Bacterial Carotenoids XXIII*

The Carotenoids of Thiorhodaceae 6.* Total Synthesis of Okenone and Related Compounds

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The structures of okenone (XIX) and its derivatives okenol (XVIII), okenol acetate (XVI), and anhydro-okenol (XVII) have been confirmed by total synthesis.

Renieral (XI), obtained by a Wittig reaction of crocetindial (X) and the ylid IX, was condensed with the ylid XIV to 4′-desoxo-okenone (XV). Treatment of XV with N-bromosuccinimide and acetic acid gave okenol acetate (XVI) and anhydro-okenol (XVII). The acetate (XVI) was saponified to okenol (XVIII) which was oxidized to okenone (XIX).

Effects of the aryl-polyen-one system of okenone (XIX) and renieral (XI) in the electronic, infrared, and proton magnetic resonance spectra are discussed.

Okenone, first isolated from *Chromatium okenii*,[1] is the characteristic carotenoid of some purple sulphur bacteria.[2]

In order to prove beyond doubt the structure XIX, suggested for okenone in the preceding paper,[3] and to provide data for comparison with the spectral properties of this carotenoid, a total synthesis of okenone and related compounds has been carried out.

RESULTS AND DISCUSSION

Total synthesis of okenone and related compounds

Triphenyl-2,3,4-trimethylbenzylphosphonium bromide (VIII) was prepared from hemimellitene (I) in five steps according to the route previously employed by Cooper, Davis and Weedon.[4] Hemimellitene (I) was brominated to 1-bromo-2,3,4-trimethylbenzene (II) by the procedure of Martin.[5] Addition of ethyl orthoformate to the corresponding Grignard reagent (III) furnished the acetal

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(IV). This was subsequently hydrolyzed by acid to give 2,3,4-trimethyl-benzaldehyde (V) in 37 % yield. The aldehyde (V) was reduced, by lithium aluminium hydride, to the corresponding benzyl alcohol (VI), which was converted to 2,3,4-trimethylbenzyl bromide (VII), and the Wittig salt (VIII) was prepared in the usual manner.[6]
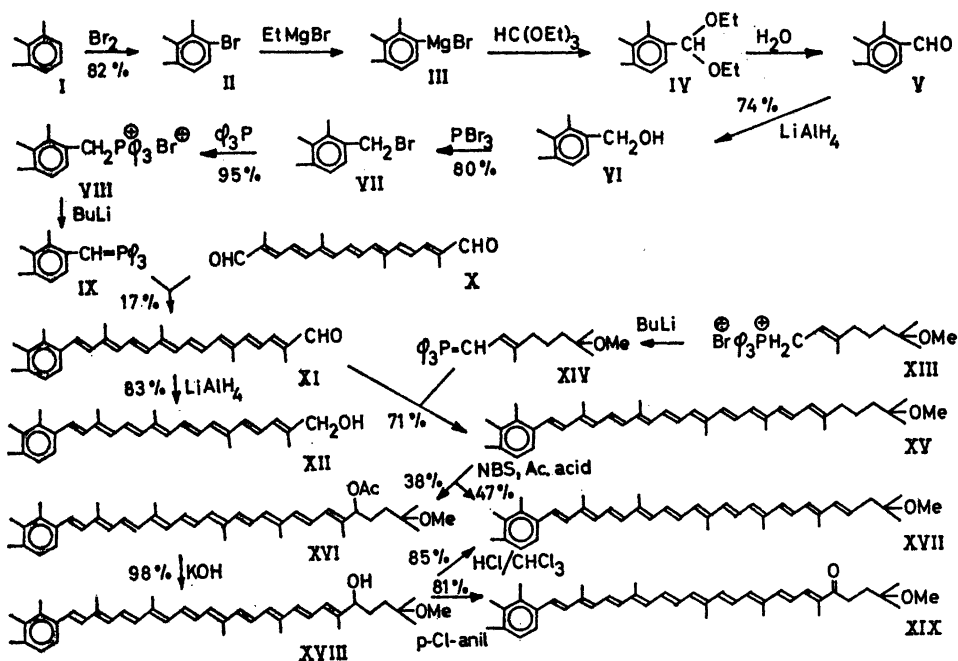
The ylid (IX) of VIII was condensed with crocetindial (X) to renieral (XI) in 17 % yield by the general method. Renieral (XI) has previously not been synthesized, but was obtained by Yamaguchi [7,8] by mild chromic acid oxidation of renieratene. A certain inconsistency in melting points and spectral data in visible light is apparent when one compares the properties reported by Yamaguchi [7] and those obtained by us. Infrared and proton magnetic resonance data, confirming structure XI for our synthetic specimen, are presented in Figs. 1 and 2. The corresponding alcohol, renierol (XII), could be prepared by hydride reduction of XI.

Wittig condensation of renieral (XI) with the ylid XIV of (7-methoxy-3,7-dimethyl-2-octen-1-yl) triphenylphosphonium bromide (XIII, prepared as described previously in connection with a synthesis of 3,4,3',4'-tetrahydro-spirilloxanthin [9]), furnished the previously undescribed 4'-desoxo-okenone (XV) in 71 % yield.

Treatment of 4'-desoxo-okenone (XV) with N-bromosuccinimide and glacial acetic acid gave okenol acetate (XVI; 38 % yield) and anhydro-okenol (XVII; 47 % yield). Under similar conditions, followed by saponification of the reaction mixture, Entschel and Karrer [10] obtained isozeaxanthin (4,4'-dihydroxy-
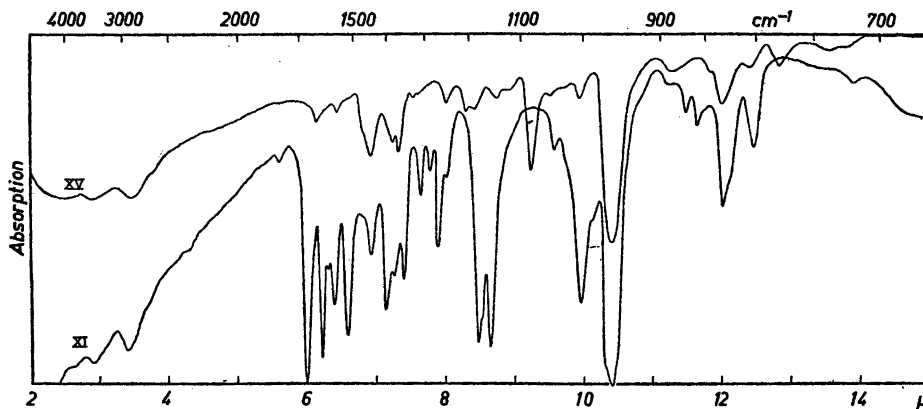
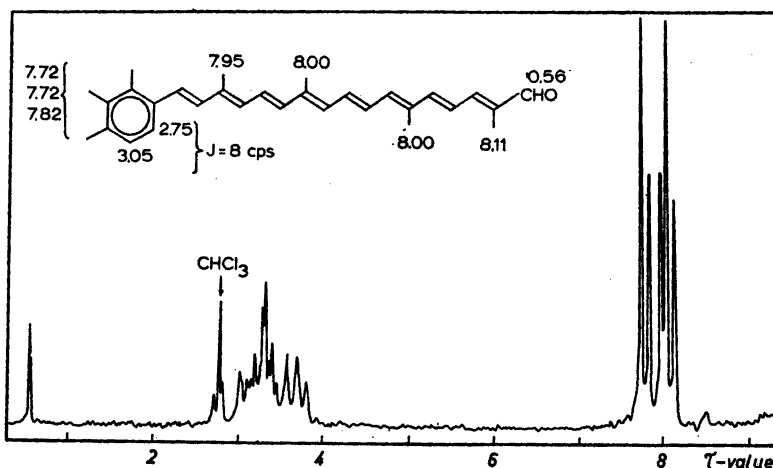*Fig. 1.* Infrared spectrum in KBr-pellet of renieral (XI) and 4'-desoxo-okonone (XV).

Fig. 2. Proton magnetic resonance spectrum at 100 Mc/sec of renieral (XI) in deutero-chloroform.

β-carotene) from β-carotene. The corresponding diacetate was not isolated, but was considered to be an intermediate. The reaction was assumed to proceed by a radical mechanism *via* the corresponding allylic bromide, which yielded the corresponding acetate by substitution. Entschel and Karrer obtained no dehydrogenation products. However, in our experiments the formation of anhydro-okenol (XVII) from XV could not be prevented. Whether or not anhydro-okenol (XVII) was formed from okenol acetate (XVI) caused by allylic elimination by acetic acid, or the hydrogen bromide liberated during the conversion of XV to XVI, or alternatively by elimination of hydrogen bromide from an intermediate allylic bromide, spontaneously or under the

Table 1. Composition of the iodine catalyzed equilibrium mixtures of natural and synthetic okenone (XIX).

Sample	Member of the stereoisomeric set	R_F-value kieselguhr paper 5 % acetone-pet. ether	In acetone Abs.max. in mμ				% D_B/D_{II}	% Of total
Natural	Neo B	0.60	378	(450)	474	(500)	59	13
	Neo A	0.48	(378)	(452)	478	(501)	26	18
	Trans	0.34		(460)	484	512	(13)	69
Synthetic	Neo B	0.60	378	(450)	474	(500)	57	17
	Neo A	0.48	(379)	(452)	478	(501)	27	17
	Trans	0.34		(460)	484	512	(12)	66

Table 2. Composition of the iodine catalyzed equilibrium mixtures of okenol derived from natural okenone, and synthetic okenol (XVIII).

Sample	Member of the stereoisomeric set	R_F-value kieselguhr paper 5 % acetone-pet. ether	In acetone Abs.max. in mμ				% D_B/D_{II}	% Of total
Natural origin	Neo A	0.30	365	(442)	465	(491)	25	43
	Trans	0.16		(448)	471.5	501	(7)	57
Synthetic	Neo A	0.30	365	(442)	465	(490)	27	41
	Trans	0.16		(448)	471.5	501	(7)	59

influence of ethyl morpholine, is not clear. In our case the gain in resonance energy obtained on introduction of a conjugated double bond at the aliphatic end of the molecule might be expected to promote the formation of the dehydrogenation product (XVII).

Okenol acetate (XVI) was saponified in quantitative yield to okenol (XVIII) which, in the final step, was oxidized to okenone (XIX) by p-chloranil[11] in 81 % yield.

Synthetic okenone was found to be identical with natural okenone isolated from *Chromatium okenii* Perty, strain Ostrau.[3] Identity criteria included adsorptive properties, stereomutation behaviour including relative abundance, R_F-values and spectral properties of the three main stereoisomers after iodine catalysis (see Table 1), electronic spectra and infrared spectra (see Fig. 3). A mixed melting point determination gave no depression.
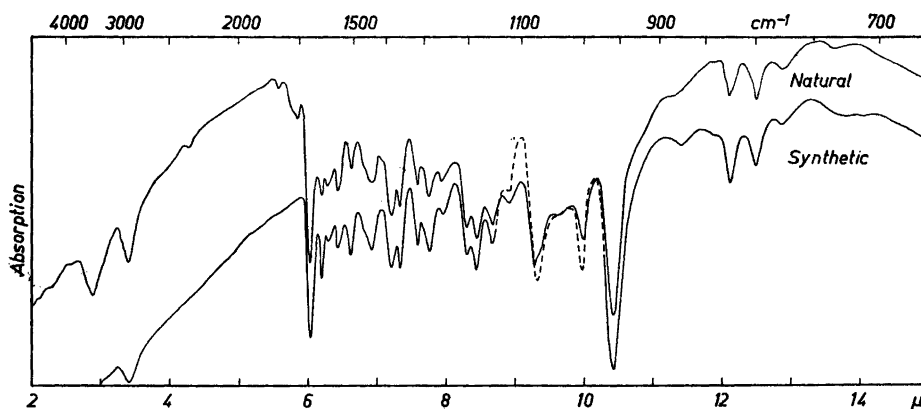

Fig. 3. Infrared spectra in KBr-pellet of natural and synthetic okenone (XIX).

Identity was also proved for synthetic okenol (XVIII) and okenol derived from natural okenone. They exhibited identical adsorptive properties and stereomutation behaviour, including relative abundance, R_F-values and spectral properties of the two main stereoisomers after iodine catalysis (see Table 2). Melting points and infrared spectra were also in satisfactory agreement. Moreover, the two samples of okenol of different origin behaved similarly on allylic oxidation to okenone (XIX) with p-chloranil, and both gave anhydro-okenol (XVII) in high yield[3] on allylic dehydration with acidified chloroform.[12]

Synthetic anhydro-okenol (XVII), obtained directly from XV or *via* okenol (XVIII), was found to be identical with anhydro-okenol derived from natural okenone.[3] Their identity was suggested by their electronic spectra, infrared spectra, melting point and from the properties listed in Table 3.

Finally, synthetic okenol acetate (XVI) was identical in adsorptive properties and electronic spectrum with okenol acetate derived from natural okenone.[3]

Table 3. Composition of the iodine catalyzed equilibrium mixtures of anhydro-okenol derived from natural okenone, and synthetic anhydro-okenol (XVII).

Sample	Member of the stereoisomeric set	R_F-value kieselguhr paper 2 % acetone-pet. ether	In acetone Abs.max. in mμ					% D_B/D_{II}	% Of total
Natural origin	Neo B	0.54	(360)	373	(448)	471	(495)	56	19
	Neo A	0.44		(375)	(449)	472.5	501.5	32	27
	Trans	0.36			(456)	480	510.5	(12)	54
Synthetic	Neo B	0.54	(360)	373	(448)	470.5	(495)	49	19
	Neo A	0.44		(373)	(448)	472	501	28	25
	Trans	0.36			(456)	480	511	(14)	56

The present synthesis of okenol acetate (XVI), okenol (XVIII), anhydro-okenol (XVII) and okenone (XIX), consequently proves the structures deduced for these carotenoids in the preceding paper.[3]

Spectral properties of okenone

The electronic spectra of okenol (XVIII) and 4'-desoxo-okenone (XV) (Fig. 4) exhibit maxima at slightly shorter wavelengths and possess less fine-structure and lower molar extinction values than does lycopene. This evidence demonstrates that substitution of an aliphatic end-group containing a con-jugated carbon-carbon double bond with a 1,2,3-trimethylphenyl residue in a carotenoid results in a slight hypsochromic effect, significant reduction of the spectral fine-structure and a decrease in the molar extinction values in visible light. This conclusion is substantiated by a comparison of the electronic spectrum of renierol (XII) (Fig. 4) with that of neurosporene. In this connec-tion it is noteworthy that the spectral effect of a 1,2,5-trimethyl-phenyl end-group is exactly equivalent to that of a so-called β-ring.[13]

As seen from Table 4, the size of the hypsochromic shift observed on reduction of the carbonyl group in conjugated ketones or aldehydes is some-what dependent on the length of the polyene chain. It has already been pointed out,[3] that the shift on reduction of okenone (XIX) to okenol (XVIII) appears to be small; cf. data compiled in Table 4 for the sets 1, 2, and 3. In petroleum ether a λ_{max} shift of 15 mμ was recorded, as against an expected value of about 23 mμ. A possible effect from the methyl group α to the keto group in okenone (XIX) may be ruled out because of the regularity of the λ_{max} shift of sets 6—10 in Table 4. However, the corresponding shift (ca. 22 mμ) from renieral (XI) to renierol (XII) is also lower than expected (ca. 28 mμ) judging from the shifts of sets 3, 8, and 9. The small spectral contribution by the carbonyl group in okenone (XV) and renieral (XI) must consequently be caused by the influence of the phenyl substituent on the other side of the polyene chain. A similar spectral effect is known to exist in conjugated ω,ω-diketones.[20]
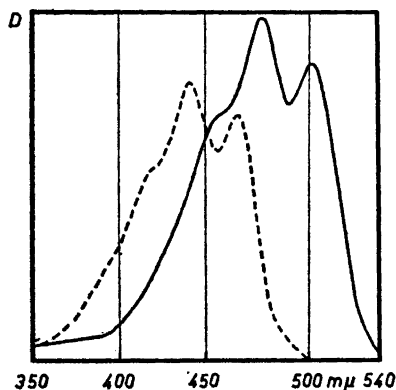

Fig. 4. Electronic spectra in acetone of ——— 4'-desoxo-okenone (XV) and – – – – renierol (XII).

Table 4. Spectral shifts (Δ) in hexane on reduction of various aliphatic conjugated carbonyl carotenoids to the corresponding alcohols.

Set No.	Conjugated ketone or aldehyde	Main middle abs.max. in mμ	Compound with corresponding polyene chromophore	Main middle abs.max. in mμ	Δ Main middle abs.max. in mμ	No. spectroscopically efficient C=C bonds in polyene chain
1	2-Keto-rhodovibrin	502[14]	Rhodovibrin	483[15]	19	12
2	Spheroidenone	483[16]	Reduced spheroidenone	454[16]	29	10
3	Apo-8'-lycopenal	488*[17]	P439	451*[18]	37*(33)	9
4	Okenone (XIX)	484	Okenol (XVIII)	470	15	$10 + \varphi$ (1,2,3)
5	Renieral (XI)	465**	Renierol (XII)	442**	23**(22)	$9 + \varphi$ (1,2,3)
6	β-Apo-2'-carotenal (C_{37})	498	β-Apo-2'-carotenol (C_{37})	473	25	11.3
7	β-Apo-4'-carotenal (C_{35})	485	β-Apo-4'-carotenol (C_{35})	459	26	10.3
8	β-Apo-6'-carotenal (C_{32})	473	β-Apo-6'-carotenol (C_{32})	443	30	9.3
9	β-Apo-8'-carotenal (C_{30})	457	β-Apo-8'-carotenol (C_{30})	426	31	8.3
10	β-Apo-10'-carotenal (C_{27})	435	β-Apo-10'-carotenol (C_{27})	403	32	7.3

* In benzene, ** in acetone. Estimated values in hexane in brackets. Data for sets 6–10 from Ref. 19.

The observed reduction in spectral fine-structure and extinction values in okenone (XIV), relative to okenol (XIII) and 4'-desoxo-okenone (XV) is a general effect caused by the conjugated keto group.[21]

Another effect of the aryl-polyen-one system may be seen on the carbonyl vibration frequency in the infrared spectrum. Measured in KBr pellet, this absorption in okenone (1652 cm^{-1}) occurs at a lower frequency than that of other aliphatic carotenoid ketones (e.g. spheroidenone 1680 cm^{-1},[16] 2'-dehydro-plectaniaxanthin 1670 cm^{-1},[22] citranaxanthin 1662 cm^{-1},[23] and sintaxanthin 1660 cm^{-1},[24]). Also, in the aldehyde series the corresponding absorption for renieral (1662 cm^{-1}) is found at a lower frequency than that of, e.g., β-apo-2'-carotenal (C$_{37}$) (1678 cm^{-1}). The low-frequency position of the carbonyl vibration in okenone (XIX) and renieral (XI) therefore seems to be connected with the aryl-polyene system of these compounds.

It has already been pointed out that the aromatic *ortho* proton at C$_5$ in okenone (XIX) comes to resonance at lower field than the aromatic protons in chlorobactene.[3] A carbonyl substituent in α-position to a phenyl ring is known to deshield an *ortho* proton by ca. 0.63 τ units.[25] On the basis of the limited data collected in Table 5, no definite conclusion may be drawn whether the observed deshielding of the C$_5$ *ortho* protons in okenone (XIX) and renieral (XI) is caused by a long-distance effect of the conjugated carbonyl group or merely reflects the closer vicinity to the polyene chain. In any case the signals
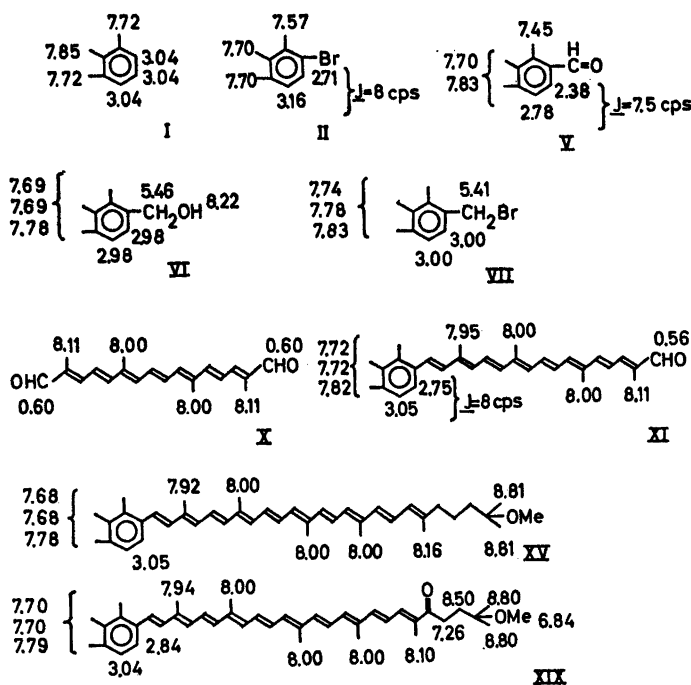

Fig. 5. Assignment of proton magnetic resonance signals for intermediates in the synthesis of okenone.

attributed to the aromatic protons were found to be more complex in the 1,2,3-than in 1,2,5-trimethylphenylsubstituted carotenoids.

In summary, the aryl-polyen-one system characteristic of okenone offers some special spectral features.

EXPERIMENTAL

Materials, methods and instruments used have been described previously.[26] Solvents used were freshly distilled. Melting points were measured using a non-abbreviated thermometer and are corrected. NMR-spectra were recorded at 60 Mc/sec unless otherwise stated. Assignment of signals are made in Fig. 5.

Table 5. Signal positions of the aromatic protons in some benzene derivatives.

Compound	τ-value			
1,2,3-Trimethylbenzene (I)	3.04			
Chlorobactene	3.05 [13]			
4'-Desoxo-okenone (XV)	3.04			
	(2.75?)			
2,3,4-Trimethylbenzaldehyde (V)	2.38	(o)	}	$J = 7$ cps
	2.78	(m)		
Renieral (XI)	2.75	(o)	}	$J = 8$ cps
	3.05	(m)		
Okenone (XIX)	ca. 2.84	(o)[3]	}	$J = ca.$ 7 cps
	ca. 3.04	(m)		

1-Bromo-2,3,4-trimethylbenzene (II). The commercial (Fluka) hemimellitene (I) used had λ_{max} 261 mμ in ether (Conrad-Bilroth [27] reported 266 m μ in hexane); IR absorption (liq.) at 760 cm^{-1} (three adjacent free hydrogens in phenyl); τ-values, see Fig. 5. (Cooper *et al.*[4] reported τ 7.84 (3 H) and 7.72 (6 H)).

II was prepared by bromination of I (105 g) by the procedure of Martin.[5] The yield of II was 142 g (82 %); b.p. 102—104°C (*ca.* 7 mm Hg); $n_D^{27} = 1.5580$; λ_{max} 268 mμ in ether; IR-property (liq.) 800 cm^{-1} (two adjacent free hydrogens in phenyl); τ-values see Fig. 5.

The following data have been reported: yield 89 %,[5] 47 %;[28] b.p. 128°C (25 mm),[5] 103—103.5°C (12 mm);[28] $n_D^{21} = 1.5618$.[28]

2,3,4-Trimethylbenzaldehyde (V) was prepared from II (142 g) by the procedure of Lowe *et al.*[6] The yield of V was 39 g (37 %); b.p. 118—119°C (8.5 mm Hg), $n_D^{21} = 1.5495$; λ_{max} 259.5 and 290 m μ in ether, 262 m μ ($\varepsilon = 12\ 800$) in ethanol; IR-properties (liq.) 2900 and 2700 (aldehydic CH) and 1685 cm^{-1} (aryl aldehyde); τ-values see Fig. 5.

The following data have been reported: yield 50 %;[4] b.p. 121.5°C (11 mm),[29] 120—122°C (0.8 mm);[4] $n_D^{22} = 1.5495$;[4] λ_{max} 265 m μ ($\varepsilon = 11\ 500$) in ethanol;[4] IR properties (CCl$_4$) 2858, 2720, and 1698 cm^{-1}.[4]

2,3,4-Trimethylbenzyl alcohol (VI). V (20 g) was reduced with lithium aluminium hydride by the procedure of Cooper *et al.*[4] The yield of VI was 14.9 g (74 %); m.p. 47°C (needles from petroleum ether); λ_{max} 264.5 mμ in ether; IR-properties (CHCl$_3$) 3280, 1010 cm^{-1} (*prim.* hydroxyl); τ-values see Fig. 5.

The following data have been reported: yield 60 %;[4] m.p. 48.5—49.5°C, [4] 49—50°C.[30]

2,3,4-Trimethylbenzyl bromide (VII) was prepared from VI (4.5 g) by the procedure of Cooper *et al.*[4] The yield of crude VII was 5.1 g (80 %); $n_D^{21} = 1.5700$; λ_{max} 240 mμ in ether; IR-properties 1445, 1200, and 815 cm^{-1} (two free adjacent hydrogens in phenyl); τ-values see Fig. 5.

Triphenyl-2,3,4-trimethylbenzylphosphonium bromide (VIII) was prepared from VII (5.1 g) by the procedure of Cooper *et al.*[4] The yield of VIII was 10.8 g (95 %), m.p. 221°C. Cooper *et al.* obtained 100 % yield, m.p. 222—223°C.

Renieral (XI). A general procedure for analogous Wittig condensations was followed.[4] To VIII (804 mg), dissolved in dry ether (14 ml), was added 0.4 N ethereal butyl lithium (6 ml). The mixture was stirred mechanically for 90 min whereupon methylene chloride (10 ml) and ether (5 ml) was added. The above solution was added dropwise to a solution of crocetindial (X, 500 mg) in methylene chloride (20 ml). The reaction mixture was stirred under reflux. Periodical paper-chromatographic analysis demonstrated that no further reaction occurred after 3 h. The reaction mixture was poured into water and the carotenoids extracted with ether. The carotenoid mixture was chromatographed on a column of alumina activity grade 3.[31] Crocetindial (X, 120 mg), requiring an eluent of 50 % ether in petroleum ether, was recovered.

XI required 10—20 % ether in petroleum ether for elution; yield 119 mg (17 %). XI was crystallized from acetone-petroleum ether; m.p. 185—187°C; λ_{max} 463 and (490) mμ in petroleum ether, 465 ($E_{1\,cm}^{1\,\%}$ = 2910) mμ in acetone and *ca.* 468 mμ in methanol; IR-properties (KBr) 1662 (conj. aldehyde) and 802 cm^{-1} (two adjacent free hydrogens in phenyl), see Fig. 1; R_F = 0.60 on kieselguhr paper (5 % acetone in petroleum ether). NMR-data (100 Mc/sec) are given in Figs. 2 and 5. The chemical shift of the aromatic *meta* proton (at C_4) was determined by double resonance.

Yamaguchi [7,8] reported a m.p. of 198—199°C; λ_{max} 501 and 540 mμ in carbon disulphide, 479 ($E_{1\,cm}^{1\,\%}$ = *ca.* 2620) and (505) mμ in benzene, 468 and 499 mμ in hexane.

The IR-spectrum (KBr) of synthetic β-apo-carotenal (C$_{37}$) was recorded for comparison.

Renierol (XII). XI (0.06 mg) in dry ether was treated with lithium aluminium hydride in the usual manner; pigment recovery 83 %. XII had abs.max. at 442 and 469.5 mμ in acetone (see Fig. 4), R_F = 0.27 (5 % acetone in petroleum ether) and R_F = 0.63 (10 % acetone in petroleum ether) on kieselguhr paper.

4'-Desoxo-okenone (XV). To (7-methoxy-3,7-dimethyl-2-octen-1-yl) triphenylphosphonium bromide (XIII, 100 mg), prepared as previously described,[26] in dry ether (15 ml) was added 1 N ethereal butyl lithium (4 ml). The mixture was stirred at room temperature for 30 min and renieral (XI, 40 mg) in methylene chloride (15 ml) was added. The mixture was stirred under reflux. Periodical paper-chromatographic examination revealed that no further reaction occurred after 3 h. The mixture was poured into water. The pigments were extracted with benzene and chromatographed on alumina; activity grade *ca.* 1.[31] Renieral (XI, 3 mg) was recovered, the required eluent beeing 85 % ether in petroleum ether.

XV required 50—75 % ether in petroleum ether for elution; yield 38 mg (71 %). XV was crystallized from acetone-petroleum ether; m.p. 158—162°C; λ_{max} 469 ($E_{1\,cm}^{1\,\%}$ = 2850) and 498 mμ in petroleum ether, 472.5 and 502.5 mμ in acetone; IR-properties 1080 (methoxyl), 960 (*trans* disubst. double bonds), 825 (*trans* trisubst. double bonds) and 800 cm^{-1} (two adjacent free hydrogens in phenyl), see Fig. 1; τ-values (100 Mc/sec.) see Fig. 5; R_F = 0.43 on kieselguhr paper (2 % acetone in petroleum ether) and R_F = 0.32 on aluminium oxide paper (same solvent system). XV was resistant towards reduction with lithium aluminium hydride in dry ether.

Okenol acetate (XVI). The procedure of Entschel and Karrer [10] was adopted. Introductory experiments revealed that the carotenoid (XV) decomposed when higher concentrations of N-bromosuccinimide and acetic acid were used.

To XV (10 mg) in dry ethanol-free chloroform (5 ml) was added N-bromosuccinimide (5 mg) and glacial acetic acid (0.15 ml) in chloroform (5 ml) at —20°C. After 30 sec ethyl morpholine (0.5 ml) was added. The pigments were transferred to petroleum ether after mixing with water; pigment recovery was 85 %. Paper-chromatographic examination revealed the presence of okenol acetate (XVI, 45 %) and anhydro-okenol (XVII, 55 %). The yield of XVI was thus 38 %.

XVI exhibited the same absorption spectrum in visible light as XV and XVIII. It had an R_F = 0.57 on kieselguhr paper (5 % acetone in petroleum ether) and could not be separated from okenol acetate derived from natural okenone.[3]

Okenol (XVIII). The above mixture of XVI and XVII was saponified for 2 h in 10 % methanolic KOH-solution. The pigments were isolated in the usual manner; pigment recovery was 98 %. By chromatography on a column of alumina, activity grade 2, anhydro-okenol (XVII) required 2 % and okenol (XVIII) 20 % acetone in petroleum ether for elution.

XVIII melted at 174—175°C; previously reported at 176—177°C.[3] On iodine catalyzed stereoisomerization traces of okenone (XIX) were produced. The properties of the stereo-isomeric set of totally synthetic XVIII directly compared with those of okenol derived from natural okenone,[3] are given in Table 2. The spectrum of XVIII was identical with that of XV (*cf.* Fig. 4). The IR-spectrum (KBr) had characteristic absorption at 1075, 954, 825, and 800 cm^{-1} and agreed with that previously reported for okenol.[3]

Anhydro-okenol (XVII) was directly prepared from XV as described above, or by treatment of XVIII (0.21 mg) with acidified chloroform according to the procedure of Entschel and Karrer;[10] yield 85 %.

Totally synthetic XVII, crystallized from acetone-petroleum ether, melted at 160—162°C; previously reported at 169—170°C.[3] Properties of the iodine catalyzed equilibrium mixture, directly compared with those of anhydro-okenol derived from natural okenone [3] are given in Table 3. The IR-spectrum (KBr) had characteristic absorption at 1120, 1080, 960, 825, and 800 cm^{-1} and agreed with that previously reported for anhydro-okenol.[3]

Okenone (XIX). Okenol (XVIII, 1.8 mg) in benzene (3 ml) was oxidized with *p*-chloranil (5.4 mg) in the presence of iodine (50 μg) in Na-light at room temperature by the procedure previously described.[11] After 8 h, complete transformation to XIX was observed; pigment recovery 81 %. In a parallel experiment okenol, obtained by hydride reduction of natural okenone, was similarly oxidized.

Synthetic XIX melted at 154—156°C, a natural sample at 154°C and a mixture of the two samples at 153—155°C; previously reported at 161—163°C.[3] The properties of the iodine catalyzed equilibrium mixture of synthetic XIX, directly compared with those of natural okenone, are presented in Table 1. The IR-spectrum (KBr) of synthetic XIX agreed completely with that of natural okenone, see Fig. 3.

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