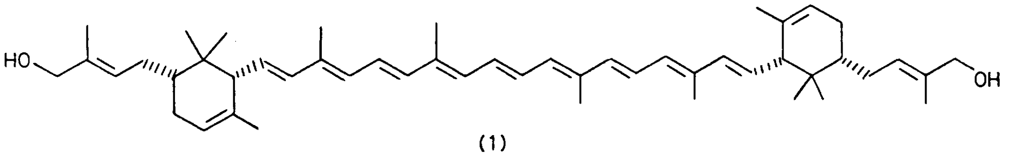
Synthesis of C$_{50}$ Carotenoids; the Structure of Decaprenoxanthin

By Akash K. Chopra, Bhupinder P. S. Khambay, Hugo Madden, Gerard P. Moss,* and Basil C. L. Weedon

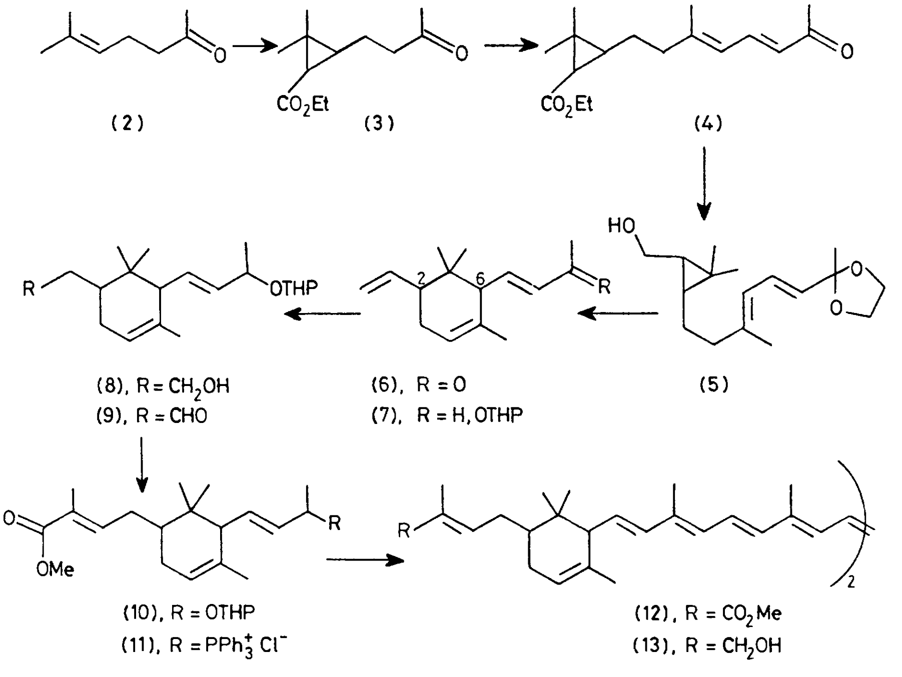
(*Department of Chemistry, Queen Mary College, Mile End Road, London* E1 4NS)

Summary Syntheses of functionalised derivatives of α-ionone have been developed which provide a route to the C$_{50}$-carotenoid, decaprenoxanthin.

The absolute stereochemistry (**1**) has been proposed[1] for decaprenoxanthin, the C$_{50}$ carotenoid[2] from *Flavobacterium dehydrogenans*. The validity of the assumption that the 1-methyl ^{1}H n.m.r. signals (δ 0·75 and 0·95) were comparable with the corresponding signals of *cis* (δ 0·62 and 0·78) and *trans* (δ 0·78 and 0·82) α-irones[3] has now been confirmed by synthesis of the isomer of decaprenoxanthin with the 2,6-*trans* end group.



(1)



(2)
(3)
(4)
(8), R = CH$_2$OH
(9), R = CHO
(6), R = O
(7), R = H,OTHP
(5)
(10), R = OTHP
(11), R = PPh$_3^+$ Cl$^-$
(12), R = CO$_2$Me
(13), R = CH$_2$OH

(THP = tetrahydropyran-2-yl)

Reaction of the ethylene acetal of (**2**) with ethyl diazoacetate, followed by hydrolysis, gave (**3**) which by chain extension[4] was converted into (**4**). Acetalisation and reduction with LiAlH$_4$ afforded (**5**) as a mixture of isomers in 28% yield from (**2**). Acid treatment (BF$_3$–AcOH–H$_3$PO$_4$) of (**5**) gave 2-vinyl-α-ionone (**6**) in yields up to 18%; the ratio of 2,6-*cis* (δ 0·79 and 0·88) to 2,6-*trans* (δ 0·84 and 0·88) isomers varied but the *trans* isomer usually predominated.

Conversion of (**6**) into the tetrahydropyranyl ether (**7**), and hydroboration with (CHMe$_2$CHMe)$_2$BH gave the alcohol (**8**), which was oxidised[5] to the aldehyde (**9**) in 34% yield from (**6**). A Wittig reaction of (**9**) yielded the *trans* α,β-unsaturated ester (**10**) (65%), which with PPh$_3$–HCl–MeOH generated the salt (**11**) (48%). Reaction with the appropriate C$_{14}$-dial[6] furnished the diester (**12**) which with LiAlH$_4$ gave a mixture of isomers of decaprenoxanthin (**13**) in which those with 2,6-*trans* end groups predominated [δ 0·88 and 0·92, *m/e* 704·552 (M^+), calc. for C$_{50}$H$_{47}$O$_2$ 704·553].

We thank the S.R.C. for studentships (to A.K.C. and H.M.), the University of London for a postgraduate studentship (to B.P.S.K.), Roche Products for financial support, F. Hoffmann-La Roche for the C_{14} dial, and Professor J. A. Elvidge, University of Surrey, for the F.T. spectrum of the final product.

(*Received, 7th March* 1977; *Com.* 218.)

---

[1] G. P. Moss, *Terpenoids & Steroids*, 1973, **3**, 230; A. G. Andrewes, S. Liaaen-Jensen, and O. B. Weeks, *Acta Chem. Scand.*, 1975, **B29**, 884.

[2] S. Liaaen-Jensen, S. Hertzberg, O. B. Weeks, and U. Schwieter, *Acta Chem. Scand.*, 1968, **22**, 1171.

[3] V. Rautenstrauch and G. Ohloff, *Helv. Chim. Acta*, 1971, **54**, 1776.

[4] G. Saucy, R. Marbet, H. Lindlar, and O. Isler, *Helv. Chim. Acta*, 1959, **42**, 1945.

[5] J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Letters*, 1968, 3363.

[6] O. Isler, H. Gutmann, H. Lindlar, M. Montavon, R. Rüegg, G. Ryser, and P. Zeller, *Helv. Chim. Acta*, 1956, **39**, 463.