# Carotenoids and Related Compounds. Part XVII.[1] Synthesis of Spirilloxanthin, "OH-Spirilloxanthin," and 3,4-Dehydrorhodopin

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Spirilloxanthin, "OH-spirilloxanthin," and 3,4-dehydrorhodopin have been synthesised. The structure proposed for α-bacterioruberin has been shown to require revision.



SPIRILLOXANTHIN, the characteristic pigment of many purple photosynthetic bacteria, was shown to have the structure (XV) by n.m.r.[1,2] in conjunction with chemical studies.[2-6] The related glycol structure (XIV) was proposed by Jensen[7] for α-bacterioruberin, the principal pigment of many *Halobacteria*. Strong support for this suggestion was provided by the observation that methylation of α-bacterioruberin with methyl iodide and silver oxide in dimethylformamide gave a product which had the same visible absorption spectrum, chromatographic properties, and stereomutation pattern as spirilloxanthin.[6,8] A further product of the same reaction was, for similar reasons, regarded[6,8] as identical with "OH-spirilloxanthin," a minor pigment of purple photosynthetic bacteria[9,10] for which structure (XVI) had been suggested.[2] Unfortunately, neither of the methylation products, which were formed in only 2·4 and 12% yield, respectively, could be crystallised.[8]

"OH-Spirilloxanthin," which is believed to be an intermediate in the biosynthesis of spirilloxanthin from lycopene, has not been fully characterised.[9-11] However, another of the supposed intermediates, 3,4-dehydrorhodopin, has been formulated as (XVII), with the same hydroxylated end-group as that postulated for "OH-spirilloxanthin" and α-bacterioruberin, from its n.m.r. spectrum and other properties.[12]

Syntheses of spirilloxanthin have been described by Surmatis and Ofner.[13] We now report a new route to this compound which also provides the first syntheses of the related hydroxy-compounds. In this way we have confirmed the structure (XVII) of dehydrorhodopin, obtained further support for the structure assigned to "OH-spirilloxanthin," but shown the need for a re-investigation of the structure of α-bacterioruberin.

A Reformatsky-type reaction of acetone (I) with prop-2-ynyl bromide (II) gave the known alcohol (III);[14] by using aluminium[15] rather than zinc[14] in this reaction, a product was obtained free from allenic impurities. Methylation in dimethyl sulphoxide with methyl iodide in the presence of barium oxide[16] furnished the corresponding methyl ether (IV). The structure of the latter was confirmed by its n.m.r. spectrum which consisted of a singlet at τ 8·74 (6H) due to $-CMe_2O-$, a singlet at 6·78 (3H) due to OMe, a doublet ($J$ = 2·5 c./sec.) at 7·63 (2H) due to prop-2-ynylic $CH_2$ (splitting being attributable to spin–spin coupling with the acetylenic hydrogen), and a triplet ($J$ = 2·5 c./sec.) at 7·98 (1H) due to the acetylenic hydrogen (spin–spin coupled with the $CH_2$ group). The lithium derivatives of (III) and (IV) reacted with methyl vinyl ketone to give the diol (V) and the alcohol (VI), respectively. These were reduced with lithium aluminium hydride to give, as expected,[17-19] the *trans*-ethylenes (VII) and (VIII). Treatment with triphenylphosphine hydrobromide then furnished the required Wittig reagents (IX) and (X). These exhibited the expected n.m.r. spectra which included a band at high field (τ 8·82 and 8·90, respectively) due to $-CMe_2O-$, a doublet ($J$ = 3·5 c./sec.) at 8·60 attributable to the olefinic methyl group, a broad band or doublet at 7·77 due to the allylic $CH_2$ group remote from the phosphorus substituent, and a doublet of doublets ($J$ = 15 and 8 c./sec.) at 5·23 attributable to the allylic $CH_2$ group which is spin–spin coupled to both the proton on the adjacent double bond and to the phosphorus atom. Analogous shielding and spin–spin coupling phenomena associated with a quaternary phosphorus substituent are observed with related Wittig salts.[20,21]

Condensation (cf. ref. 13) of the reagent (X) with crocetindial (XI)[22] gave spirilloxanthin (XV) identical with the natural pigment isolated from *Rhodospirillum rubrum*.[1,2] A similar condensation of the reagent (IX)

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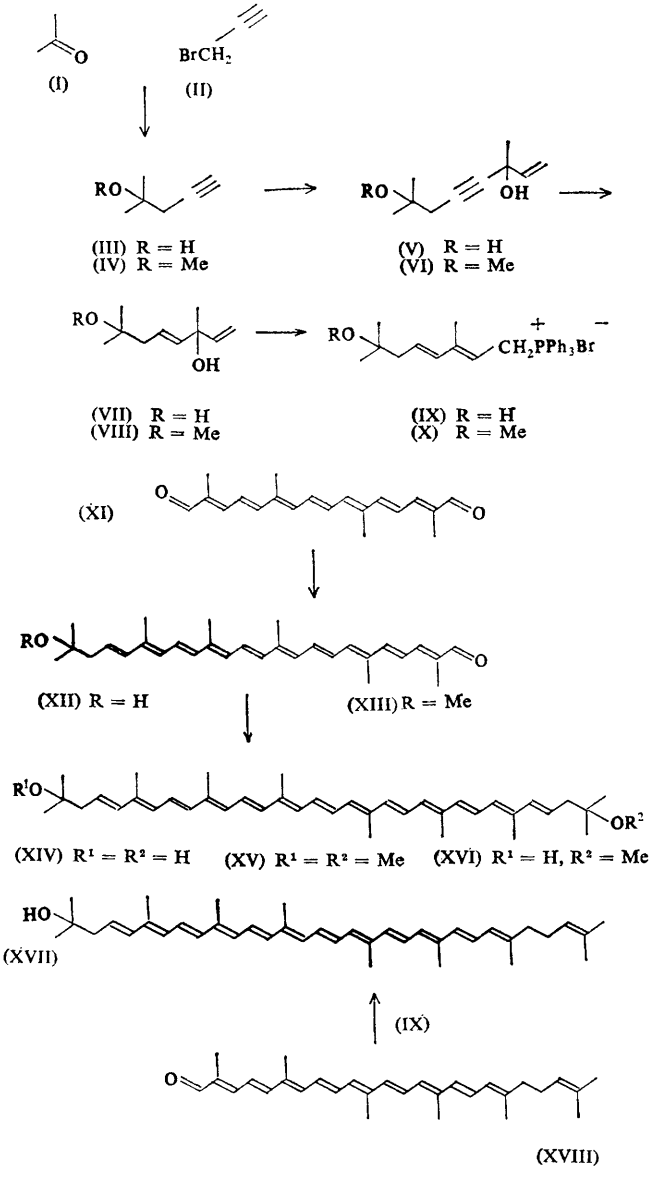
with crocetindial (XI) gave a mixture of stereoisomers from which the all-*trans*-diol (XIV) was isolated. Its composition was confirmed by precision mass spectrometry, and it exhibited the expected n.m.r. bands at τ 8·77 ($-CMe_2OH$), 8·02 (in-chain methyls) and 7·69 (doublet, $J = 6$ c./sec.; allylic $CH_2$) with the required relative intensities of *ca.* 6 : 9 : 2. However, its melting point and partition properties were markedly different




from those reported for α-bacterioruberin. Moreover a direct comparison of the natural and synthetic pigments, carried out by Dr. S. L. Jensen, revealed significant differences in chromatographic behaviour and stereomutation pattern. We conclude that α-bacterioruberin does not have the structure (XIV).

Reaction of the reagent (IX) with crocetindial (XI) under controlled conditions furnished the $C_{30}$ hydroxyaldehyde (XII) which was then treated with the reagent (X) to give the required hydroxy-ether (XVI). Its composition was confirmed by precision mass spectrometry, and it exhibited the expected n.m.r. bands at τ 8·86 ($-CMe_2OC<$), 8·78 ($-CMe_2OH$), 8·03 (in-chain methyls), 7·69 (doublet, $J = 6·5$ c./sec.; allylic $CH_2$), and 6·78 (OMe), with the required relative intensities. Although it has not, as yet, been possible to carry out a direct comparison of the natural and synthetic pigments, the good agreement in m. p., partition ratio, and visible and i.r. absorption spectra, provides reasonable grounds for assuming that the two are identical.

Reaction of the reagent (IX) with $C_{30}$ apo-8-lycopenal (XVIII)[23,24] gave 3,4-dehydrorhodopin. Its properties, and in particular its n.m.r. spectrum, were in excellent agreement with those[12] for the natural pigment.

## EXPERIMENTAL

All operations were, as far as possible, carried out under nitrogen. Solutions were evaporated under reduced pressure. Alumina for chromatography was washed[25] and graded.[26] Melting points were determined in evacuated capillaries. Except where indicated to the contrary, i.r. absorption data were determined for liquid films or KBr discs, and n.m.r. data for deuteriochloroform solutions; only bands useful for identification are quoted.

*2-Methylpent-4-yn-2-ol* (III).—Prop-2-ynyl bromide (342 g.) in tetrahydrofuran was added dropwise to a well stirred and cooled mixture of aluminium powder[15] (54 g.) and mercuric chloride (250 mg.) in tetrahydrofuran (250 ml.) at such a rate that the temperature of the mixture was maintained at *ca.* 30°. The mixture was stirred for 1 hr. at 25—30°, and then cooled to 0°. Acetone (246 ml.) in tetrahydrofuran (200 ml.) was added slowly at 0°. The temperature of the mixture was then allowed to rise to 50°, and when it had dropped to 20° saturated ammonium chloride solution was added. The mixture was extracted with ether, and the extracts were dried ($Na_2SO_4$) and evaporated. Distillation (short Fenske column) gave a liquid (200 g., 71%), b. p. 126—128°, which was shown by g.l.c. to be contaminated with *ca.* 2% of 4-methylpent-3-en-2-one. The latter was removed by treatment with an excess of semicarbazide acetate leaving the acetylenic alcohol, b. p. 128°, $\nu_{max.}$ 3420 (OH), 3313 (C:CH), and 2135 (C:C) $cm.^{-1}$; no allenic impurities were detected.

When the condensation was carried out using zinc, a mixture of acetylenic and allenic alcohols was obtained (cf. ref. 14 which gives b. p. 124—127°).

*2-Methoxy-2-methylpent-4-yne* (IV).—The above alcohol (42 g.) in dimethyl sulphoxide (20 ml.) was added dropwise to a stirred suspension of barium oxide (300 g.) in dimethyl sulphoxide (120 ml.) and methyl iodide (250 ml.). After the mixture had been stirred for 2 hr. a vigorous reaction commenced which was controlled by cooling (ice–salt bath).

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When the reaction had subsided the mixture was stirred for 4 hr. at 20°, and then left overnight. The mixture was filtered, and the solid was washed thoroughly with ether. The filtrate and washings were combined, washed thoroughly with water, dried ($Na_2SO_4$), and evaporated (Vigreux column) giving a mixture of the acetylenic alcohol and the required ether. Repeated chromatography in light petroleum (b. p. 40—50°) on alumina (Grade I) yielded the acetylenic ether (18 g.), b. p. 120—121°, $\nu_{max.}$ 3320 (C:CH), 2840 (OMe), 2130 (C:C), and 1090 (C–O) cm.$^{-1}$; $\tau$ 8·74 (–$CMe_2O$–), 7·98 (triplet, $J$ = 2·5 c./sec.) (C:CH), 7·63 (doublet, $J$ = 2·5 c./sec.), and 6·78 (OMe), relative intensities *ca.* 6 : 1 : 2 : 3. The ether was unstable and formed coloured impurities on distillation, and even on storage at −20° under nitrogen.

2,6-*Dimethyloct-7-en-4-yne-2,6-diol* (V).—Ethereal 0·95N-phenyl-lithium (426 ml.) was added dropwise to a well stirred (Hirschberg) solution of 2-methylpent-4-yn-2-ol (19·6 g.) in benzene (400 ml.). The mixture was stirred at 20° for 30 min., boiled under reflux for 30 min., and then cooled to 0°. Methyl vinyl ketone (15 g.) in ether (60 ml.) was added during 1 hr. at 0°. The mixture was warmed (60° bath temp.) for 4 hr., and then cooled. Saturated ammonium chloride was added cautiously, the organic layer was separated and the aqueous layer was extracted with ether. The ethereal layer and extracts were combined, dried ($Na_2SO_4$), and evaporated giving a residue which showed strong carbonyl absorption ($\nu_{max.}$ 1700 cm.$^{-1}$). Treatment of the crude product in aqueous alcohol with an excess of semicarbazide acetate at 20° overnight, isolation of the unreacted product and chromatography on alumina (Grade IV) using petrol and subsequently ether as eluent, gave the *diol* (1·5 g.) as a viscous oil, b. p. 100° (bath)/2·2 × $10^{-2}$ mm., $n_D^{20}$ 1·480, $\nu_{max.}$ 3400 (OH), 2250 (C:C), 995 and 925 (–CH:$CH_2$) cm.$^{-1}$; $\tau$ 8·70 (–$CMe_2O$–), 8·46 (Me at C-6), 7·61 ($CH_2$), relative intensities *ca.* 6 : 3 : 2 (Found: C, 71·45; H, 9·4. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·5%).

When the reaction was carried out by the Grignard method the product was almost entirely ketonic.

7-*Methoxy-3,7-dimethyloct-1-en-4-yn-3-ol* (VI).—Ethereal 0·845N-phenyl-lithium (160 ml.) was added during 2 hr. to a stirred and cooled (0°) solution of 2-methoxy-2-methylpent-4-yne (15 g.) in ether (300 ml.). After the mixture had been stirred at 0° for 2 hr., methyl vinyl ketone (10 g.) in ether (40 ml.) was added during 45 min., and the mixture was stirred at 20° for 4 hr. and then cooled. Cold saturated ammonium chloride was added, and the crude product was isolated with ether in the usual way. Distillation gave the *hydroxy-ether* (4·8 g.), b. p. 78—82°/$10^{-1}$ mm., $\nu_{max.}$ 3420 (OH), 2840 (OMe), 2265 (C:C), 990 and 925 (–CH:$CH_2$) cm.$^{-1}$; $\tau$ 8·76 (–$CMe_2O$–), 8·50 (Me at C-6), 7·61 ($CH_2$), and 6·79 (OMe), relative intensities *ca.* 6 : 3 : 2 : 3 (n.m.r. bands at 8·18 and 7·5 indicated the presence of *ca.* 15% of the isomeric primary alcohol formed by anionotropic rearrangement) (Found: C, 72·3; H, 9·9. $C_{11}H_{18}O_2$ requires C, 72·5; H, 9·9%).

6,6-*Dimethylocta-4,7-diene-2,6-diol* (VII).—The acetylenic glycol (V) (1·3 g.) in tetrahydrofuran (5 ml.) was added dropwise to a stirred solution of lithium aluminium hydride (0·37 g.) in ether (15 ml.). The mixture was boiled under reflux for 16 hr. and then cooled. Ethyl acetate was added to decompose the excess of hydride, followed by saturated ammonium chloride solution. Isolation of the product with ether, and distillation, gave the diol (1·0 g.), b. p. 95° (bath)/2 × $10^{-2}$ mm., $\nu_{max.}$ 3400 (OH), 980 and 920 (–CH:$CH_2$) cm.$^{-1}$; $\tau$ 8·81 (–$CMe_2O$–), 8·62 (Me at C-6), and 7·80 (multiplet) ($CH_2$), relative intensities *ca.* 6 : 3 : 2 (no bands due to the acetylenic glycol were detected).

7-*Methoxy-3,7-dimethylocta-1,4-dien-3-ol* (VIII).— The acetylenic hydroxy-ether (VI) (4·4 g.) in tetrahydrofuran (50 ml.) was added during 1 hr. to a stirred suspension of lithium aluminium hydride (0·6 g.) in ether (50 ml.) at 0°. The mixture was stirred for 5 hr. at 0°, overnight at 20°, and then cooled (ice-bath). Cold saturated ammonium chloride was added cautiously. Isolation of the product with ether in the usual way, and distillation, gave the hydroxy-ether (3·8 g.), b. p. 95°/$10^{-1}$ mm., $\nu_{max.}$ 3420 (OH), 2840 (OMe), 1084 (C–O), 978, and 920 (–CH:$CH_2$) cm.$^{-1}$; $\tau$ 8·88 (–$CMe_2O$–), 8·63 (Me at C-6), 7·80 (multiplet) ($CH_2$), and 6·82 (OMe), relative intensities *ca.* 6 : 3 : 2 : 3 (bands due to small amounts of the isomeric primary alcohol were also observed).

(7-*Hydroxy-3,7-dimethylocta-2,4-dienyl*)*triphenylphosphonium Bromide* (IX).—The glycol (VII) (2·0 g.) in methanol (10 ml.) was added slowly to a stirred suspension of triphenylphosphine hydrobromide (3·5 g.) in methanol (50 ml.), and the mixture was stirred at 20° in the dark for 56 hr. The solvent was removed under reduced pressure giving a viscous oil which solidified under high vacuum. Repeated crystallisation from ethyl acetate–methylene dichloride gave the *phosphonium salt* (3·0 g.), m. p. 186°, $\nu_{max.}$ ($CHCl_3$) 3390 cm.$^{-1}$; $\tau$ 8·82 (–$CMe_2O$–), 8·60 (doublet, $J$ = 3·5 c./sec.) (Me at C-3), 7·70—7·82 ($CH_2$ at C-6), 5·25 (doublet of doublets, $J$ = 15 and 8 c./sec.), and 2·0—2·5 (multiplet) (aryl H), with the expected relative intensities (Found: C, 68·1; H, 6·6; P, 6·5. $C_{28}H_{32}BrOP$ requires C, 67·9; H, 6·5; P, 6·3%).

(7-*Methoxy-3,7-dimethylocta-2,4-dienyl*)*triphenylphosphonium Bromide* (X).—Reaction of the alcohol (VIII) (2·0 g.) in methanol (15 ml.) with triphenylphosphine hydrobromide (3·6 g.) in methanol (50 ml.), and isolation of the product, in the manner described for the previous experiment, gave the phosphonium salt (2·5 g.), m. p. 173° (lit.,[13] m. p. 168°); $\tau$ 8·90 (–$CMe_2O$–), 8·60 (doublet, $J$ = 3·5 c./sec) (Me at C-3), 7·76 (doublet, $J$ = 6·5 c./sec.) ($CH_2$ at C-6), 6·82 (OMe), 5·23 (doublet of doublets, $J$ = 15 and 8 c./sec.), and 2·0—2·5 (multiplet) (aryl H) (Found: C, 68·35; H, 6·5; P, 6·3; OMe, 6·0. Calc. for $C_{29}H_{34}BrOP$: C, 68·4; H, 6·7; P, 6·1; OMe, 6·1%).

1,1′-*Dihydroxy-3,4,3′,4′-tetradehydro-1,2,1′,2′-tetrahydrolycopene* (XIV).—A 0·42N-solution of sodium methoxide in methanol (5·8 ml.) was added to the phosphonium bromide (IX) (0·58 g.) in methanol (10 ml.), and the mixture was stirred for 15 min. at 20°. Crocetindial[22] (164 mg.) in methanol (30 ml.) was added, and the mixture was boiled under reflux in the dark. The course of the reaction was followed by t.l.c. and visible absorption spectroscopy. After 4 hr. the mixture was cooled and poured into water. The product was extracted with methylene chloride, and the extract was evaporated. Preparative t.l.c. on silica gel, using 10% acetone in benzene as eluent, isolation of the main band (of the ten bands observed this was the most strongly adsorbed and exhibited the longest wavelength absorption maxima), elution of the product with methylene dichloride, and repeated crystallisation from the same solvent gave the all-*trans*-isomer of the *diol* (30 mg.), m. p. 225°, $\lambda_{max.}$ (acetone) 531, 497, and 469 mμ ($10^{-3}\varepsilon$ 135, 157, and 112); $E^{1\%}_{1cm}$ (497) = 2762; $\nu_{max.}$ 961·5 (*trans* –CH:CH–) cm.$^{-1}$; $\tau$ 8·77 (–$CMe_2O$–), 8·02 (in-chain methyls),

and 7·69 (doublet, $J$ = 6 c./sec.) (C$H_2$·CH:), relative intensities *ca.* 6 : 9 : 2; molecular ion, *m/e* 568·430 ($C_{40}H_{56}O_2$ requires 568·428). Partition ratio [6] between light petroleum and 95% methanol, 17 : 83.

For α-bacterioruberin Jensen [6,8] gives m. p. 183·5°, $\lambda_{max.}$ (acetone) 533·5, 500, and 470 mμ, $E^{1\%}_{1cm}$ (500) = 2620, partition ratio 1 : 99. In a direct comparison Dr. S. L. Jensen reported that α-bacterioruberin was more strongly adsorbed than the synthetic diol on kieselguhr paper ($R_F$ = 0·20 and 0·44, respectively, on Schleicher and Schüll no. 287 paper), and that whereas stereomutation of the former gave neo A (20%), neo B (1%), and neo U (42%) isomers, the synthetic diol gave neo A and neo B isomers, but no neo U isomer. The i.r. spectra of the two pigments in KBr discs were similar.

*Spirilloxanthin* (XVI).—A 0·423N-solution of sodium methoxide in methanol (8 ml.) was added dropwise to the phosphonium bromide (X) (0·96 g.) in methanol (80 ml.), and the mixture was stirred for 10 min. at 20°. Crocetindial [22] (250 mg.) was added. The mixture was boiled under reflux for 5 hr. and then kept at −50° overnight. The solid which had separated was filtered off. Repeated crystallisation from benzene gave all-*trans*-spirilloxanthin (154 mg.), m. p. 219·5—220°, $\lambda_{max.}$ ($C_6H_6$) 546, 510, and 480 mμ ($10^{-3}\varepsilon$ 146, 169, and 118), $\nu_{max.}$ 971 cm.$^{-1}$; τ 8·86 (−C$Me_2$O−), 8·04 (in-chain methyls), 7·69 (doublet, $J$ = 6·5 c./sec.) (−C$H_2$·CH:), and 6·79 (OMe), relative intensities 6 : 9 : 2 : 3; molecular ion *m/e* 596·455 (calc. for $C_{42}H_{60}O_2$: 596·459). The product was identical (m. p., mixed m.p., t.l.c. on silica gel using 10% acetone in benzene as eluent, visible and n.m.r. spectra) with the natural pigment [1,2] from *Rhodospirillum rubrum*.

1-*Hydroxy*-3,4-*dehydro*-1,2-*dihydro*-*apo*-8′-*lycopenal* (XII).—To a well stirred, boiling, solution of crocetindial [22] (500 mg.) in benzene (30 ml.) was added, slowly and simultaneously, the phosphonium salt (IX) (0·7 g.) in methanol (15 ml.) and 0·123N-sodium methoxide in methanol (14 ml.). The mixture was heated under reflux for 3 hr., and then cooled. The organic layer was separated, and the aqueous layer was extracted with benzene. The benzene solutions were combined, washed, dried, and evaporated. Chromatography of the residue in benzene on alumina (Grade IV), elution of the main band with 10% acetone in benzene, evaporation, and crystallisation from light petroleum–benzene and finally from benzene gave the $C_{30}$ *aldehyde* (150 mg.), m. p. 189°, $\lambda_{max.}$ ($C_6H_6$) 493 mμ ($10^{-3}\varepsilon$ 112) (inflexions at 521 and 468 mμ), $\nu_{max.}$ 1667 and 966 cm.$^{-1}$; τ 8·78 (−C$Me_2$O−), 8·09 (:CMe·C:O), 8·02 (in-chain methyls), 7·70 (doublet, $J$ = 6·5 c./sec.) (−C$H_2$·CH:), and 0·57 (CHO), relative intensities *ca.* 6 : 3 : 12 : 2 : 1; molecular ion *m/e* 432·301 ($C_{30}H_{40}O_2$ requires 432·303).

"OH-*Spirilloxanthin*" (XVI).—A 0·439N-solution of sodium methoxide in methanol (0·70 ml.) was added dropwise to the phosphonium salt (IX) (135 mg.) in methanol (10 ml.), and the mixture was stirred for 10 min. at 20°. A hot suspension of the preceding $C_{30}$ hydroxy-aldehyde (100 mg.) in methanol (15 ml.) was added slowly. The mixture was boiled under reflux for 4 hr., and then kept at −50° overnight. The solid which had separated was filtered off. Repeated crystallisation from benzene gave "OH-spirilloxanthin" (45 mg.), m. p. 214—214·5°, $\lambda_{max.}$ (acetone) 531, 498, and 469 mμ ($10^{-3}\varepsilon$ 161, 184, and 128), $\nu_{max.}$ 966 cm.$^{-1}$; τ 8·86 (−C$Me_2$OC<), 8·78 (−C$Me_2$OH), 8·03 (in-chain methyls), 7·69 (doublet, $J$ = 6·5 c./sec.) (−C$H_2$–CH:), and 6·78 (OMe), relative intensities *ca.* 6 : 6 : 18 : 4 : 3; molecular ion *m/e* 582·441 (calc. for $C_{41}H_{58}O_2$: 582·444). Partition ratio [6] between light petroleum and 95% methanol, 41 : 59. For natural "OH-spirilloxanthin" Jensen [6,8,11] gives m. p. 208·5—209°; $\lambda_{max.}$ (acetone) 533, 499, and 467 mμ; partition ratio 44 : 56. The i.r. spectra of the two pigments in KBr discs were similar.

3,4-*Dehydrorhodopin* (XVII).—A 0·437N-solution of sodium methoxide in methanol (1·0 ml.) was added dropwise to the phosphonium salt (IX) (0·19 g.) in methanol (15 ml.), and the mixture was stirred for 10 min. at 20°. Apo-8′-lycopenal [23,24] (130 mg.) in methanol (20 ml.) was added. The mixture was boiled under reflux for 4 hr., and then kept at −50° overnight. The solid which had separated was filtered off. Repeated crystallisation from benzene–light petroleum (b. p. 60—80°) gave 3,4-dehydrorhodopin (70 mg.), m. p. 194°, $\lambda_{max.}$ (petrol) 517, 482, and 455 mμ; $\lambda_{max.}$ (acetone) 520, 486, and 459 mμ ($10^{-3}\varepsilon$ 175, 195, and 133); $\nu_{max.}$ 963 cm.$^{-1}$; τ 8·78 (−C$Me_2$O−), 8·39, 8·32 (C$Me_2$:C−), 8·19 (end-of-chain methyl), 8·05 (in-chain methyls), and 7·69 (doublet, $J$ = 6·5 c./sec.) (−C$H_2$·CH:), relative intensities *ca.* 6 : 3 : 3 : 3 : 5 : 2; molecular ion, *m/e* 552·440 (calc. for $C_{40}H_{56}O$: 552·433.)

For natural 3,4-dehydrorhodopin, Jackman and Jensen [12] give m. p. 186—190°, $\lambda_{max.}$ (petrol) 517, 483, and 455 mμ; τ 8·76, 8·39, 8·32, 8·19, 8·03, and 7·70.

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