Rubixanthin and Gazaniaxanthin

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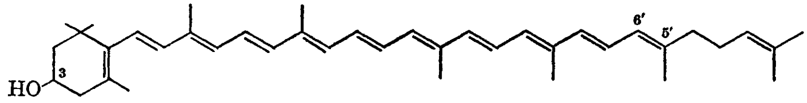
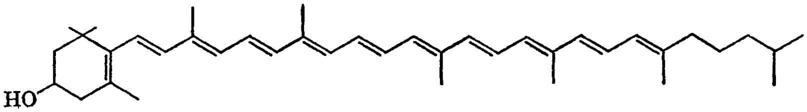
RUBIXANTHIN, m.p. 160°, was isolated from rose hips by Kuhn and Grundmann,[1] who proposed the structure (I). From pigments of the petals of *Gazania rigens*, grown in Portugal, Schön[2] isolated rubixanthin, m.p. 160°, and gazaniaxanthin, m.p. 136—137° by chromatography on alumina. Zechmeister and Schroeder[3] detected no rubixanthin in petals of the same plant grown in Southern California, but obtained gazaniaxanthin, m.p. 133—134°, as the main pigment for which they suggested structure (II). The evidence for neither of these structures was conclusive, and (II) contains an acyclic end group that has not as yet been established for any natural carotenoid.

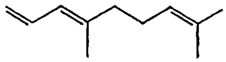
Professor L. Zechmeister kindly supplied us with samples of his gazaniaxanthin and of Schön's rubixanthin. We also obtained a small sample of the original rubixanthin from the specimen collection of the late Professor R. Kuhn. Attempts to separate these pigments by chromatography (both column and thin layer) on alumina and a variety of other adsorbents, or on kieselgel paper, were abortive. All three samples exhibited molecular ions (*m/e* 552·434, 552·431 and 552·432 respectively) corresponding to a molecular formula $C_{40}H_{56}O$ (Calc. *m/e* 552·433), and qualitatively similar cracking patterns; ions at M — 69 indicated the presence of an end group of the lycopene type,[4] and weak ions at $M-18$ were consistent with a 3-hydroxy-end group of the zeaxanthin type.[5] The visible light absorption curves (light petroleum) had identical maxima (λ_{max} 490, 460, and 434 mμ), with the same relative intensities, and no "*cis*-peak". The n.m.r. spectra ($CDCl_3$) were similar, but with gazaniaxanthin the absorption near τ 7·90, attributable to the allylic methylene groups, was more complex than with the rubixanthin samples. The positions (τ 8·95, 8·42, 8·34, 8·30, 8·21, and 8·06) and intensities of the methyl bands were those expected for (I).



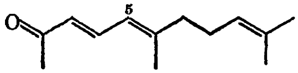
(I)



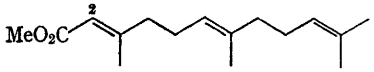
(II)



(III)



(IV)



(V)

Further comparisons were made between Schön's rubixanthin and Zechmeister's gazaniaxanthin. The latter crystallised unchanged on seeding with rubixanthin, and its m.p. was not depressed on admixture (4 : 1) with rubixanthin. However the m.p. of rubixanthin was depressed (*ca.* 10°) on admixture (4 : 1) with gazaniaxanthin. Both carotenoids had similar o.r.d. curves resembling that of zeaxanthin, but with smaller amplitudes. The i.r. spectra ($CHCl_3$ and KBr disc) were also similar. Both pigments yielded an acetate (no separation on t.l.c.) and both reacted only slowly, on treatment with chloroformic hydrogen chloride, giving chromatographically similar mixtures.

Iodine-catalysed stereomutation[6] of the two carotenoids gave mixtures of isomers which exhibited similar patterns on chromatography (t.l.c., calcium hydroxide). Fractional crystallisation of the pigment from the most strongly-adsorbed band in the gazaniaxanthin set yielded a solid m.p. 152—154°, with n.m.r. absorption near τ 7·90 resembling that of rubixanthin. After recrystallisation the product had the same m.p. (and mixed m.p.), λ_{max}, and chromatographic properties as rubixanthin.

We conclude that both natural carotenoids have structure (I), and suggest that their properties are consistent with rubixanthin being the all-*trans* form and gazaniaxanthin the isomer with a *cis*-configuration about the 5′,6′-double bond. No instance of stereoisomerism about the terminal double bond of the chromophore has been reported in carotenoids.[6] However, the n.m.r. differences observed resemble those between *cis*- and *trans*-(III),[7] between *cis*-5- and *trans*-5-ψ-ionone (IV),[8] and (as regards spin–spin coupling in the allylic methylene region) between the *cis*-2- and *trans*-2-methyl farnesoates (V).[9] Other *cis*-carotenoids exhibit a "*cis*-peak" and visible light absorption maxima at shorter wavelengths than their "all-*trans*" isomers.[6] Such effects would not necessarily be expected if the stereochemical difference resulted in no change in the distance between the ends of the conjugated system.

(*Received, February 12th,* 1968; *Com.* 167.)

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