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SHORT COMMUNICATION

THE CONSTITUTION OF APHANIZOPHYLL*

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Abstract—Chemical and physical evidence in favour of aphanizophyll being 4-hydroxymyxoxanthophyll (I) is discussed.

APHANIZOPHYLL, m.p. 172–173°; C, 70·14; H, 9·42 (calc. for $C_{46}H_{66}O_8$; C, 73·89; H, 8·86) λ_{max} 444, 475 and 507 nm in methanol, was first isolated by Tischer[1,2] from *Aphanizomenon flos-aquae* and described as a strongly polar carotenoid. Aphanizophyll yielded an epiphasic palmitate and a presumed oxime with unchanged electronic spectrum, neither of which was fully characterized.

The possible identity of myxoxanthophyll (*Oscillatoria rubescens*)[3] and aphanizophyll was disputed,[1,4,5] and subsequently disproved by chromatographic evidence.[6] Myxoxanthophyll has since been assigned the structure myxol-2′-rhamnoside.[7,8]

The occurrence of aphanizophyll has recently been reported in three other blue-green algae *Microcystis aeruginosa*, *Oscillatoria tenui* and *Anabaena aerulosa oscillatoriaoides*.[9] We observed both myxoxanthophyll (R_f 0·75, 50% AP) and aphanizophyll (R_f 0·64 in the same system) in *Aphonizomenon flos-aquae*, aphanizophyll being in greater abundance.[6] All R_f values refer to Schleicher and Schüll No. 287 kieselguhr-containing paper and AP is acetone in petroleum ether.

Aphanizophyll (*ca.* 1 mg) remaining from the previous study[6] was used for these experiments. Aphanizophyll acetate (R_f 0·40, 10% AP) was prepared in the usual manner[6] and differed from myxoxanthophyll tetraacetate (R_f 0·56, 10% AP) in adsorptive properties. No significant difference in the electronic spectra of the two acetates was observed, see Refs. 6, 7. Aphanizophyll acetate gave a monotrimethylsilyl ether (R_f 0·80, 10% AP) on silylation,[10] slightly more polar than the monotrimethylsilyl ether of myxoxanthophyll tetraacetate. Following prolonged treatment of aphanizophyll acetate with $LiAlH_4$,[8] 50 per cent of the pigment was recovered. The reaction mixture contained aphanizophyll, Product

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* Part VIII in the series "Carotenoids of Blue-Green Algae". For Part VII see ref. 12.

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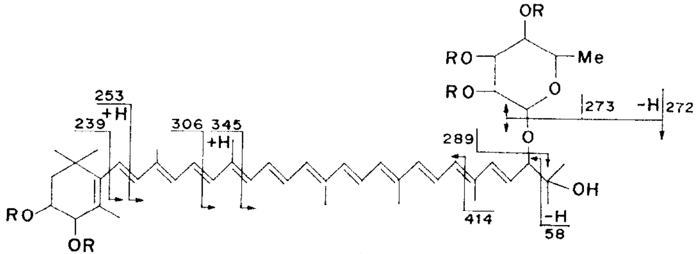
A and Product B. Paper chromatographically purified Product B exhibited R_f 0·15 in 10% AP, λ_{max} 365, 450, 476 and 507 nm (acetone) in satisfactory spectral agreement with saproxanthin (1′,2′-dihydro-3′,4′-dehydro-3,1′-dihydroxy-γ-carotene),[11] but was more strongly adsorbed than saproxanthin (R_f 0·47 in the same system). Product A had R_f 0·34 in 10% AP and λ_{max} 365, 388, 460, 486 and 519 nm (acetone) in good spectral agreement with torulene, but was more strongly adsorbed than 3-hydroxytorulene (= anhydro-saprozanthin = 3-hydroxy-3′,4′-dehydrorubixanthin[10]) with R_f 0·63 in 10% AP. Myxoxanthophyll tetraacetate is known to give saproxanthin and 3-hydroxytorulene on similar treatment.[8] $LiAlH_4$ reduction of acetylated 4-keto-myxol-methylpentoside was recently found to give an aphanizophyll-like product.[12]

The above evidence, together with mass spectral data for aphanizophyll acetate discussed below, suggests that aphanizophyll might be a myxol-2′-methylpentoside with an additional hydroxy group in the β-ring, tentatively placed by analogy in the 4-position (I). Further evidence for the hypothesis that P483 from *Oscillatoria limosa*[7] is 4-keto-myxoxanthophyll and aphanizophyll is 4-hydroxy-myxoxanthophyll may be sought by glycoside hydrolysis.

The mass spectrum of aphanizophyll acetate exhibited diagnostically useful peaks at *m/e* 956 (M, corresponding to $C_{46}H_{66}O_8$), M-60, M-92, M-106, M-152 (M-92-60), M-164 (M-106-58), M-212 (M-92-60-60), M-226 (M-106-60-60), M-239, M-253, M-272, M-273, M-289, M-306 (ion c^7?), M-331 (M-273-58), M-345, 331?, 273 (100%), 153 (65%) and 111 (43%) *cf.* Ref. 8, 105 (32%), 91 (43%), 60 (22%). These ions are compatible with the characteristic losses of 92 and 106 mass units from the central polyene chain,[13,14] further fragmentation of the *m/e* 273 oxonium ion[15] and fragmentation of the pentaacetate (II) as indicated below.



(II) R = CH₃CO
(I) R = H

The *m/e* 331 ion, however, is indicative of a tetraacetyloxonium ion and is not readily explained by structure II. No molecular ion corresponding to mixture with a hydroxy-myxol-2′-hexoside hexaacetate (M = 1014) was observed. Alternatively contamination with a myxol-2′-hexoside pentaacetate (M = 956) is not likely, due to the different chromatographic properties of the latter.[8] The occurrence of *m/e* 331 ions also from other acetylated presumed carotenoid methylpentosides[7,12] remains to be explained.

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