

Phytochemistry, 1972, Vol. 11, pp. 2347 to 2348. Pergamon Press. Printed in England.

## CYANOPHYTA OSCILLATORIACEAE

### $\gamma$ -CAROTENE AND LYCOPENE *OSCILLATORIA PRINCEPS*

G. W. FRANCIS

Department of Chemistry, University of Bergen, Bergen, Norway

and

L. N. HALFEN

Department of Biochemistry, Norway Institute of Technology, University of Trondheim,  
Trondheim, Norway

(Received 18 January 1972)

**Key Word Index**—*Oscillatoria princeps*; Cyanophyta; blue-green algae; carotenoids;  $\gamma$ -carotene; lycopene.

Goodwin<sup>1</sup> emphasized that the carotenoids may provide significant taxonomic data for algae. The variations in carotenoids in the various algae<sup>2</sup> are believed to be due to the occurrence of different enzyme systems. Inherent in this argument is the assumption of a common carotenoid precursor, such as phytoene, in all algae. The possible involvement of lycopene has also been suggested.<sup>1</sup> However, although several hundred species of algae from different divisions have been examined, lycopene has been found only in three species of Chlorophyta.<sup>3,4</sup> The lack of acyclic carotenoids in the blue-green algae may be explained by the presence of highly effective cyclizing enzymes.<sup>1</sup>

Perhaps the oldest group of algae is the Cyanophyta, which have pigments produced by 'beta cyclase' activity<sup>2</sup> as well as carotenoid glycosides otherwise found only in bacteria.<sup>5-7</sup> These organisms might be used, therefore, to demonstrate the precursors of cyclic carotenoids.

The carotenoid content of the hot spring species, *Oscillatoria princeps*<sup>8</sup> was examined. The alga was grown axenically at 40° in Medium D<sup>9</sup> and harvested during exponential growth.

The carotenoids were extracted from a packed mass of wet cells with methanol-acetone and saponified by normal procedures.<sup>10</sup> The pigments (0.4% on a dry weight basis) were separated by TLC on silica gel and identified by their chromatographic behaviour, MS and visible spectra as described in previous investigations.<sup>6,10-12</sup>

<sup>1</sup> T. W. GOODWIN, in *Aspects of Terpenoid Chemistry and Biochemistry*, Academic Press, New York (1971).

<sup>2</sup> J. W. PORTER and R. E. LINCOLN, *Arch. Biochem.* **27**, 390 (1950).

<sup>3</sup> P. KARRER, W. FATZER, M. FAVARGER and E. JUCKER, *Helv. Chim. Acta* **26**, 2121 (1943).

<sup>4</sup> H. H. STRAIN, 32nd Annual Priestley Lectures. Penn. State University (1958).

<sup>5</sup> S. HERTZBERG and S. LIAAEN-JENSEN, *Phytochem.* **8**, 1259 (1969).

<sup>6</sup> S. HERTZBERG and S. LIAAEN-JENSEN, *Phytochem.* **8**, 1281 (1969).

<sup>7</sup> G. W. FRANCIS, S. HERTZBERG, K. ANDERSEN and S. LIAAEN-JENSEN, *Phytochem.* **9**, 629 (1970).

<sup>8</sup> L. N. HALFEN and R. W. CASTENHOLZ, *Nature, Lond.* **225**, 1163 (1970).

<sup>9</sup> R. W. CASTENHOLZ, *Bacteriol. Rev.* **33**, 476 (1969).

<sup>10</sup> L. N. HALFEN and G. W. FRANCIS, *Arch. fur. Mikrobiol.* **81**, 25 (1972).

<sup>11</sup> L. N. HALFEN, B. K. PIERSON and G. W. FRANCIS, *Arch. fur. Mikrobiol.* **82**, 240 (1972).

<sup>12</sup> C. R. ENZELL, G. W. FRANCIS and S. LIAAEN-JENSEN, *Acta Chem. Scand.* **22**, 1054 (1968).

The results are presented in Table 1. Pigment II was identified as  $\gamma$ -carotene on the basis of the visible spectrum, co-chromatography with a genuine sample and the MS which showed a molecular ion at  $m/e$  536 together with ions at M-92 and M-106 (M-92/M-106 = 1).<sup>13</sup>

TABLE 1. THE CAROTENOID COMPOSITION OF *Oscillatoria princeps*

Pigment	%	Visible abs. <sub>max</sub> in acetone	TLC (Merck Kieselgel G) % Acetone in light petroleum					MW by MS <sup>1,2</sup>
			0%	5%	10%	20%	30%	
$\beta$ -Carotene	65.0	478, 452, (429)*	0.34	0.98	—	—	—†	536
$\gamma$ -Carotene	1.0	491, 461, (439)*	0.22	0.94	—	—	—†	536
Lycopene	0.6	504, 472, 447*	0.14	0.92	—	—	—†	536
Echinenone	2.6	460*	—	0.25	0.43	0.63	—†	550
iso-Cryptoxanthin	0.6	472, 449, (425)†	—	0.08	0.20	0.42	—†	552
Glycoside acetate	0.4	505, 473, (448)†	—	—	—	0.33	0.60	—
Glycoside acetate	0.4	504, 473, (450)†	—	—	—	0.30	0.57	—
Myxoxanthophyll peracetate	26.4	508, 476, 451*	—	—	—	0.23	0.50	898
Glycoside acetate	0.3	504, 474, (450)†	—	—	—	0.14	0.42	—
Oscillaxanthin peracetate	2.7	532, 499, 469*	—	—	—	0.05	0.23	1144

\* Vis. maxima of all-*trans* pigment obtained by preparative paper chromatography.

† Vis. maxima of *cis-trans* pigment mixture.

‡ Co-chromatographed with genuine or synthetic material.

Pigment III was identified as lycopene from evidence provided by visible spectra, co-chromatography with synthetic lycopene and MS which showed ions at M = 536 (16%), M-69 (0.7%), M-92 (0.8%), M-106 (2.7%) and  $m/e$  69 (100%) with M-92/M-106 = 0.30.

The above results indicate that *O. princeps* is a typical cyanophyte in that it contains a high percentage of  $\beta$ -carotene, together with echinenone and the glycosidic carotenoids myxoxanthophyll and oscillaxanthin. The presence of lycopene, not previously found in this group of algae, is of importance because it lends support to the hypothesis that this compound may be the precursor of the cyclic carotenoids found in this group of organisms. Support for this contention is derived from the presence of  $\gamma$ -carotene which is the monocyclic compound expected to be an intermediate in the double cyclization leading from lycopene to  $\beta$ -carotene.  $\gamma$ -Carotene has not been found previously in a cyanophyte<sup>1</sup> although it is of limited occurrence in other algal groups.

*Acknowledgement*—We thank the Royal Norwegian Council for Scientific and Industrial Research for a Post-doctoral Fellowship to L.N.H. during the period of this work.

<sup>13</sup> G. W. FRANCIS, *Acta Chem. Scand.* in press.