Tetrahedron. Vol 33, pp. 381 to 383. Pergamon Press 1977 Printed in Great Britain

TOTAL SYNTHESES OF CROSS-CONJUGATED CAROTENALS

JON EIGILL JOHANSEN and SYNNØVE LIAAEN-JENSEN
Organic Chemistry Laboratories, Norwegian Institute of Technology, University of Trondheim, N-7034 Trondheim-NTH, Norway

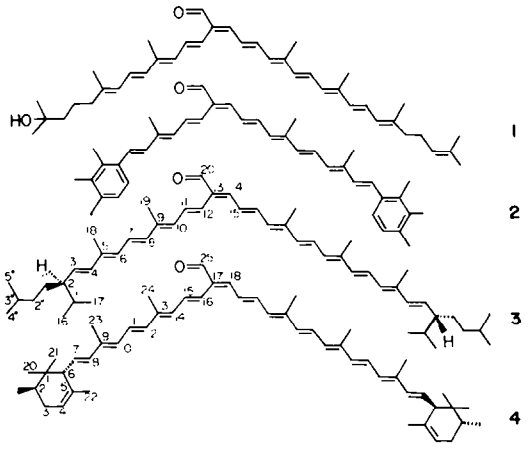
(*Received in USA* 11 *June* 1976; *Received in UK for publication* 23 *September* 1976)

Abstract—Total syntheses of the cross-conjugated carotenals renierapurpurin-20-al (χ,χ-caroten-20-al, **2**), (2*R*,2′*R*)-tetradesoxybacterioruberin-20-al ((2*R*,2′*R*)-2,2′-bis-(3-methylbutyl)-3,4,3′,4′-tetrahydro-ψ,ψ-caroten-20-al, **3**) and (2*R*,6*R*,2′*R*,6′*R*)-2,2′-dimethyl-decapreno-ϵ,ϵ-caroten-25-al (**4**) from the common intermediate 8,8′-diapo-20-acetoxycarotene-8,8′-dial (**5**) are described. The cross-conjugated 20-(2,3,4-trimethylbenzal)renierapurpurin (**16**) has also been synthesized.

Cross-conjugated carotenals of the rhodopinal (**1**) type are encountered in many photosynthetic bacteria.[1] These carotenals exhibit peculiar electronic spectra and are known to have the 13-double bond in *cis* configuration.[2-4] Small scale total synthesis of aliphatic carotenals of this type has recently been effected in our laboratory.[5]

Since the general instability of these aliphatic cross-conjugated carotenals does not allow a full characterization, total synthesis of a related, more stable carotenal with aryl end groups, namely renierapurpurin-20-al (**2**) has now been effected with the special purpose of configurational studies.[6]

For the investigation of chiroptical properties of such carotenoids with bent polyene chain two cross-conjugated carotenals with chiral end groups have also been prepared, the aliphatic bacterioruberin derivative **3** and the bicyclic C_{52}-carotenal **4**.



Scheme 1.

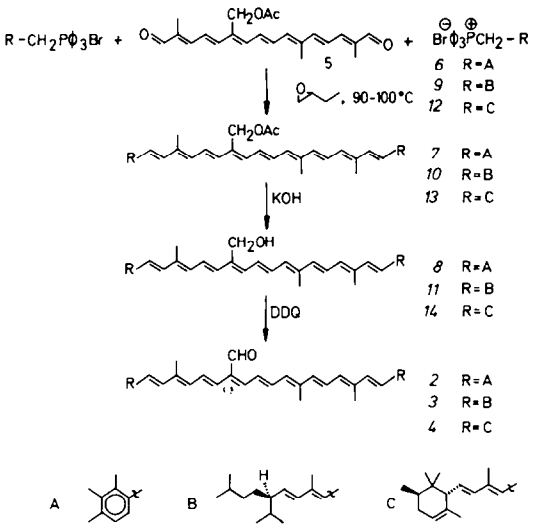
RESULTS AND DISCUSSION

We have recently reported the synthesis of the key intermediate 8,8′-diapo-20-acetoxycarotene-8,8′-dial (**5**) from the corresponding dial.[7] The synthesis of the cross-conjugated carotenals **2**–**4** (Scheme 1) followed the route outlined in Scheme 2.

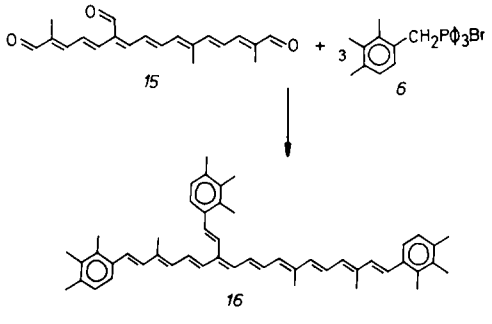
The phosphonium salts **6** and **12** were available[8,9] and the chiral phosphonium salt **9** was synthesized as described elsewhere.[10,11]

Test experiments showed that the free C_{20}-alcohol corresponding to the acetate **5** readily was oxidized during Wittig condensation with the phosphonium salt **6**, thus resulting in undesired condensation products such as **16** (Scheme 3).

However, Wittig condensation of the acetylated dialdehyde **5** with the appropriate phosphonium salts, using 1,2-butylene oxide to avoid excess base, provided the desired di-condensation products **7**, **10** and **13** without complications. Hydrolysis of the acetates to the free alcohols **8**, **11** and **14** followed by allylic oxidation with



Scheme 2.



Scheme 3.

DDQ gave the cross-conjugated carotenals **2**, **3** and **4**. All intermediates are fully spectroscopically characterized.

Renierapurpurin-20-al (**2**) was obtained as crystals, m.p. 185–186° and was characterized by electronic, IR, ^{1}H NMR and mass spectra. The 13-*cis* configuration of the polyene chain is now established.[6]

The aliphatic bacterioruberin derivative **3** and the bicyclic carotenal **4** could not be crystallized, but were characterized by the same criteria. From their electronic and ^{1}H NMR spectra and by analogy with **1**[4] and **2**[6] *cis*-configuration of the double bond α to the carbonyl is assumed.[6] CD properties of the two chiral aldehydes **3** and **4** will be reported elsewhere.

Finally the cross-conjugated triaryl carotene **16** was prepared by Wittig condensation of the previously prepared trial **15** with 2,3,4-trimethylbenzyl triphenylphosphonium bromide (**6**, Scheme 3) and now shown to be 13-*cis*.[6]

Linear dichroic spectra of **2**, **15** and **16** are reported elsewhere.[6]

EXPERIMENTAL

Materials and methods were as described elsewhere.[7] Yields were calculated from absorption spectra using extinction coefficients obtained for the crystalline products. However, due to the ready *cis-trans* isomerization of these compounds calculation of concentrations in soln is approximative. For products not obtained in the crystalline state $E_{1\%,1cm} = 2500$ at λ_{max} was used when not otherwise stated.

20-*Acetoxy-renierapurpurin* (**7**). Compounds **5** (7.7 mg) and **6** (140 mg) were transferred to a test tube and dissolved in chloroform-1,2-butylene oxide (1:1, 1 ml). The tube was filled with N_2, sealed and kept at 100° for 3 hr. The solvents were removed and the products chromatographed on a silica gel column developed with benzene to give **7**, yield 3.7 mg (29%). The combined products from several experiments (24.5 mg) were rechromatographed in the same system and crystallized from ether-methanol to give **7**, yield 6.3 mg, m.p. 172–173°; UV-visible λ_{max} (acetone) 471.5 nm ($E_{1\%,1cm} = 2230$, $\epsilon = 130{,}000$), % $D_B/D_{II}^3 = 9$; λ_{max} (hexane) 296, (363) and 468 nm; IR (KBr) ν_{max} 3015, 2990, 2910 (w), 1736 (s), 1466, 1440 (w), 1369 (m), 1225 (s), 1049 (w), 1022 (m), 962 (s), 828, 802 and 778 (w); ^{1}H NMR δ ($CDCl_3$) 2.02 (3H, H-20'), 2.08s (–$OCOCH_3$), 2.10s (H-19,19'), 2.08 and 2.10 (9H), 2.22s (6H, H-16,16'), 2.32 s (12H, H-17,18,17',18'), 5.02 s (2H, –CH_2OAc), 6.15–7.0 (14 olefinic H), 7.00 d (2H, H-4,4' (5,5'), $J_{4-5} = 8.5$ Hz) and 7.31 d (2H, H-5,5' (4,4'), $J_{4-5} = 8.5$ Hz); MS *m/e* (220°) 586 (M, 47%) 526 (M-60, 5.1%), 511 (M-75, 0.8%), 494 (M-92, 0.8%), 470 (M-106, 6.2%), 436 (M-150, 4.1%), 422 (M-164, 34%) and 133 (100%).

Renierapurpurin-20-ol (**8**). Compound **7** (17.4 mg) was treated with ether–10% KOH in MeOH (1:1, 50 ml) for 2 hr. The mixture was diluted with ether and washed until neutral with 5% NaCl aq. The solvents were removed and the product dried and purified on a silica gel column developed with 10% ether in chloroform, yield 16.1 mg (100%, *cis-trans* mixture); UV-visible λ_{max} (acetone) 462.5 nm; ^{1}H NMR δ ($CDCl_3$) 1.99 s (3H, H-20'), 2.07 s (6H, H-19,19'), 2.21 s (6H, H-16,16'), 2.30 s (12H, H-17,18,17',18'), 4.43 and 4.55 (2H, –CH_2OH), 6.1–7.1 (14 olefinic H), 6.98 (2H, H-4,4'(5,5'), $J_{4-5} = 8.5$ Hz) and 7.29(2H,H-5,5'(4.4'), $J_{4-5} = 8.5$ Hz).

All-*trans* **8** was crystallized from chloroform-ether, yield 4.0 mg, m.p. 195–196°; UV-visible λ_{max} (CS_2) 504 ($E_{1\%,1cm} = 2060$) 536.5 nm, λ_{max} (acetone) 472.5 ($E_{1\%,1cm} = 2580$, $\epsilon = 140{,}000$) and 501.5 nm, % $D_B/D_{II} = 7$, % III/II = 7, λ_{max} (hexane) 298.5, 470 and 498 nm; IR (KBr) ν_{max} 3440 (m), 3030, 2995 (w), 2915 (m), 2860, 1476, 1444, 1392, 1251, 1050 (w), 1006 (m), 960 (s), 883, 828, 803 and 779 (w) cm^{-1}; ^{1}H NMR δ ($CDCl_3$, 100 MHz) 2.00 s, 2.06 s, 2.20 s, 2.29 s, 4.56 s (–CH_2OH, no signal at 4.43), 7.02 d and 7.30 d (H-4,5,4',5', $J_{4-5} = 8$ Hz); MS *m/e* (210°) 544 (M, 53%), 526 (M-18, 6.1%), 513 (M-31, 0.7%), 465 (M-79, 0.2%), 452 (M-92, 0.6%), 438 (M-106, 4.2%), 436 (M-108, 3.3%), 422 (M-122, 2.8%) and 133 (100%).

Renierapurpurin-20-al (**2**). DDQ in ether-dioxane (2.9 ml, 2.9 mg DDQ) was added dropwise to a soln of **8** (1.85 mg) in ether–dioxane (1:1, 2 ml) at ÷5–÷10°. The reaction was monitored by TLC and addition of DDQ was stopped when the conversion was considered complete. The mixture was chromatographed on a silica gel column developed with chloroform, yield of **2** was 1.80 mg (97%). The combined product from several experiments was rechromatographed on silica gel (benzene). Crystallization from acetone–methanol gave 5.7 mg of **2**, m.p. 185–186°; UV-visible λ_{max} (acetone) 365 and 496.5 nm ($E_{1\%,1cm} = 1450$, $\epsilon = 79{,}000$), % $D_B/D_{II} = 42$; λ_{max} (hexane) 232), 314, 369 and 490.5 nm; IR (KBr) ν_{max} 2915, 2830 (w), 1676 (s), 1580, 1583 (m), 1371, 1216, 1165 (m), 965 (s), 904 and 800 cm^{-1}; ^{1}H NMR δ ($CDCl_3$) 2.09 s (9H, H-19,19',20'), 2.21 s (6H, H-16,16'), 2.29 (12H, H-17,18,17'), 6.10–7.80 (aromatic and olefinic H), 6.99 (H-4,4' (5,5'), $J_{4-5} = 8.5$ Hz), 7.28 (H-5,5' (4,4'), $J_{4-5} = 8.5$ Hz), 7.70 dd (H-11?, $J_{10-11} = 5$ Hz, $J_{11-12} = 12$ Hz) and 9.58 d (1H, –CHO, $J = ca.$ 1.9 Hz); MS *m/e* (210°) 542 (M, 76%), 450 (M-92, 1.0%), 436 (M-106, 4.6%), 422 (M-120, 21%), 408 (M-134, 2.7%) and 133 (100%).

(2R,2'R) - 2,2' - Bis(3 - *methylbutyl*) - 3,4,3',4' - *tetradihydro* - *ψ,ψ* - *caroten* - 20 - *acetate* (**10**). Compounds **5** (20.1 mg) and **9**[10,11] (230 mg) were dissolved in a test tube with chloroform-1,2-butylene oxide (1:1, 1 ml). The tube was filled with N_2, sealed and kept at 90° for 2.5 hr, the solvents removed and the product chromatographed on TLC (silica gel G, 4% acetone in hexane = AH). Several zones of approximately the same polarity were observed. Two fractions were collected. The less polar fraction **10A** consisted of zone 1 (yellow) and 2 (orange), yield 3.0 mg (4%); UV-visible λ_{max} (ether) (372), 388 and 481 nm.

Fraction **10B**, zone 3–8 (red); yield 27.0 mg (39%); UV-visible λ_{max} (ether) 371, 387, 488.5, 518 nm. IR(KBr) ν_{max} 3035, 2955, 2930, 2970 (m), 1730 (s), 1467, 1385, 1367 (w), 1223, 1023 (m) and 964 (s); ^{1}H NMR δ ($CDCl_3$) 0.86 d (24H, isopropyl CH_3, $J_{1-16} = J_{3'-4'} = 5.5$ Hz), 1.3–1.9 (12H, >CH– and –CH_2–, complex), 1.93 s (6H, H-18,18'), 1.98 (9H, H-19,19',20', broad), 2.07 and 2.08 (3H, –$OCOCH_3$), *ca.* 2.25 (2H, H-2,2', complex), *ca.* 4.86 and 4.99 (2H, broad), *ca.* 5.52 dd (2H, H-3,3', $J_{2-3} = 9$ Hz, $J_{3-4} = 16$ Hz), and 5.9–7.0 (18 olefinic H); MS *m/e* (240°) 734 (M, 35%), 674 (M-60, 3.1%), 642 (M-92, 0.9%), 628 (M-106, 20%), 584 (M-150, 3.4%), 576 (M-158, 0.9%), 570 (M-164, 18%), 518 (M-216, 5.4%) and 43 (100%).

(2R,2'R) - 2,2' - Bis(3 - *methylbutyl*) - 3,4,3',4' - *tetrahydro* - *ψ,ψ* - *caroten* - 20 - *ol* (**11**). Hydrolysis of **10A** (3.0 mg) and **10B** (25.5 mg) was effected with ether–10% KOH in MeOH (1:1, 20 + 50 ml). Co-chromatography prior to work-up indicated identity. Hydrolyzed **10A** and **10B** were combined and worked up after 2.5 hr according to the procedure described for **8**. Chromatography on TLC (silica gel, 8% AH) gave 7 zones which were collected in two fractions. The less polar fraction **11A**; zone 1 (yellow) and zone 2 and 3 (orange); yield 2.8 mg (10%); UV-visible λ_{max} (ether) 370.5, 387 and 481 nm.

The main fraction (**11B**) consisted of four red zones, yield 20.6 mg (77%); UV-visible λ_{max} (ether) 370, 386.5, 487.5 and 516.5 nm; IR (KBr) ν_{max} 3035 (w), 2955, 2925, 2870 (m), 1467, 1384, 1368, 1004 (w) and 964 (s), ^{1}H NMR δ ($CDCl_3$) 0.87 d (24H, isopropyl CH_3), $J_{1-16} = J_{3'-4'} = 5.5$ Hz), 1.3–1.9 (12H, >CH– and –CH_2–, complex), 1.93 s (6H, H-18,18'), 2.00 (9H, H-19,19',20', broad), *ca.* 2.25 (2H, H-2,2', complex), *ca.* 4.43 and 4.54 (2H, –CH_2OH, broad), *ca.* 5.56 dd (2H, H-3,3, $J_{2,3} = 9$ Hz, $J_{3-4} = 16$ Hz) and 5.95–7.0 (18 olefinic H); MS *m/e* (235°) 692 (M, 32%), 674 (M-18, 1.3%), 600 (M-92, 0.8%), 586 (M-106, 27%), 584 (M-108, 3.7%), 570 (M-122, 18%), 534 (M-158, 0.7%), 518 (M-216, 5.4%) and 43 (100%).

(2R,2'R) - 2,2' - Bis(3 - *methylbutyl*) - 3,4,3',4' - *tetrahydro* - *ψ,ψ* - *caroten* - 20 - *al* (**3**). Combined **11A** and **11B** (16.7 mg) was oxidized with DDQ (21 mg) according to the procedure described for **8**. The mixture was chromatographed on a silica gel column (benzene) and the crude product rechromatographed on TLC (silica gel, 6% AH) giving three major zones (blue–violet). The product was collected in one fraction, Yield 7.3 mg (44%, $E_{1\%,1cm} = 1400$ used); UV-visible λ_{max} (acetone) 391 and 520 nm; IR (KBr) ν_{max} 2955, 2925, 2830 (m), 1736 (imp.), 1680 (s), 1466, 1377 (m), 1280, 1220, 1169, 1074 (w), 967 (s) and 910 (w); ^{1}H

NMR δ ($CDCl_3$) 0.87 d (24H, isopropyl, $J_{1-16} = J_{1'-4'} = 5.5$ Hz), 1.26 imp., 1.3–1.9 (12H, >CH–, and $-CH_2-$, complex), 1.93 s (6H, H-18,18'), 2.03 (9H, H-19,19',20', broad), *ca.* 2.25 (2H, H-2,2', complex), *ca.* 4.0 imp., 5.5–7.00 (20 olefinic H) and 9.56 d (1H, –CHO, $J_{14-20} = ca.$ 1.9 Hz, broad); MS *m/e* (230°) 690 (M, 54%), 688 (M-2, 35%), 598 (M-92), 1.8%), 584 (M-106, 7.5%), 570 (M-120, 8.8%), 518 (M-172, 9.1%) and 43 (100%).

Upon rechromatography the eluted pigment from the main zone had UV-visible λ_{max} (acetone) 392 and 529, % D_B/D_{II} = 63, λ_{max} (ether) 354, 390.5 and 518 nm. Crystallization before and after rechromatography was unsuccessful.

(2R,6R,2'R,6'R) - 25 - *Acetoxy* - 2,2' - *dimethyl* - *decapreno* - ϵ,ϵ - *carotene* (**13**) was prepared from **5** (15 mg) and **12**[9] (200 mg) according to the procedure described for **9**. Chromatography on TLC (silica gel G, 3% AH) gave fraction **13A** (least polar, two orange zones), yield 2.3 mg (5%); UV-visible λ_{max} (ether) 374, 388 and 485 nm.

Fraction **13B** (most polar, one broad band), yield 18.2 mg (41%); UV-visible λ_{max} (ether) 373.5, 389, 491 and 520. IR (KBr) ν_{max} 3030, 2960, 2915, 2875 (m), 2835 (w), 1740 (s), 1447, 1366, 1376 (w), 1228 (s), 1052, 1024 (w), 964 (s) and 810 (w); ^{1}H NMR δ ($CDCl_3$) 0.82 s (isopropyl CH_3), 0.83 d (CH_3-2,2', J = 5 Hz), 0.82 and 0.83 (24H), 1.61 (H-22,22', broad), 1.92 s (6H, H-23,23'), 1.99 s (9H, H-24,24',25'), 2.08 (3H, $-OCOCH_3$, broad), 1.6–2.4 (8H, H-2,3,6,2',3',6', complex), *ca.* 4.84 and 4.99 (2H, broad), *ca.* 5.41 (2H, H-4,4'), 5.58 dd (2H, H-7,7', $J_{5-7} = 9$ Hz, $J_{7-8} = 16$ Hz) and 5.9–7.0 (18 olefinic H); MS *m/e* (230°) 754 (M, 66%), 694 (M-60, 61%), 662 (M-92, 2.3%), 648 (M-106, 9.3%), 618 (M-136, 2.3%), 604 (M-150, 6.8%), 596 (M-158, 1.4%), 590 (M-164, 34%), 538 (M-216, 10.5%) and 137 (100%).

(2R,6R,2'R,6'R) - 2,2' - *Dimethyl* - *decapreno* - ϵ,ϵ - *caroten* - 25 - *ol* (**14**). **13A** and **13B** (20 mg) were combined, hydrolyzed and chromatographed as described for **11**. The product was collected in two fractions. Fraction **14A** (least polar, orange); yield 1.4 mg (7%); UV-visible λ_{max} (ether) 472, 388, 482 and (509) nm.

Fraction **14B** (most polar, red), yield 17.0 mg (90%); UV-visible λ_{max} 371.5, 388, 487.5 and 517 nm. IR (KBr) ν_{max} 3420, 3030, 2960, 2915, 2875 (m), 2830, 1705, 1548 (w), 1447 (m), 1366, 1376, 1387, 1184, 1153, 1007 (w), 964 (s), 912, 886 and 809 (w); ^{1}H NMR δ ($CDCl_3$) 0.82 s (isopropyl CH_3), 0.84 D (CH_3-2,2', J = 5 Hz), 0.82 and 0.84 (24H), 1.59 (6 H, H-22,22', broad), 1.91 s (6H, H-23,23'), 1.98 s (9H, H-24,24',25'), 1.6–2.4 (8H, H-2,3,6,2',3',6', complex), *ca.* 4.41 and 4.53 (2H, broad), *ca.* 5.38 (2H, H-4,4', broad), *ca.* 5.57 dd (2H, H-7,7', $J_{6-7} = 9$ Hz, $J_{7-8} = 16$ Hz) and 5.9–7.0 (18 olefinic H), MS *m/e* (220°) 712 (M, 40%), 684 (M-18, 2.7%), 642 (M-70, 2.3%), 620 (M-92, 2.1%), 606 (M-106, 8.1%), 604 (M-108, 7.8%), 590 (M-122, 29%), 538 (M-174, 8.2%) and 137 (100%).

(2R,6R,2'R,6'R) - 2,2' - *Dimethyl-decapreno* - ϵ,ϵ - *caroten* - 25 - *al* (**4**). Combined **14A** and **14B** (180 mg) was oxidized with DDQ (17 mg) and purified according to the procedure described for **11**. TLC yielded three main zones (all blue-violet) which were collected together, yield 17.0 mg (95%); ^{1}H NMR δ ($CDCl_3$) 0.82 s (isopropyl CH_3), 0.84 d (CH_3-2,2', J = 5 Hz), 0.82 and 0.84 (24H), 1.59 (6H, H-22,22', broad), 1.92s (6H, H-23,23'), 2.03 (9H, H-24,24',25', broad), 1.6–2.4 (H-2,3,6,2',3',6', complex), *ca.* 5.39 (H-4,4', broad), *ca.* 5.58 (H-7,7', $J_{6-7} = 9$ Hz, $J_{7-8} = 16$ Hz), 5.9–7.0 (18 olefinic H) and 9.56 d (1H, –CHO, $J_{14-20} = ca.$ 1.9 Hz, broad).

Attempted crystallization from acetone-methanol gave a solid ppt; yield 7.9 mg (m.p. unsharp at 102–110°); UV-visible λ_{max} (hexane) 333, 392.5 and 515 ($E_{1\%,1\,cm} = 1290$, $\epsilon = 92{,}000$), λ_{max} (acetone) 392 and 518 nm; MS *m/e* (220°) 710 (M, 60%), 708 (M-2, 2.7%), 640 (M-70, 3.6%), 618 (M-92, 1.7%), 604 (M-106, 4.6%), 590 (M-120, 9.8%) 573 (M-137, 7.9%), 552 (M-158, 0.7%), 538 (M-170, 8.8%) and 137 (100%).

The mother liquor was purified by TLC (silica gel G, 5% AH). The pigments from the three zones, numbered 4A–C from top, were isolated. **4A** (*ca.* 5%), two zones on Merck silica gel 60 pre-coated plates (0.2 mm thick); had; UV-visible λ_{max} (acetone) 392 and 512.5 nm; **4B** (*ca.* 15%) had UV-visible λ_{max} (acetone) 391.5 and 518.5 nm; **4C** (80%) showed UV-visible λ_{max} (acetone) 392 and 525, % D_B/D_{II} = 61; λ_{max} (hexane) 340, 392 and 520, % D_B/D_{II} = 55; Attempted crystallization of **4C** from acetone-methanol was unsuccessful.

20-(2,3,4-*Trimethylbenzal*)-*renierapurpurin* (**16**) was prepared from **15** (31.4 mg) and **6** (1.35 g) according to the procedure described for the preparation of **7**. The product was chromatographed on a column of silica gel (3% AH), yield 34.5 mg (52%).

Rechromatography on TLC (silica gel G, 1% acetone in CS_2) gave two zones. The least polar zone **16A** (65%) had UV-visible λ_{max} (acetone) 481.5 nm and the most polar zone **16B** (35%) had UV-visible λ_{max} (acetone) 476 nm.

16A was crystallized from acetone-CS_2-methanol, yield 4.5 mg, m.p. 165–167°; UV-visible λ_{max} (acetone) 370 and 485 nm ($E_{1\%,1\,cm} = 1670$, $\epsilon = 110{,}000$); λ_{max} (hexane) 362.5 and 478.5 nm; IR (KBr) ν_{max} 3030 (w), 2920 (m), 2855 (w), 1441, 1387, 1247, 1170, 1049, 1004 (w), 969 (s), 885, 843, 825 (w), 803 (m), 778 and 723 (w); MS *m/e* (230°) 658 (M, 41%), 566 (M-92, 6.7%), 552 M-106, 8.4%), 525 (M-133, 5.5%), 422 (M-236, 22%) and 133 (100%).

A second batch of crystals was obtained from the mother liquor, yield 5.9 mg from acetone-methanol; ^{1}H NMR δ ($CDCl_3$) *ca.* 2.01 and 2.06 (9H, H-19,19',20'), 221 (9H, H-16,16',16"), 2.29 (18H, H-17,18,17',18',17",18") and 6.2–7.3 (aromatic and olefinic H).

16B was not further investigated.

Acknowledgements—J.E.J. was supported by a personal grant from the University of Trondheim and by a grant from the Norwegian Council of Science and the Humanities to S.L.J.

REFERENCES

[1]K. Schmidt, *Biosynthesis of carotenoids.* In *Photosynthetic Bacteria* (Edited by R. K. Clayton and W. R. Sistrom). Plenum Press, New York (1976).

[2]A. J. Aasen and S. Liaaen-Jensen, *Acta Chem. Scand.* **21**, 2185 (1967).

[3]B. Ke, F. Imsgaard, H. Kjøsen and S. Liaaen-Jensen, *Biochim. Biophys. Acta* **210**, 139 (1970).

[4]C.-A. Chin and P.-S. Song, *J. Molec. Spectros.* **52**, 216 (1974).

[5]O. Puntervold and S. Liaaen-Jensen, *Acta Chem. Scand. B* **28**, 1096 (1974).

[6]Q. Chae, P.-S. Song, J. E. Johansen and S. Liaaen-Jensen, to be published.

[7]J. E. Johansen and S. Liaaen-Jensen, *Acta Chem. Scand. B* **29**, 315 (1975).

[8]A. J. Aasen and S. Liaaen-Jensen, *Ibid.* **21**, 970 (1967).

[9]A. G. Andrewes, G. Borch and S. Liaaen-Jensen, *Ibid. B* **30**, In press. (1976).

[10]J. E. Johansen and S. Liaaen-Jensen, *Tetrahedron Letters* 995 (1976).

[11]J. E. Johansen, *Thesis*, Norw. Inst. Technology, Univ. Trondheim, 1977.