

Bacterial Carotenoids. XLVIII.\* C<sub>50</sub>-Carotenoids. 16.\*

## Synthesis and Chiroptical Properties of the Model

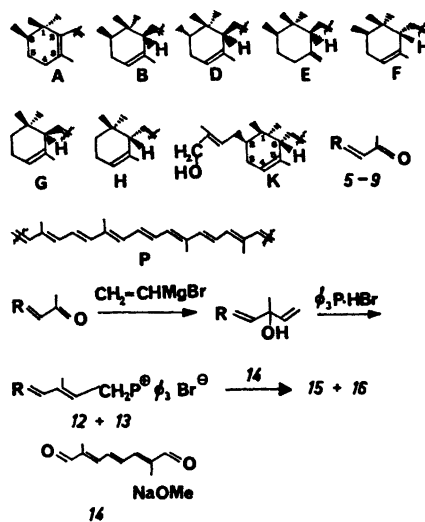
Compounds (2*R*, 6*R*, 2'*R*, 6'*R*)-2,2'-Dimethyl- $\epsilon,\epsilon$ -caroteneand (2*R*, 6*S*, 2'*R*, 6'*S*)-2,2'-Dimethyl- $\epsilon,\epsilon$ -caroteneA. G. ANDREWES<sup>a\*\*</sup>, G. BORCH<sup>b</sup> and S. LIAAEN-JENSEN<sup>a</sup>

<sup>a</sup> Organic Chemistry Laboratories, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway and <sup>b</sup> Chemistry Department A, Technical University of Denmark, DK-2800 Lyngby, Denmark

(2*R*, 6*S*, 2'*R*, 6'*S*)-2,2'-Dimethyl- $\epsilon,\epsilon$ -carotene (15) and (2*R*, 6*R*, 2'*R*, 6'*R*)-2,2'-dimethyl- $\epsilon,\epsilon$ -carotene (16) were synthesized from the corresponding optically active irones (6, 9). <sup>1</sup>H NMR and CD properties of the optically active C<sub>42</sub>-carotenes and synthetic intermediates are reported. The absolute configuration 2*R*, 6*R*, 2'*R*, 6'*R* of the bacterial C<sub>50</sub>-carotenoid decaprenoxanthin (3*a*) is based on these results.

Recently<sup>1</sup> we reported the synthesis and CD properties of (2*R*, 2'*R*)-2,2'-dimethyl- $\beta,\beta$ -carotene (1) from which the absolute configuration of *C.p.* 450<sup>2</sup> = (2*R*, 2'*R*)-2-(4-hydroxy-3-hydroxymethyl-2-butenyl)-2'-(3-methyl-2-butenyl)- $\beta,\beta$ -carotene (2, with opposite configuration at C-2, 2' relative to 1) was established, Scheme 1. The synthesis was based on the isolation of optically active  $\beta$ -irones (5) from Iris oil.<sup>3</sup> Optically active  $\alpha$ -irones (6 and 7) of known absolute configuration are also present in Iris oil.<sup>3</sup>

An obvious extension to our earlier work was the synthesis of optically active 2-methyl substituted  $\epsilon,\epsilon$ -carotenes in order to illuminate the absolute configurations of C<sub>50</sub>-carotenoids containing  $\epsilon$ -ring systems,<sup>4,5</sup> particularly of decaprenoxanthin (3).<sup>6,7</sup> Simpler, appropriate



Scheme 1. 1, A-P-A; 3, K-P-K (chirality unknown); 3*a*, K-P-K; 4*a*, G-P-G; 4*b*, H-P-H; 5, R=A; 6, R=B; 7, R=D; 8, R=E; 9, R=F; 12, R=B; 13, R=F; 15, B-P-B; 16, F-P-F.

models for CD-comparison already available were the enantiomeric  $\epsilon,\epsilon$ -carotenes (4*a*, *b*).<sup>8-10</sup>

Optically inactive 2,2'-dimethyl- $\epsilon,\epsilon$ -carotene has previously been synthesized by a different approach<sup>11</sup> than that reported below.

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\*\* Present address: Department of Bacteriology, University of California, Davis, California 95616, USA.

## RESULTS AND DISCUSSION

The irones 5, 6, 7 and 8 are constituents of natural Iris oil.<sup>3</sup> (2*S*,6*R*)-*cis*- $\alpha$ -Irone (6, numbering and nomenclature of the irones follow those used by Rautenstrauch and Ohloff,<sup>3</sup> cf. A, and differ from those of the carotenoids,<sup>12</sup> cf. K) was isolated by direct preparative GLC of Iris oil. The C-2 epimeric (2*R*,6*R*)-*trans*- $\alpha$ -irone (9) was isolated by preparative GLC of a base isomerized mixture of natural irones. The optical purity of 9 used in the synthesis of (2*R*,6*R*,2'*R*,6'*R*)-2,2'-dimethyl- $\epsilon$ , $\epsilon$ -carotene was diluted to some extent by the presence of a small amount of its enantiomer 7.

The route utilized for the synthesis of optically active dimethyl- $\epsilon$ , $\epsilon$ -carotenes is illustrated in Scheme 1. In reactions known to retain stereochemical integrity at position C-2 of irones,<sup>13</sup> 6 and 9 were successively treated with excess vinyl magnesium bromide and triphenyl phosphonium bromide to yield the phosphonium salts 12 and 13. CD curves of the

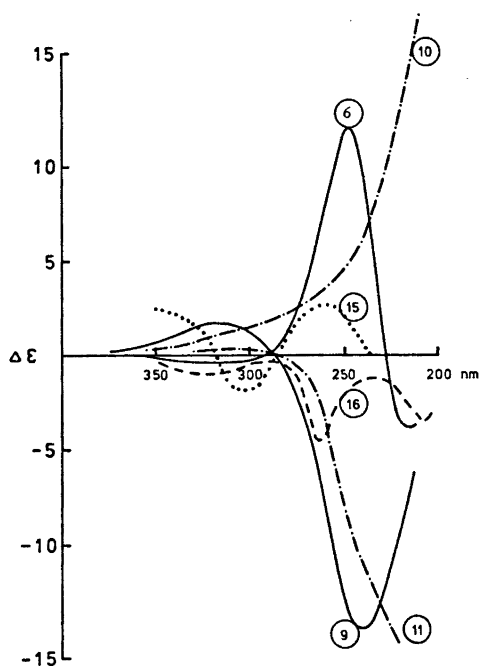


Fig. 1. CD spectra of (2*S*,6*R*)-*cis*- $\alpha$ -irone (6), (2*R*,6*R*)-*trans*- $\alpha$ -irone (9), (2*S*,6*R*)-*cis*-vinyl- $\alpha$ -ironol (10), (2*R*,6*R*)-*trans*-vinyl- $\alpha$ -ironol (11), (2*R*,6*S*,2'*R*,6'*S*)-2,2'-dimethyl- $\epsilon$ , $\epsilon$ -carotene (15), and (2*R*,6*R*,2'*R*,6'*R*)-2,2'-dimethyl- $\epsilon$ , $\epsilon$ -carotene (16) in EPA solution.

Table 1. Diagnostically useful <sup>1</sup>H NMR signals ( $\delta$  values) in the 2,6-*cis* (6, 10, 15) and 2,6-*trans* (9, 11, 16) series (carotenoid numbering used).

Compound	Methyl at C-2,2'	16,17,16',17'- <i>gem</i> dimethyl $\Delta$		
<i>2,6-cis</i>				
6	0.87	0.72	0.87	0.15
10	0.85	0.63	0.85	0.22
15	0.87	0.68	0.87	0.19
<i>2,6-trans</i>				
9	0.85	0.83	0.87	0.04
11	0.82	0.77	0.81	0.04
16	0.82	0.81	0.82	0.01

intermediate vinyl alcohols 10 and 11 are given in Fig. 1 and have the same sign as the irone precursors 6 and 9, respectively. Reaction of the ylids of the phosphonium salts 12 and 13, generated in the presence of sodium methoxide, with the dial 14 gave (2*R*,6*S*,2'*R*,6'*S*)-2,2'-dimethyl- $\epsilon$ , $\epsilon$ -carotene (15) and (2*R*,6*R*,2'*R*,6'*R*)-2,2'-dimethyl- $\epsilon$ , $\epsilon$ -carotene (16), respectively.

The dimethyl carotenes 15 and 16 had electronic spectra identical with that of  $\epsilon$ , $\epsilon$ -carotene.<sup>8,14</sup> Mass spectra of the here synthesized optically active dimethyl-carotenes 15 and 16 were identical and consistent with the fragmentation pattern reported for racemic 2,2'-dimethyl- $\epsilon$ , $\epsilon$ -carotene.<sup>14,15</sup> The <sup>1</sup>H NMR signals of 15 and 16 are given in the Experimental part. Signals assigned to the *gem* dimethyl and adjacent methyl groups of the irones 6 and 9, vinyl-ironols 10 and 11 and the synthesized C<sub>42</sub>-carotenes 15 and 16 are compared in Table 1. There is a clear distinction between the chemical shifts of the *gem* dimethyl groups associated with the 2,6-*cis* and 2,6-*trans* isomers which are consistent with the starting irones, intermediate vinyl-ironols and product carotenes within each isomeric group. Mention should be made that the <sup>1</sup>H NMR signals reported by Vetter *et al.*<sup>14</sup> for synthetic, racemic <sup>16</sup> 2,2'-dimethyl- $\epsilon$ , $\epsilon$ -carotene correlate with the 2,6-*trans*-isomer.

The chromatographic behaviour of the dimethyl-carotenes 15 and 16 were very similar on alumina paper and alumina plates. Both 15 and 16 were less strongly adsorbed than

synthetic  $\epsilon,\epsilon$ -carotene,  $\beta,\epsilon$ -carotene, and  $\beta,\beta$ -carotene.

CD spectra of 15 and 16 are included in Fig. 1.

In a separate report<sup>17</sup> comparison of the present <sup>1</sup>H NMR results (Table 1) with data for decaprenoxanthin (3)<sup>6</sup> has led to 2,6-*cis* (2',6'-*cis*) assignment for decaprenoxanthin. Furthermore comparison of CD data for the synthetic dimethyl-carotenes 15 and 16 (Fig. 1), decaprenoxanthin (3),<sup>18</sup> and synthetic 6S,6'S- $\epsilon,\epsilon$ -carotene (4b)<sup>10</sup> has revealed that the chiral center at C-2(C-2') does not contribute significantly to the CD of 15, 16 and 3. This is consistent with previous findings by Rautenstrauch and Ohloff in the  $\alpha$ -ionone/ $\alpha$ -ionone series.<sup>3</sup> Consequently decaprenoxanthin has been assigned the 2*R*,6*R*,2'*R*,6'*R*-configuration 3a,<sup>17</sup> Scheme 1.

Whereas the sign of the Cotton effect of 15 below 280 nm is as predicted, the lower magnitude could partly be due to some presence of its enantiomer derived from 7. Further differences in shape and magnitude relative to 16 could be sought in a conformational preference of quasiaxial polyene chain,<sup>19</sup> in which case an axial methyl group at C-2 of 15 should destabilize the preferred conformation and could alter the CD. However, it seems questionable (*cf.* conformations discussed in Ref. 17) that this finding for enones of the  $\alpha$ -ionone/ $\alpha$ -ionone series<sup>19</sup> may be extended to the carotenes.

## EXPERIMENTAL

**Materials and methods.** All solvents were of analytical grade or distilled before use. Separation and purification of synthetic carotenes were accomplished on alumina plates (1 mm) developed with petroleum ether-ethyl ether mixtures. Comparative TLC was on Merck HF<sub>254</sub> pre-coated alumina plates (0.2 mm).

Instruments used were as specified elsewhere.<sup>20</sup> Specific rotations of carotenoid intermediates were obtained on a Perkin-Elmer 141 polarimeter and CD spectra recorded in EPA (ether-isopentane-ethanol, 5+5+2) on a Roussel-Jouane Dicrographe.

The composition of Iris oil before and after base isomerization has been reported;<sup>1,3</sup> GLC separation of the irones has also been described.<sup>1,3</sup>

(+)-(2*S*,6*R*)-*cis*- $\alpha$ -Irone (6). (6) isolated from natural Iris oil by preparative GLC had the following physical characteristics:  $[\alpha]_D^{20}$  (EPA)

589 nm = 9°, 578 nm = 10°, 546 nm = 11°, 436 nm = 23° and 365 nm = 43°;  $\lambda_{max}$  225 nm (EPA), 228 nm (MeOH); IR (liq.) 3015 (m), 2980, 2935, 2880, 1695, 1675, 1620, 1450, 1365, 1255 (s), 1210, 1170, 1065, 1000, 985 (m), 910, 885, 795 and 740 (w) cm<sup>-1</sup>;  $\delta$  (CDCl<sub>3</sub>) 0.72, 0.87 (6 H, *gem.* dimethyl), 0.87 d (3 H, *J* = 5 Hz, >CH-CH<sub>3</sub>), 1.54 (3 H, =C-CH<sub>3</sub>), 1.9-1.7 (3 H, -CH<sub>2</sub> and CH<sub>2</sub>CH<), 2.25 O=C-CH<sub>3</sub>, 2.53 d (1 H, *J* = 10.5 Hz, >CH-C=C), 5.39 (1 H, broad, -CH=C-CH<sub>3</sub>), 6.08 d (1 H, *J* = 15 Hz, =CH-C=O) and 6.27 q (1 H, *J*<sub>1</sub> = 16 Hz, *J*<sub>2</sub> = 10 Hz, CH=CH-C=O; *m/e* 206 (M), 136 (M-70, 121 (M-85) and 93 (M-113).

(+)-(2*S*,6*R*)-*cis*-Vinyl- $\alpha$ -ironol (10). Vinyl magnesium bromide (5 g) in tetrahydrofuran (THF, 30 ml) was added to a stirred solution of 4 (544 mg) in THF (5 ml). After 1.5 h at 25 °C saturated NH<sub>4</sub>Cl (5 ml) was added and the mixture extracted with ether. The organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, concentrated under reduced pressure and chromatographed on a silica gel column developed with benzene-CHCl<sub>3</sub> mixtures to give 8 (625 mg, quantitative yield). Product 10 had  $[\alpha]_D^{20}$  (EPA) 589 nm = 7°, 578 nm = 8°, 546 nm = 9°, 436 nm = 17° and 365 nm = 33°; IR (liq.) 3400, 2980, 2900, 2800 (s), 1455, 1375 (w), 1100, 1060, 1000, 925, 890 (m) and 810 (w) cm<sup>-1</sup>;  $\delta$  (CDCl<sub>3</sub>) 0.63, 0.85 (6 H, *gem.* dimethyl), 0.85 d (3 H, *J* = *ca.* 5 Hz, >CH-CH<sub>3</sub>), 1.54 (3 H, =C-CH<sub>3</sub>), 1.38 (3 H, CH<sub>2</sub>-C-OH), 1.9-1.5 (3 H, complex, -CH<sub>2</sub>, CH<sub>2</sub>-CH<), 2.1-2.2 (1 H, broad >CH-C=C<), 3.65 (1 H, broad, OH), 5.03 q (1 H, *J*<sub>1</sub> = 10.5 Hz, *J*<sub>2</sub> = 1.5 Hz, *cis* CH=CH<sub>2</sub>), 5.22 q (1 H, *J*<sub>1</sub> = 16.5 Hz, *J*<sub>2</sub> = 1.5 Hz, *trans* CH=CH<sub>2</sub>), *ca.* 5.37 (1 H, CH=C-CH<sub>3</sub>), *ca.* 5.50 (1 H, -CH=CH<sub>2</sub>), 5.58 (1 H, =CH-COH) and 6.02 q (1 H, *J*<sub>1</sub> = 17.5 Hz, *J*<sub>2</sub> = 10.5 Hz, CH=CH-COH); *m/e* 234 (M), 216 (M-18) and 263 (M-71).

(-)-(2*R*,6*R*)-*trans*- $\alpha$ -Irone (9). 9 isolated from a base isomerized mixture of irones as described earlier<sup>1,3</sup> had the following properties:  $[\alpha]_D^{20}$  (EPA) 589 nm = -421°, 578 nm = -440°, 546 nm = -506°, 436 nm = -898°;  $\lambda_{max}$  225 nm (EPA), 228 nm (MeOH); IR (liq.) 3035 (w), 2960, 2935, 2910, 2880 (s), 2835 (m), 1697, 1675, 1620 (s), 1450, 1430, 1390 (m), 1365, 1255 (s), 1200, 1170, 1140, 1120, 1080, 1050 (w), 995, 980 (m) 910 and 810 (w) cm<sup>-1</sup>;  $\delta$  (CDCl<sub>3</sub>) 0.83, 0.87 (6 H, *gem.* dimethyl), *ca.* 0.85 d (3 H, *J* = 5 Hz, >CH-CH<sub>3</sub>), 1.58 (3 H, =C-CH<sub>3</sub>), 2.1-1.7 (3 H, complex, -CH<sub>2</sub>, CH<sub>2</sub>CH<), 2.22 (3 H, O=C-CH<sub>3</sub>), 2.31 d (1 H, *J* = *ca.* 8 Hz, >CH-C=C), 5.47 (1 H, broad, CH=C-CH<sub>3</sub>), 6.08 d (1 H, *J* = 16 Hz, =CH-C=O), and 6.70 q (1 H, *J*<sub>1</sub> = 16 Hz, *J*<sub>2</sub> = 9 Hz, CH=CH-C=O); *m/e* 208 (M), 136 (M-70), 121 (M-85) and 93 (M-113).

(-)-(2*R*,6*R*)-*trans*-Vinyl- $\alpha$ -ironol (11). (11) was prepared from 9 (636 mg) and vinyl magnesium bromide by the procedure earlier described for the preparation of 10;<sup>3</sup> yield 715 mg (quantitative);  $[\alpha]_D^{20}$  (EPA) 589 nm =

-48°, 578 nm = -50°, 546 nm = -57°, 436 nm = -103°; IR (liq.) 3400, 2980, 2900, 2800 (s), 1455, 1375 (w), 1100, 1050, 890 (m) and 810 (w)  $\text{cm}^{-1}$ ;  $\delta$  ( $\text{CDCl}_3$ ) 0.77, 0.81 (6 H, *gem.* dimethyl), *ca.* 0.82 d (3 H,  $J = \text{ca. } 5 \text{ Hz}$ , >CH- $\text{CH}_3$ ), 1.58 (3 H, =C- $\text{CH}_3$ ), 1.35 (3 H,  $\text{CH}_3$ -C-OH), 1.3-1.8 (3 H, complex, - $\text{CH}_2$ ,  $\text{CH}_2$ -CH <), 2.1 (1 H, broad >CH-C=C), 3.65 (1 H, broad, -OH), 5.00 (q, 1 H,  $J_1 = 10 \text{ Hz}$ ,  $J_2 = 2 \text{ Hz}$ , *cis* CH=CH $_2$ ), 5.18 (q, 1 H,  $J_1 = 18 \text{ Hz}$ ,  $J_2 = 1.5 \text{ Hz}$ , *trans* CH=CH $_2$ ), *ca.* 5.37 (1 H, CH=C- $\text{CH}_3$ ), *ca.* 5.49 (1 H, CH=CH $_2$ ), 5.56 (1 H, =CH-COH) and 5.97 (q, 1 H,  $J_1 = 17.5 \text{ Hz}$ ,  $J_2 = 10.5 \text{ Hz}$ , CH=CH-COH; *m/e* 234 (M), 216 (M-18) and 263 (M-71).

(2S,6R)-*cis*- $\alpha$ -Ironylidene-ethyltriphenylphosphonium bromide (12). A solution of 10 (0.6 g) and triphenylphosphonium bromide (1.1 g) in dry MeOH (15 ml) was stirred at 20 °C for 48 h under nitrogen. The solvent was removed under reduced pressure, the oily residue dissolved in a minimum amount of acetone and chromatographed on a silica gel column. Elution with acetone removed unreacted 10 and triphenylphosphine. 12 was eluted with MeOH and obtained as an amorphous powder after solvent evaporation. Yield of 12 was 1.02 g (62 %).

(2R,6R)-*trans*- $\alpha$ -Ironylidene-ethyltriphenylphosphonium bromide (13). 13 was prepared from 11 (0.56 g) according to the procedure described for 12; yield 0.91 g (70 %).

(2R,6S,2'R,6'S)-2,2'-Dimethyl- $\epsilon$ , $\epsilon$ -carotene (15). NaOMe (0.6 M) was slowly added to a stirred solution of 12 (250 mg) in dry MeOH (5 ml) until the phosphonium salt was completely converted to the deep red phosphorane. A solution of 2,7-dimethylocta-2,4,6-triene-1,8-dial (14, 15 mg, prepared from the acetylenic analogue<sup>21</sup>) in  $\text{CH}_2\text{Cl}_2$  (1 ml) was added and the mixture stirred at room temperature. Progress of the reaction was monitored by TLC and additional phosphorane, generated externally, was added until 14 was completely consumed. Water was added, the crude product extracted into ether, concentrated under vacuum and chromatographed on alumina plates. Yield of 15 (*cis-trans*-mixture) was 25.2 mg (47 % based on dial 14). All *trans*-15 was obtained after rechromatography on alumina plates followed by crystallization from MeOH- $\text{CHCl}_3$  solution. 15 melted at 197 °C;  $\lambda_{\text{max}}$  (petroleum ether) 268, (396), 417, 440 [ $E(1\%, 1 \text{ cm}) = 2600$ ;  $\epsilon = 147\,000$  compared to 151\,700 reported for racemic 2,2'-dimethyl- $\epsilon$ , $\epsilon$ -carotene<sup>11</sup>], 471 [ $E(1\%, 1 \text{ cm}) = 2680$ ;  $\epsilon = 149\,000$  compared to 152\,300<sup>11</sup>], (acetone) 416, (426), 441 [ $E(1\%, 1 \text{ cm}) = 2520$ ], and 472 nm [ $E(1\%, 1 \text{ cm}) = 2510$ ]; IR (KBr) 3030 (w), 2980, 2920, 2880 (s), 1730, 1440 (w), 1390, 1365 (m), 1210, 1120, 1060, 1030, 1010 (w), 965 (s), 910, 890, 860, 835, 820 and 800  $\text{cm}^{-1}$  (w);  $\delta$  ( $\text{CDCl}_3$ ) 0.68, 0.87 (6 H + 6 H, *gem.* dimethyl), 0.87 (6 H, d,  $J = 5 \text{ Hz}$ ,  $\text{CH}_3$  at C-2,2'), 1.53 (6 H,  $\text{CH}_3$ -18,18'), 1.93 (6 H,  $\text{CH}_3$ -19,19'), 1.97 (6 H,  $\text{CH}_3$ -20,20'),

*ca.* 2.4 (2 H, H-6,6'), *ca.* 5.5 (2 H, H-4,4'), 5.58 (2 H, dd,  $J_1 = 16 \text{ Hz}$ ,  $J_2 = 7 \text{ Hz}$ , H-7,7') and 6.0-7.0 (in-chain olefinic H); *m/e* 364 (M), 494 (M-70), 472 (M-92), 458 (M-106), 406 (M-158) and 402 (M-70-92); CD spectrum Fig. 1;  $R_F = 0.42$  on alumina plates developed with petroleum ether-ether (97:3) compared to 0.38 for  $\epsilon$ , $\epsilon$ -carotene, 0.32 for  $\beta$ , $\epsilon$ -carotene, and 0.25 for  $\beta$ , $\beta$ -carotene; on Schleicher and Schüll No. 288 alumina paper 15 had  $R_F = 0.50$  when developed in petroleum ether.

(2R,6R,2'R,6'R)-2,2'-Dimethyl- $\epsilon$ , $\epsilon$ -carotene (16). 16 was prepared from 13 and 14 (15 mg), isolated, purified and crystallized by using the procedures described for the preparation of 15; yield 15.75 mg (29.3 %). The electronic, IR and mass spectra could not be distinguished from those of 15;  $\delta$  ( $\text{CDCl}_3$ ) 0.81 (12 H, *gem.* dimethyl), 0.82 (6 H, d,  $J = 5 \text{ Hz}$ ,  $\text{CH}_3$  at C-2,2'), 1.59 (6 H,  $\text{CH}_3$ -18,18'), 1.81 (6 H,  $\text{CH}_3$ -19,19'), 1.97 (6 H,  $\text{CH}_3$ -20,20'), 2.18 (d,  $J = 9 \text{ Hz}$ , C-6,6'), *ca.* 5.4 (2 H, C-4,4'), 5.52 (2 H, dd,  $J_1 = 16 \text{ Hz}$ ,  $J_2 = 7 \text{ Hz}$ , H-7,7') and 6.0-7.0 (in-chain olefinic H). Crystalline all-*trans*-16 melted at 222-223 °C. The CD spectrum is reproduced in Fig. 1. On Schleicher and Schüll No. 288 paper 16 had  $R_F = 0.49$  when developed in petroleum ether and could only be distinguished from 15 by careful chromatography; on alumina plates 16 had  $R_F = 0.42$  when developed in petroleum ether-ether (97:3) and was difficult to distinguish from 15 on co-chromatography.

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