acetone/Et_3N 200:1. HPLC Analysis of oscillol revealed a mixture of five (*E*/*Z*)-isomers. The (all-*E*)-isomer **1** was obtained by recrystallization from warm benzene in 3.7% yield relative to **7**. The *Wittig* reaction of **6** with 15,15′-didehydrocrocetindialdehyde (**5**) to 15,15′-didehydrooscillol (**18**) allowed milder reaction conditions (room temperature *vs.* reflux) with a similar yield (38%) compared to the reaction of **6** with **4**. However, the *Lindlar* hydrogenation did not proceed quantitatively, and due to the similar chromatographical behavior of **1** and **18**, these compounds could not be separated on a preparative scale. As the formation of (*E*/*Z*)-isomers occurs in both reactions, the second reaction sequence was not further investigated (*Scheme 2*).

Scheme 2



a) 2N NaOH, CH_2Cl_2, reflux. *b*) 2N NaOH, CH_2Cl_2, r.t. *c*) H_2, *Lindlar* catalyst, I_2, sunlight.

3. Spectroscopical Studies. – All ^{1}H- and ^{13}C-signals in the NMR spectra of (all-*E*,2*R*,2′*R*)-oscillol (**1**), with the exception of the C(10) and C(12) signal, can be unambiguously assigned by 400-MHz ^{1}H-NMR, ^{13}C-NMR, DEPT, and ^{1}H,^{1}H-COSY experiments (*Table*).

Table. *^{1}H- and ^{13}C-NMR of* **1** (400 and 100.6 MHz, resp.; $CDCl_3$): *Chemical Shifts and Coupling Constants*

	δ [ppm]	Multiplicity	Coupling constants [Hz]		δ [ppm]
HO–C(1)	*ca.* 2.08[a])	*s*		C(1)	73.07
HO–C(2)	*ca.* 2.08[a])	*s*		C(2)	80.06
H–C(2)	4.00	*d*	$J(2,3) = 7.61$	C(3)	126.30
H–C(3)	5.71	*dd*	$J(3,2) = 7.61$, $J(3,4) = 15.64$	C(4)	138.12
H–C(4)	6.38	*d*	$J(4,3) = 15.64$	C(5)	134.09
H–C(6)	6.20	*d*	$J(6,7) = 11.46$	C(6)	138.35
H–C(7)	6.58	*dd*	$J(7,6) = 11.46$, $J(7,8) = 15.08$	C(7)	124.27
H–C(8)	6.39	*d*	$J(8,7) = 15.08$	C(8)	138.73
H–C(10)	6.26	*d*	$J(10,11) = 11.64$	C(9)	135.97
H–C(11)	6.65	*dd*	$J(11,10) = 11.64$, $J(11,12) = 14.66$	C(10)[b])	133.24
H–C(12)	6.40	*d*	$J(12,11) = 14.66$	C(11)	125.11
H–C(14)	6.28	*AA′XX′*		C(12)[b])	133.32
H–C(15)	6.65	*AA′XX′*		C(13)	136.72
CH_3(16)	1.18	*s*		C(14)	132.96
CH_3(17)	1.24	*s*		C(15)	130.38
CH_3(18)	1.92	*s*		C(16)	26.48
CH_3(19)	1.97	*s*		C(17)	23.96
CH_3(20)	1.98	*s*		C(18)	12.98
				C(19)	12.89
				C(20)	12.81

[a]) Broad *s*, integration 4 H. [b]) Assignment uncertain.

The UV/VIS spectrum of **1** in MeOH shows a fine structure typical for acyclic carotenoids with maxima at 523, 493, and 468 nm which are in agreement with the data for natural oscillaxanthin (**2**) [10]. The CD spectrum in Et_2O/isopentane/EtOH 5:5:2 (EPA) at −180° shows maxima and minima at 282 (−2.5), 301 (+9.1), 482 (−9.3), 501 (−3.0), 511.5 (−4.6), 531 (+4.5), 552.5 (−0.4), and 572 nm (+7.0). As no CD spectrum of oscillol (**1**) from natural sources is known, no conclusion on the configuration of **1** as aglycone of **2** can be drawn. As shown in the *Figure*, the CD spectrum of oscillaxanthin hexaacetate [8] shows no similarity to the spectrum of **1**. But the spectra have to be compared with reservations as the spectrum of oscillaxanthin hexaacetate was measured at room temperature [11] and that of **1** at −180°. The comparison with plectaniaxanthin (**3**) which also possesses a 3,4-didehydro-1,2-dihydro-1,2-dihydroxy-ψ-end group shows that the CD spectrum of **3** and for the corresponding 2′-glycoside are similar [12] [13]. On the other hand, it was demonstrated that the CD spectrum of **3** is strongly temperature-dependent. Additionally, the comparison of the monocyclic chromophore of **3** with the acyclic chromophore of oscillol (**1**) may not be reliable [14] [15]. Considering these limitations on the CD correlations, only a direct comparison of natural and synthetic oscillol (**1**) or oscillaxanthin (**2**) will unambiguously determine the configuration of natural **1**. These investigations are in progress.

Figure. *CD Spectra of oscillaxanthin hexaacetate* (---; redrawn from [8]) *and of (all-*E,*2*R,*2'* R*)-oscillol* (**1**; —)

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Experimental Part

1. General. All experiments were carried out under N_2 or Ar. Solvents were distilled prior to use or purchased in HPLC quality. TLC: Silica gel *KG 60, F_{254}* (*Merck*). Flash chromatography (FC): Silica gel *60* (*J.T. Baker*, 0.040–0.063 mm). Anal. high-pressure liquid chromatography (HPLC): *Altex-110A* pump, *Kontron 720-LC* spectrometer, *HP-3392A* integrator; columns: *Macherey-Nagel 720055.6 Nucl. 120-3 C18* and *Macherey-Nagel 715.0022 250/VP/10 Nucl. 5 C18*. GC: *HP-5890*; t_R in min. M.p.: *Büchi 510*, not corrected. $[\alpha]_D$: *Perkin-Elmer-241* polarimeter. UV Spectra: *Perkin-Elmer 554*; λ_{max} in nm. CD Spectra: modified *Jobin-Yvon Dichrograph II*, wavelength in nm ($\Delta\varepsilon$). IR Spectra: *Perkin-Elmer-782* spectrometer, $\tilde{\nu}$ in cm^{-1}. ^{1}H- and ^{13}C-NMR Spectra: *Bruker AC-300* (300 and 75.5 MHz, resp.), *Bruker AM-400* (400 and 100.6 MHz, resp.); in $CDCl_3$; chemical shifts in ppm as δ values relative to $CDCl_3$ (= 7.26 ppm), *J* in Hz. Mass spectra: *Varian MAT CH-7A*; *m/z* (rel. intensity in %); ionization energy 70 eV.

2. *3-Methylbut-2-enyl 4-Nitrobenzoate* (**8**). To a soln. of 4-nitrobenzoyl chloride (4.3 g, 23 mmol) in dry pyridine (30 ml) cooled to 0° was added dropwise 3-methylbut-2-en-1-ol **7**; (2.0 g, 23 mmol). The mixture was stirred for 30 min, the cooling bath removed, and stirring continued for additional 90 min. The mixture was partitioned between Et_2O and 0.5M HCl, washed with sat. aq. $NaHCO_3$ soln. and brine, dried ($MgSO_4$), and evaporated. Recrystallization from hot AcOEt/EtOH 1:1 gave 4.75 g (88%) of **8**. Light-yellow needles. M.p. 63°. IR (KBr): 1715*s*, 1670*w*, 1610*m*, 1530*s*, 1350*m*, 1280*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.80 (*s*, Me–C(3')); 1.84 (*s*, 3 H–C(4')); 4.88 (*d*, *J* = 9, 2 H–C(1')); 5.48 (*t*, *J* = 9, H–C(2')); 8.27 (*m*, H–C(2), H–C(3), H–C(5), H–C(6)). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 18.16 (*Me*–C(3')); 25.83 (C(4')); 62.80 (C(1')); 116.01 (C(2')); 123.50 (C(3), C(5)); 130.74 (C(2), C(6)); 135.96 (C(1)); 140.21 (C(3')); 150.50 (C(4)); 164.78 (C=O). MS: 235 (28, M^+), 150 (100), 134 (32), 120 (22), 104 (41), 92 (11), 85 (10), 76 (20), 68 (79), 53 (16), 41 (33).

3. *(2R)-2,3-Dihydroxy-3-methylbutyl 4-Nitrobenzoate* (**9**). A soln. of AD-mix β[2]) (1.4 g) and methanesulfonamide (95 mg, 1 mmol) in *t*-BuOH/H_2O 1:1 (10 ml) was cooled to 0°. Ester **8** (235 mg, 1 mmol) was added to the orange slurry and stirred for 23 h. Afterwards, Na_2SO_3 (1.5 g, 11.9 mmol) was added, the cooling bath removed, and stirring continued for an additional h. The soln. was extracted with AcOEt and the org. phase washed with 10% aq. KOH soln. and dried ($MgSO_4$). Purification by FC afforded 160 mg (59%) of **9**. White powder. M.p. 93–94°. $[\alpha]_D^{20} = +5.8$ ($c = 0.04$, $CHCl_3$). IR (KBr): 3520*m*, 3110*w*, 1720*s*, 1610*w*, 1525*s*, 1350*m*, 1275*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.30 (*s*, *Me*–C(3′)); 1.46 (*s*, 3 H–C(4′)); 2.21, 2.82 (2br. *s*, HO–C(2′), HO–C(3′)); 3.86 (*dd*, $J = 9, 3$, H–C(2′)); 4.38 (*dd*, $J = 12, 9$, H–C(1′)); 4.57 (*dd*, $J = 12, 3$, H–C(1′)); 8.27 (*m*, H–C(2), H–C(3), H–C(5), H–C(6)). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 24.50 (*Me*–C(3′)); 26.52 (C(4′)); 67.03 (C(1′)); 71.71 (C(3′)); 76.20 (C(2′)); 123.55 (C(3), C(5)); 130.75 (C(2), C(6)); 135.15 (C(1)); 150.60 (C(4)); 164.98 (C=O). MS: 270 (1, M^+), 254 (3), 236 (4), 208 (7), 168 (62), 150 (100), 134 (25), 104 (48), 59 (97).

4. *(4′R)-(2′,2′,5′,5′-Tetramethyl-1′,3′-dioxolan-4′-yl)methyl 4-Nitrobenzoate* (**10**). To a soln. of **9** (100 mg, 0.37 mmol) in acetone (20 ml), dimethoxypropane (1.1 ml, 9 mmol) and toluene-4-sulfonic acid (10 mg, 0.05 mmol) were added and stirred for 17 h at r.t. Afterwards Et_3N (1 ml) was added and the soln. evaporated. The residue was partitioned between Et_2O and H_2O and the org. phase washed with brine, dried (Na_2SO_4), and evaporated. Drying under h.v. gave 88 mg (77%) of **10**. Light-yellow powder. GC (150°, 30% *DEXY1* in *OV-1701*, 10 m): t_R 106.5 ((*R*)-**10**), 109.3 ((*S*)-**10**); enantiomeric excess 91.4%. M.p. 98°. $[\alpha]_D^{20} = +26.4$ ($c = 0.0027$, $CHCl_3$). IR (KBr): 2990*w*, 2960*w*, 1730*s*, 1615*w*, 1530*s*, 1350*m*, 1120*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.22 (*s*, Me–C(2′)); 1.39, 1.41 (2*s*, 2 Me–C(5′)); 1.49 (*s*, Me–C(2′)); 4.13 (*dd*, $J = 7, 5$, H–C(4′)); 4.46 (*m*, CH_2–C(4′)); 8.27 (*m*, H–C(2), H–C(3), H–C(5), H–C(6)). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 22.95 (*Me*–C(2′)); 26.52, 26.97 (2 *Me*–C(5′)); 28.43 (*Me*–C(2′)); 64.41 (CH_2–C(4′)); 79.63 (C(5′)); 80.54 (C(4′)); 108.24 (C(2′)); 123.55 (C(3), C(5)); 130.83 (C(2), C(6)); 135.06 (C(1)); 150.65 (C(4)); 164.64 (C=O). MS: 294 (66, $[M - 15]^+$), 234 (16), 208 (8), 193 (5), 150 (100), 127 (16), 120 (12), 104 (13), 85 (19), 43 (20).

5. *(4′R)-(2′,2′,5′,5′-Tetramethyl-1′,3′-dioxolan-4′-yl)methanol* (**11**). To a soln. of **10** (600 mg, 1.94 mmol) in *t*-BuOH (15 ml), 2N NaOH (4 ml) was added and the mixture stirred for 2 h at r.t. The soln. was extracted with Et_2O and the org. phase dried ($MgSO_4$) and evaporated. Drying under h.v. for 15 min resulted in 280 mg (90%) of **11**. Colorless oil. $[\alpha]_D^{20} = -11.6$ ($c = 0.164$, MeOH). IR (NaCl): 3440*m*, 2990*s*, 2885*m*, 1470*w*, 1370*s*, 1220*s*, 1195*s*, 1135*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.15 (*s*, Me–C(2′)); 1.33, 1.39 (2*s*, 2 Me–C(5′)); 1.47 (*s*, Me–C(2′)); 2.70 (br. *s*, HO–C(1)); 3.63 (*dd*, $J = 5, 11$, H–C(1)); 3.76 (*dd*, $J = 10, 11$, H–C(4′)); 3.92 (*dd*, $J = 5, 10$, H–C(1)). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 22.98 (*Me*–C(2′)); 26.67, 26.97 (2 Me–C(5′)); 28.52 (*Me*–C(2′)); 61.52 (C(1)); 79.56 (C(5′)); 83.78 (C(4′)); 107.66 (C(2′)). MS: 145 (100, $[M - 15]^+$), 129 (56), 115 (38), 105 (58), 85 (73), 77 (38), 71 (41), 59 (88), 43 (73).

6. *(4′R,3E)-4-(2′,2′,5′,5′-Tetramethyl-1′,3′-dioxolan-4′-yl)but-3-en-2-one* (**13**). To a soln. of $(COCl)_2$ (300 mg, 2 mmol) in CH_2Cl_2 (2.5 ml), DMSO (0.3 ml, 4.5 mmol) in CH_2Cl_2 (1.2 ml) was added and stirred for 15 min at –65°. A soln. of **11** (280 mg, 1.75 mmol) in CH_2Cl_2 (3 ml) was added and the mixture stirred for 1 h. Et_3N (1.3 ml) and, after 10 min stirring, (acetylmethylidene)triphenylphosphorane (930 mg, 2.8 mmol) in CH_2Cl_2 (3 ml) were added, and the soln. was allowed to warm to r.t. The mixture was partitioned between CH_2Cl_2 and half-sat. brine and the org. phase dried ($MgSO_4$) and evaporated. FC afforded 150 mg (52%) of **13** and 70 mg (24%) of its (*Z*)-isomer, colorless liquids. **13**: $[\alpha]_D^{20} = -140.5$ ($c = 0.04$, MeOH). IR (NaCl): 2980*m*, 2935*w*, 2870*w*, 1740*w*, 1675*s*, 1635*w*, 1370*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.01 (*s*, Me–C(2′)); 1.27, 1.31 (2*s*, 2 *Me*-C(5′)); 1.41 (*s*, Me–C(2′)); 2.23 (*s*, 3 H–C(1)); 4.30 (*d*, $J = 5$, H–C(4′)); 6.31 (*d*, $J = 16$, H–C(3)); 6.59 (*dd*, $J = 5, 16$, H–C(4)). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 23.72 (*Me*–C(2′)); 25.80, 26.80 (2 *Me*–C(5′)); 27.40 (C(1)); 28.17 (*Me*–C(2′)); 80.92 (C(5′)); 82.63 (C(4′)); 108.04 (C(2′)); 131.15 (C(3)); 140.10 (C(4)); 197.38 (C(2)). MS: 183 (29, $[M - 15]^+$), 141 (20), 123 (8), 97 (9), 82 (100), 43 (53).

7. *(4′R,4E)-3-Methyl-5-(2′,2′,5′,5′-tetramethyl-1′,3′-dioxolan-4′-yl)penta-1,4-dien-3-ol* (**14**). A soln. of **13** (7.92 g, 40 mmol) in THF (50 ml) was added to 1M vinylmagnesium bromide in THF (100 ml) at –10 to –6°. The mixture was stirred for 2 h at 0° and hydrolyzed with cold sat. NH_4Cl soln. (20 ml) so that the temp. did not exceed 8°. The mixture was warmed to r.t. and partitioned between Et_2O and H_2O. The org. phase was dried with $MgSO_4$ and evaporated. Drying under h.v. for 15 min gave 8.92 g (99%) of **14** (diastereoisomers). Colorless oil. $[\alpha]_D^{20} = -24.8$ ($c = 0.0025$, $CHCl_3$). IR (NaCl): 3440*m*, 3085*w*, 2980*s*, 2935*m*, 2870*w*, 1715*w*, 1645*w*, 1460*w*, 1370*s*,

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[2]) The applied AD-mix β consists of $K_3Fe(CN)_6$, K_2CO_3, $(DHQD)_2$-PHAL, and $K_2OsO_2(OH)_4$ in a molar ratio of 1500:1500:5:1.

1265*m*, 1220*s*, 1195*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.02 (*s*, Me–C(2′)); 1.18 (*s*, Me–C(3)); 1.28, 1.33 (2*s*, 2 Me–C(5′)); 1.38 (*s*, Me–C(2′)); 4.13 (*d*, J = 8, H–C(4′)); 5.00 (*d*, J = 10, H–C(2)); 5.23 (*d*, J = 10, H–C(4)); 5.60 (*dd*, J = 8, 10, H–C(5)); 5.87 (*m*, 2 H–C(1)). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 23.49 (*Me*–C(2′)); 25.66, 26.90 (2 *Me*–C(5′)); 27.75 (*Me*–C(3)); 28.34 (*Me*–C(2′)); 72.80 (C(3)); 80.83 (C(5′)); 84.00 (C(4′)); 107.26 (C(2′)); 112.45 (C(1)); 122.87 (C(5)); 140.02 (C(4)); 143.42 (C(2)). MS: 211 (21, $[M - 15]^+$), 168 (10), 151 (16), 129 (9), 110 (38), 95 (73), 81 (41), 71 (19), 59 (44), 43 (100).

8. *(4′R,4E)-[3-Methyl-5-(2′,2′,5′,5′-tetramethyl-1′,3′-dioxolan-4′-yl)penta-2,4-dien-1-yl]triphenylphosphonium Bromide* (**16**). To a soln. of **14** (530 mg, 2.35 mmol) in light petroleum ether at −14°, pyridine (0.1 ml) and a soln. of PBr_3 (0.21 ml, 2.35 mmol) in light petroleum ether (3 ml) were added and stirred for 45 min at −10°. The mixture was hydrolyzed with sat. aq. $NaHCO_3$ soln. and extracted with Et_2O. The org. phase was washed with brine, dried ($MgSO_4$), and evaporated. The residue was immediately dissolved in Et_2O (5 ml), and PPh_3 (750 mg, 2.86 mmol) was added. The soln. was stirred for 46 h at r.t. under exclusion of light and the precipitation filtered off and washed with cold Et_2O. Drying under h.v. (12 h) afforded 502 mg (39%) of **16**. Light-yellow powder[3]). M.p. 89°. $[\alpha]_D^{20} = +9.9$ (c = 0.005, $CHCl_3$). IR (KBr): 2980*m*, 1630*w*, 1585*w*, 1435*s*, 1365*m*, 1260*w*, 1195*m*, 1110*s*. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.99 (*s*, Me–C(2′)); 1.18, 1.27 (2*s*, 2 Me–C(5′)); 1.48 (*s*, Me–C(2′), Me–C(3)); 4.12 (*d*, J = 8, H–C(4′)); 4.63 (*m*, H–C(1)); 4.85 (*m*, H–C(1)); 5.95 (*m*, H–C(5), H–C(2)); 6.23 (*d*, J = 13, H–C(4)); 7.66–7.85 (*m*, 15 arom. H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 13.40 (C(1)); 23.76 (*Me*–C(2′)); 24.90 (*Me*–C(3)); 25.95, 27.13 (2 *Me*–C(5′)); 28.54 (*Me*–C(2′)); 81.23 (C(5′)); 84.41 (C(4′)); 107.62 (C(2′)); 117.55 (C(4)); 118.68 (C(2)); 125.28 (3 C(4″)); 130.62 (3 C(3″), 3 C(5″)); 134.03 (3 C(2″), 3 C(5″)); 136.10 (C(5)); 136.17 (3 C(1″)); 142.32 (C(3)). MS: 551 (2, M^+), 339 (15), 313 (10), 277 (19), 262 (100), 183 (57), 152 (14), 135 (16), 108 (23), 95 (30), 81 (32), 67 (22), 55 (23), 44 (28).

9. *(6R,4E)-(6,7-Dihydroxy-3,7-dimethylocta-2,4-dien-1-yl)triphenylphosphonium Bromide* (**6**). A soln. of **16** (5.02 g, 1.11 mmol) in 10% aq. AcOH (220 ml) was stirred for 2 h under exclusion of light at 65°. The soln. was evaporated and the residue dissolved in little MeOH and precipitated in Et_2O (500 ml). The precipitation was filtered off, washed with cold Et_2O, and dried under h.v. The filtrate was evaporated and purified by FC (silica gel, AcOEt/acetone/HCOOH 8:1:1). Total yield: 4.54 g (97%) of **6**. White powder. M.p. 132–135°. $[\alpha]_D^{20} = +11.4$ (c = 0.004, MeOH). IR (KBr): 3420*s*, 2940*m*, 1715*w*, 1635*w*, 1440*m*, 1380*w*, 1115*m*. ^{1}H-NMR (300 MHz, $CDCl_3$): 1.00, 1.08 (2*s*, 3 H–C(8), Me–C(7)); 1.28 (*s*, Me–C(3)); 3.91 (*d*, J = 8, H–C(6)); 4.40 (*m*, 2 H–C(1)); 5.29 (*m*, H–C(2)); 5.61 (*m*, H–C(5)); 6.14 (*d*, J = 13, H–C(4)); 6.75 (br. *s*, HO–C(6), HO–C(7)); 7.57–7.82 (*m*, 15 arom. H). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 12.80 (C(1)); 23.56 (*Me*–C(7)); 24.64 (*Me*–C(3)); 26.22 (C(8)); 72.88 (C(7)); 78.66 (C(6)); 117.05 (C(4)); 118.17 (C(2)); 130.09 (3 C(4′)); 130.25 (3 C(3′), 3 C(5′)); 133.54 (3 C(2′), 3 C(6′)); 134.00 (C(1′)); 135.01 (C(5)); 142.88 (C(3)). MS: 413 (7, $[M - 98]^+$), 369 (9), 277 (49), 262 (100), 249 (12), 199 (18), 183 (63), 170 (15), 157 (27), 152 (29), 131 (17), 115 (14), 108 (34), 82 (20).

10. *(2R,2′R)-3,4,15,3′,4′,15′-Hexadehydro-1,2,1′,2′-tetrahydro-ψ,ψ-carotene-1,2,1′,2′-tetrol* (= *(2R,2′R)-15,15′-Didehydrooscillol*; **18**). To a soln. of 15,15′-didehydrocrocetindialdehyde (**5**; 10 mg, 34 μmol) in CH_2Cl_2 (2 ml) at 0°, 2N NaOH (2 ml) was added. A soln. of **6** (76.4 mg, 149.5 μmol) in CH_2Cl_2 (2 ml) was added dropwise to the mixture. The reaction was protected from light, warmed to r.t., and stirred for 3 h. The soln. was extracted with Et_2O and the org. phase washed with phosphate buffer (pH 7) and evaporated. With FC (silica gel, acetone/Et_3N 200:1), triphenylphosphine oxide was separated from the carotenoids. A second FC (silica gel, hexane/AcOEt 1:1 + 0.5% Et_3N) and drying under h.v. (12 h) resulted in 7.8 mg (38%) of **18**. Red powder. M.p. 196°. UV/VIS (AcOEt): 498, 470, 432, 383, 317. IR (KBr): 3430*s*, 2960*s*, 2865*m*, 1760*w*, 1675*s*, 1625*m*, 1455*m*, 1385*s*, 1365*s*, 1255*s*, 1220*m*. ^{1}H-NMR (300 MHz, CDCl): 1.13 (*s*, 6 H, Me(16,16′)); 1.20 (*s*, 6 H, Me(17,17′)); 1.58 (br. *s*, 4 H, HO–C(1,1′), HO–C(2,2′)); 1.87 (*s*, 6 H, Me(18,18′)); 2.05 (*s*, 12 H, Me (19,19′), Me (20,20′)); 3.93 (*m*, 2 H, H–C(2,2′)); 5.68 (*m*, 4 H, H–C(3,3′), H–C(14,14′)); 6.20 (*m*, 4 H, H–C(6,6′), H–C(10,10′)); 6.32 (*m*, 6 H, H–C(4,4′), H–C(8,8′), H–C(12,12′)); 6.61 (*m*, 4 H, H–C(7,7′), H–C(11,11′)). MS: 598 (31, M^+), 580 (5), 562 (2), 521 (4), 504 (10), 492 (16), 402 (15), 325 (17), 247 (30), 196 (60), 181 (69), 106 (79), 91 (100), 59 (49).

11. *(all-E,2R,2′R)-3,4,3′,4′-Tetradehydro-1,2,1′,2′-tetrahydro-ψ,ψ-carotene-1,2,1′,2′-tetrol* (= *(all-E,2R,2′R)-Oscillol*; **1**). To a soln. of crocetindialdehyde (**4**; 91.6 mg, 0.3 mmol) in CH_2Cl_2 (12 ml), 2N NaOH (10 ml) and a soln. of **6** (700 mg, 1.27 mmol) in CH_2Cl_2 (14 ml) were carefully and dropwise added at 0°. The soln. was protected from light, refluxed for 2 h, and extracted with CH_2Cl_2. The org. layer was washed with phosphate buffer (pH 7)

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[3]) A brownish extremely viscous oil was sometimes obtained. It was dissolved in little CH_2Cl_2 and precipitated in vigorously stirred ice-cold 10% Et_2O/hexane.

and evaporated. FC (silica gel, acetone/Et_3N 200:1) separated the carotenoids from triphenylphosphine oxide, and FC (silica gel, hexane/AcOEt 1:1 + 0.5% Et_3N) resulted in 77 mg (41%) of **1** and 96 mg (51%) of C_{30}-monoadduct **17** after drying under h.v. (12 h). **1**: Deep red powder. An anal. sample was recrystallized from warm benzene to give (all-*E*)-isomer **1**. M.p. 225°. UV/VIS (MeOH): 523, 493, 468, 388, 315. CD (EPA, −180°; $\Delta\varepsilon$): 282 (−2.5), 288 (0), 301 (+9.1), 330 (0), 482 (−9.3), 501 (−3.0), 511.5 (−4.6), 519 (0), 531 (+4.9), 550 (0), 552.5 (−0.4), 556.5 (0), 572 (+7.0), 581.5 (0). ^{1}H-NMR (400 MHz, $CDCl_3$): *Table*. ^{13}C-NMR (100.6 MHz, $CDCl_3$): *Table*. MS: 600 (10, M^+), 582 (1), 506 (4), 494 (42), 417 (6), 400 (8), 388 (13), 157 (52), 145 (67), 105 (76), 91 (100), 59 (68).

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