

The molecule may be considered as built of four main planar or approximately planar groups, *p*-methyl-thiophenyl, prolyl, peptide + pyrrolidine and carboxyl, all of which tend to lie at approximately right angles to one another. In the case of the prolyl ring it would appear that the carbon atom opposite the N-C<sub>α</sub> bond does not show any tendency to occupy alternate sites as noted by Leung and Marsh in the analysis of leucylprolyl-glycine monohydrate.<sup>12</sup> Neither does it maintain the position observed in proline<sup>10</sup> or hydroxyproline,<sup>11</sup> *i.e.*, *trans* with respect to the carboxyl group. In this compound it appears to have swung to the same side as the peptide C=O, providing further evidence of the flexibility of the pyrrolidine ring system in the prolyl group.

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RECEIVED MAY 5, 1958

### PHOTOSYNTHESIS OF GALACTOLIPIDS

Sir:

An appreciable portion of the products of brief photosynthesis in C<sup>14</sup>O<sub>2</sub> is lipid in nature.<sup>1</sup> Chromatograms of these products exhibit several separable lipids<sup>2</sup> which had been assumed to be fatty acid-labeled phosphatides. However, we wish to report that the phosphatides constitute but a fraction of these labeled products. We have examined the lipids of *Chlorella* and find that the glycolipid concentration exceeds that of the phospholipids by a factor of four. These glycolipids include the β-D-galactosyl and the α-D-galactosyl-(1 → 6)-β-D-galactosyl monoglycerides which had been identified in wheat flour lipids by Carter, *et al.*,<sup>3</sup> and 3'-*O*-oleyl-glycerol-1-β-D-galactopyranoside-6-sulfate.<sup>4</sup> Glycerolphosphatides<sup>5</sup> and lesser amounts of a galactotriosyl monoglyceride are observed.

Radiograms of deacylated<sup>5,6</sup> products of five minutes and of thirty seconds of photosynthesis in C<sup>14</sup>O<sub>2</sub> by *Chlorella* revealed that the galactolipids are labeled very rapidly with C<sup>14</sup>. In five minutes photosynthesis over half of the C<sup>14</sup> in the lipids was found in the galactose moieties. These lipids had the following C<sup>14</sup> distribution: fatty acids, 40%; galactosylglycerol, 39%; galactosylgalactosylglycerol, 10%; galactosyl-6-sulfate glycerol, 2%; diglycerophosphate, 3%; glycerol, 4%. The galactolipids were identified by examination of radiograms of the deacylated lipids and then acid hydrolysis of the uniformly-labeled galactosyl glycerols to yield simple ratios of C<sup>14</sup> in galactose and glycerol. Glycerol β-D-galactoside and its digalactose homolog cochromatographed precisely with au-

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thentic samples generously provided by Professor H. E. Carter. The glyceryl galactotrioside was found in a chromatographic position (*R*<sub>f</sub> = 0.50 in phenol-water and *R*<sub>f</sub> = 0.14 in butanol-propionic acid-water<sup>2</sup>) characteristic of a third member of the homologous series of galactosyl glycerides. Hydrolysis by thirty minutes in 3 *N* hydrochloric acid at 100° of the uniformly labeled unknown formed during eight days of photosynthesis gave galactose and glycerol in an activity ratio of 6.1 to 1, thus indicating that there are three galactose units bound to a monoglyceride in the original lipid.

The only precursor available in appreciable concentration in *Chlorella* for biosynthesis of these glycolipids is uridine diphosphate galactose.<sup>7,8</sup> Biosynthesis of galactosyl glycerides is probably analogous to that of the uridine diphosphate galactose-mediated saccharide syntheses.<sup>9</sup>

We are indebted to Mr. M. S. Brown for valuable assistance. This work was supported by the Atomic Energy Commission and the Pennsylvania Agricultural Experiment Station.

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RECEIVED JULY 24, 1958

### STEREOCHEMISTRY OF DIELS-ALDER ADDUCTS. I. THE REARRANGEMENT OF 2-*exo*-BROMONORBORNANE-2-*endo*-CARBOXAMIDE

Sir:

A recent communication<sup>1</sup> describing the rearrangement of 2-*exo*-bromonorborene-2-*endo*-carboxylic acid (I, R = OH) and its methyl ester (I, R = OCH<sub>3</sub>) upon catalytic or chemical hydrogenolysis prompts us to report our observations upon the rearrangement of the corresponding carboxamide. 2-*exo*-Bromonorborene-2-*endo*-carboxamide (I, R = NH<sub>2</sub>) does not rearrange upon hydrogenolysis and yields only norbornane-2-*endocarboxamide* (III, R = NH<sub>2</sub>), identified by analysis, mixed melting point and comparison of the infrared spectrum with that of an authentic sample. When I (R = NH<sub>2</sub>) was heated above its melting point, resolidification took place and a second melting point was observed. The isomeric bromocarboxamide (II, R = NH<sub>2</sub>) obtained from the melt gave norbornane-1-carboxamide (IV, R = NH<sub>2</sub>) upon hydrogenolysis. The rearrangement of I (R = NH<sub>2</sub>) to II (R = NH<sub>2</sub>) was also catalyzed by alcoholic alkali. On the basis of Wagner-Meerwein rearrangements undergone by 2,2-disubstituted bicyclo[2,2,1]heptane derivatives<sup>2-4</sup> we have tentatively designated the rearrangement product II (R = NH<sub>2</sub>) as 2-*exo*-bromo-

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