carried out in two stages: the photoreduction of ferredoxin-reducing substance followed by the dark reduction of NADP (or ferredoxin) by photo-reduced ferredoxin-reducing substance.

The reaction partner for the photoreduction of ferredoxin-reducing substance is the specialized form of chlorophyll *a*, chlorophyll *P*-700. After a 1 ns flash to oxidize chlorophyll *P*-700 to chlorophyll *P*-700*, the dark kinetics of the reduction of chlorophyll *P*-700* are consistent with this reaction scheme.

Additional information on the characteristic potential, amino acid composition and other properties of ferredoxin-reducing substance will be presented.

Biosynthesis of Fatty Acids by Isolated Chloroplasts

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Because of the importance of lipids in the structural components of chloroplasts in higher plants, studies on the biosynthesis of these compounds will provide a better understanding of the functional properties of the organelles.

Since the discovery by Smirnov (1960) of the capacity of chloroplasts to synthesize fatty acids from acetate, a number of investigators have extended our knowledge in this area. At present, isolated class I spinach chloroplasts (with intact outer envelope) readily incorporate [¹⁴C]acetate into palmitate and oleate in the presence of ATP, CoA, Mg²⁺, CO₂ and light (Stumpf *et al.*, 1967). In the absence of light, little if any synthesis occurs. When Triton X-100 or one of a number of other detergents is added to the reaction at very low concentrations, a large increase in fatty acid synthesis occurs as well as a marked increase in the formation of oleate. This effect is reversed specifically by increasing the concentration of ATP, which lowers the rate of synthesis as well as the extent of desaturation (Stumpf & Boardman, 1970). Further studies revealed that the site of regulation of Triton X-100 and ATP is at the C₁₆ → C₁₈ elongation step (Givan & Stumpf, 1971) and is not directly related to the desaturation reaction.

Very recently we have detected rather significant accumulation of acyl thiol esters in intact chloroplasts formed *de novo* from [¹⁴C]acetate. These acyl thiol esters have a fivefold higher amount of unsaturated acyl components than do the oxygen esters, suggesting that desaturation takes place on an acyl thiol ester level. Also present in chloroplasts are acyl-CoA synthetases, acyl-CoA hydrolase and transacylases (C. G. Kannagara & P. K. Stumpf, unpublished work). The interaction of these and other

enzymes in the biosynthetic capacity of isolated chloroplasts will be further described.

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The Sulphoglycolytic Pathway in Plants

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The ubiquity of sulpholipid in green plants and of sulphopropanediol in all diatoms implies the existence of biodegradative pathways for such compounds. Martelli & Benson (1964) have outlined the terminal portions of the pathway for bacterial degradation of sulphoquinovose (6-deoxyglucose-6-sulphonate). Martelli & Souza (1970) established the ultimate conversion into glyoxylate-sulphite addition product followed by production of sulphate ion.

In experiments with intact leaves of alfalfa (*lucerne*; *Medicago sativa*) and the coral tree (*Erythrina crista-galli*) we have observed that glycerol sulphoquinovoside is readily degraded whereas sulphoquinovose is relatively resistant. Sulpholactaldehyde, sulpholactate, sulphopropanediol, analogues of glyceraldehyde 3-phosphate, 3-phosphoglycerate and glycerol 1-phosphate were identified among the intermediates. The first step appears to be a phosphorylation of glycerol sulphoquinovoside, since free sulphoquinovose was only slowly metabolized by any system yet examined. Hydrolysis of glycerol sulphoquinovoside would be expected to yield appreciable concentrations of sulphoquinovose since the observed rate of degradation of the latter was relatively low.

A striking difference was observed between the metabolism of glycerol [³⁵S]sulphoquinovoside by leaves of alfalfa and the Indian shrub *Erythrina*. The major compound produced by *Erythrina* was sulphoacetate, analogue of phosphoglycollate. Alfalfa and other plants produced first sulpholactaldehyde and then, after about 24 h, sulpholactate. Sulphate ion appeared slowly thereafter. We presume that *Erythrina* leaves utilize the sulphoglycolytic pathway but possess a more active system for decarboxylating sulpholactate than do most plants. The alkaloids of *Erythrina* bark are esters of sulphoacetate (Folkers, 1944; Mondon, 1970). Massive accumulation of sulpholactate in spores of *Bacillus subtilis* was observed by Bensen *et al.* (1969). Relative activities of enzymes in the sulphoglycolytic pathway determine

the steady-state concentrations of its sulphonic acid intermediates. The pathway appears to serve for degradation and not for synthesis of the sulpholipid.

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Biochemistry of the Sex Attractants of Marine Plants

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The chemotactic sperm attractants of the female gametes of lower plants may be generically termed 'sirenins' (Köhler, 1967). Apparently the sirenins form a family of remarkable cyclic molecules with and without functional groups. Their chemistry and biochemistry will be discussed.

The first chemical elucidation of such a molecule was achieved in the case of the *Allomyces* sirenin by Machlis and co-workers (Nutting *et al.*, 1968). In the meantime Müller (1968) had isolated the sirenin from the brown alga *Ectocarpus siliculosus*. It is a volatile hydrocarbon, C₁₁H₁₆, with an aromatic terpenoid odour, formed only during a short period of the generation cycle between maturation and fertilization of the female gametes. A 100g wet wt. batch of sexual algal thalli produces about 6mg of the near-homogeneous compound, which was separated by condensing the gas phase above the plants and purified by g.l.c. By means of chemical degradations, mass spectroscopy, i.r. spectroscopy and n.m.r. spectroscopy, its structure was found to be all-*cis*-1-(cyclohepta-2',5'-dienyl)but-1-ene (Müller *et al.*, 1971).

The compound is optically active by virtue of the centre of asymmetry at the branching carbon atom C-1: $[\alpha]_D^{25}$ is 71.75°. Its absolute configuration was established by chemical means and comparison with authentic compounds as *S*, which is in accordance with the globular conformation of the volatile molecule. The formula was established by partial transformations of the natural compound and comparison with synthetic derivatives (Akintobi, 1970), and finally by the total synthesis of the cyclic hydrocarbon from divinylcyclopropanes and appropriate unsaturated halogeno hydrocarbons, followed by Cope rearrangement (Jaenicke *et al.*, 1971). By way of this versatile synthesis it is possible to prepare various homologues and steric relatives of the *Ectocarpus*

sirenin. In a semi-quantitative assay system most of them proved to be biologically inactive. From the structure of the *Ectocarpus* sirenin it may be inferred that it is biosynthetically derived from the hydrocarbon end of highly unsaturated fatty acids such as linolenate, with their penta-2,4-dienyl sequence preserved. It has been established that the native compound possesses the cycloheptadiene structure.

On the other hand there is great similarity to the dictyopterenes, isolated from *Dictyopteris plagiogramma* and studied extensively by Moore *et al.* (1968). They are mostly divinylcyclopropane derivatives, which can be transformed artificially into cycloheptadienes of similar structure (see Pettus & Moore, 1971). In the genus *Fucus* was found a cluster of volatile compounds and sex attractants that seem to be closely related to the sirenin from *Ectocarpus*. Their structure has not yet been determined unequivocally.

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Oxidation of Catechol in Plants

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A wide range of structurally diverse natural products found in higher plants and micro-organisms (lignins, tannins, antibiotics, alkaloids, melanins, pigments) are recognized to be derived from hydroxy aromatic compounds by oxidative coupling involving C-C and C-O linkages (Brown, 1967; Scott, 1967). We decided to test whether such oxidation products were formed from catechol in the leaves of *Tecoma stans*. It had already been demonstrated in our laboratory that anthranilate was converted into catechol in *Tecoma* leaves (Nair & Vaidyanathan, 1964). In the present study we have observed that leaf extracts of *T. stans* can carry out the oxidation of catechol to yield biphenylene dioxide 2,3-quinone and 3,4,3',4'-tetrahydroxybiphenyl (Kandaswami *et al.*, 1969). The occurrence of two distinct enzymes, one involved in the conversion of catechol into biphenylene dioxide 2,3-quinone and the other