scanner unit, have been performed with 620, 350 and 280nm light. At all wavelengths sedimentation-velocity measurements gave identical results. Because of the magnitude of the extinction coefficient of the 620nm absorption band of phycocyanin, measurements could be made at concentrations as low as 0.005mg/ml. The monomer is not the only species present above concentrations of 0.01mg/ml. It is possible to stimulate disaggregation to monomer only by employing a pH of 3.9. Band sedimentation and conventional sedimentation-velocity measurements indicate that hexamer is the first aggregate formed. The aggregation process is analogous to a micellar process. The behaviour is consistent with a structural role for phycocyanin in addition to its known function as an energy-transfer pigment. Fluorescence measurements also indicate that the largest aggregates have the highest fluorescence efficiency (Lee & Berns, 1968*a*). The aggregation process in phycocyanin may be a prototype for membrane-forming systems.

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Structure of Phycocyanobilin

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Phycocyanobilin, the prosthetic group of the algal biliprotein C-phycocyanin, is a linear tetrapyrrolic compound. An extensive study by Ó hEocha (1963) revealed that three different phycobilins can be obtained, depending on the conditions of the hydrolysis of the protein. The three different phycobilins were designated phycobilins 630, 655 and 608. Phycobilin 630 is considered to be the native form (hence the 'real' phycocyanobilin), whereas phycobilins 655 and 608 are derivatives obtained after prolonged treatment with concentrated acid. In view of its u.v. spectrum phycocyanobilin should be structurally intermediate between mesobiliverdin and mesobiliviolin.

A structure for phycocyanobilin has been proposed based on the information obtained from mass and n.m.r. spectra (Cole, Chapman & Siegelman, 1967, 1968; Crespi, Boucher, Norman, Katz & Dougherty, 1967; Crespi, Smith & Katz, 1968). According to these workers the molecule has a molecular weight of 586, or more precisely a molecular weight of 614 for its dimethyl ester.

Our results (B. L. Schram & H. H. Kroes, unpublished work) indicate that the acid form of phycocyanobilin has a molecular weight of 588 and that the dimethyl ester has a molecular weight of 614 (2 less than expected for a dimethyl ester of a dibasic acid with molecular weight 588).

A close look at the mass spectrum of the acid reveals several properties inconsistent with the structure previously proposed. We therefore present a new structure for phycocyanobilin that has two hydrogen atoms more and that has an internal hydrogen bond.

The new structure can better explain the chemical properties of phycocyanobilin. In the first place, breaking of the internal hydrogen bond, e.g. by esterification or treatment with concentrated acid, causes the molecule to be converted into a more stable dehydrogenated form. The structure given by Cole *et al.* (1967, 1968) will be that of phycobilin 655, since it is the stable form of the ester. It also explains the irreversibility of the transition of phycobilin 630 into phycobilin 655. The n.m.r. spectra are obtained with a solution of phycocyanobilin in trifluoroacetic acid or in deuterated pyridine; the molecule is probably converted readily into its dehydrogenated form in these solvents and the two extra hydrogen atoms will not be observed.

Phycobilin 608 has a violinoid structure and is isomeric with phycobilin 655. A tentative structure will be given, based on an analysis of the electronegative properties of the individual pyrrole rings in phycobilin 655.

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Some Aspects of the Localization of Phycobiliproteins in the Rhodophyceae and the Cyanophyceae

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The phycobiliproteins observed in the Rhodophyceae appear in general in the form of globules (*Porphyridium cruentum, Rhodomela subfusca, Antithamnion glanduliferum*) but sometimes in the form