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PHOTOSYNTHETIC CARBON DIOXIDE ASSIMILATION VIA THE REDUCTIVE PENTOSE PHOSPHATE CYCLE (C_3 CYCLE)

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for

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Handbook of Biosolar Resources

All photosynthetic green plants and cyanobacteria (blue-green "algae") capable of using sunlight to convert carbon dioxide and water to oxygen and carbohydrates employ the reductive pentose phosphate cycle (also called the C_3 cycle or the Calvin cycle).[1-3] Most available evidence indicates that the RPP cycle is the principal pathway for initial fixation of carbon dioxide in all plants except those which have either the C_4 pathway[4,5] (see), Crassulacean Acid Metabolism (CAM)[6] or both. Even in those species in which most of the carbon dioxide is initially incorporated by C_4 metabolism or by CAM, most of the carbon dioxide is released inside chloroplasts where it is reincorporated via the RPP cycle.[7] This is necessary since neither the C_4 cycle nor CAM can bring about a net conversion of carbon dioxide to sugar phosphate or carbohydrates.

The RPP cycle can be considered as consisting of three phases: The first phase is the conversion of a C_5 sugar, ribulose 5-phosphate with ATP to ribulose 1,5-bisphosphate (Reaction M) followed by carboxylation to give two molecules of the C_3 acid, 3-phosphoglycerate (3-PGA) in Reaction A. The second phase is the conversion of 3-PGA to triose phosphate which occurs in two steps: formation of the acyl phosphate with ATP (Reaction B), and reduction of the acyl phosphate to aldehyde with release of inorganic phosphate (Reaction C). The third phase of the RPP cycle consists of all the remaining reactions (D through L) which convert five molecules of C_3 sugar phosphate to three molecules of pentose phosphate.

One complete cycle (in which each reaction occurs at least once) requires that three ribulose 5-phosphate molecules are phosphorylated, carboxylated, and split to give a total of six molecules of 3-PGA which are in turn converted to six molecules of the triose phosphate, glyceraldehyde-phosphate. Since only five triose phosphate molecules are required to regenerate the three pentose phosphates, one triose phosphate is left over and represents the product of the fixation and reduction of three molecules of carbon dioxide. The overall reaction of one complete cycle may therefore be represented as

$$3\ CO_2 + 9\ ATP^{4-} + 6\ NADPH \longrightarrow 9\ ADP^{3-} + \underset{\text{(glyceraldehyde-3-phosphate)}}{OCH\text{-}CHOH\text{-}CH_2OPO_3H^-} + 8\ HPO_3^{2-} + 2\ H^+.$$

ATP is regenerated from ADP and P_i by photophosphorylation in the chloroplast thylakoids, while NADPH is regenerated from $NADP^+$ by reduction with reduced ferredoxin which is in turn reduced by electron transport from water by the light reactions and electron transport in the thylakoids.

The triose phosphate product of the RPP cycle is to a large extent translocated out of the chloroplast (in exchange for inorganic phosphate)[8] to be used for various biosynthetic needs of the plant including synthesis of sucrose for export to other parts of the plant in the case of multicellular plants. Under conditions where photosynthesis exceeds the needs of the plant, some of the triose phosphate is converted to fructose-6-phosphate (via reactions D, E, and F), thence to glucose phosphates and finally to the storage product, starch, which accumulates in the chloroplasts. Some biosynthetic reactions starting with intermediate compounds of the RPP cycle also occur in the chloroplasts. For example, triose phosphate may be reduced to glycerol phosphate and used in fat synthesis, and ribose 5-phosphate can be used in ribonucleotide and deoxyribonucleotide biosynthesis.

The most distinctive reaction of the RPP Cycle is the carboxylation of ribulose 1,5 bisphosphate to give two molecules of 3-PGA.[9] The enzyme, ribulose 1,5-bisphosphate carboxylase (RuBPCase) constitutes a major fraction of the soluble protein in green cells, and may be the most abundant protein in the biosphere. It is generally accepted that the enzyme mediates the addition of carbon dioxide to the carbon atom 2 of the RuBP molecule,[10] forming an enzyme-bound 6-carbon intermediate. This undergoes an internal oxidation-reduction reaction (the enzyme was once called "carboxydismutase"[11]) so that hydrolytic splitting of the molecule results in the formation of two identical molecules of 3-PGA. One 3-PGA molecule is composed of carbon atoms 1 and 2 of the RuBP plus the newly incorporated carbon dioxide which becomes the carboxyl group. The other 3-PGA product is made from carbons 3, 4, and 5 of RuBP, with carbon 3 becoming the carboxyl group.

An interesting and important property of the RuBPCase is its ability to function as an oxygenase.[12,13] At low levels of CO_2 and atmospheric levels of O_2 (20%), O_2 can bind competitively at the active site of the enzyme and react with the RuBP at the carbon 2 position, oxidatively splitting it to one molecule of 3-PGA (from carbon atoms 3, 4, and 5) and one molecule of 2-phosphoglycolate. The latter compound is converted to glycolate in the chloroplast[14] from which it is mainly exported. Glycolate is widely believed to be the principal if not the exclusive substrate for photorespiration.[15] This alternate oxygenase activity of RuBPCase thus competes with carbon assimilation and at the same time leads to conversion of some of the reduced carbon back to carbon dioxide, via photorespiration. This limits the maximum rate of photosynthetic carbon assimilation under conditions of high light intensity, high temperature, low CO_2 and atmospheric O_2 level in plants lacking C_4 metabolism.

REACTIONS

A. Ribulose 1,5-bisphosphate adds CO_2 at C-2 and splits hydrolytically to give 2 molecules of 3-phosphoglycerate.

B. The carboxyl group of 3-phosphoglycerate is converted to an acyl phosphate in a reaction utilizing the terminal phosphate of ATP.

C. The acyl phosphate group is reduced in the presence of NADPH to give P_i and an aldehyde group, thus converting the 3-C-atom compound to glyceraldehyde 3-phosphate.

D. The aldo-sugar is converted into a keto-sugar by the transfer of 2 H atoms from C-2 to C-1

E. The aldol condensation between aldotriose and ketotriose gives fructose 1, 6-bisphosphate.

F. The phosphate group on C-1 is removed by hydrolysis.

G. 2 H atoms plus the glycolyl group (C-1 and C-2) of fructose 6-phosphate are transferred to glyceraldehyde 3-phosphate to form xylulose 5-phosphate, leaving erythrose 4-phosphate.

H. An aldol condensation between erythrose 4-phosphate gives sedoheptulose 1, 7-bisphosphate.

I. Hydrolysis of the phosphate on C-1 gives sedoheptulose 7-phosphate.

J. Transfer of the glycolyl group (C-1 and C-2) plus 2 H atoms from sedo-heptulose 7-phosphate to C-1 of glyceraldehyde 3-phosphate gives xylulose 5-phosphate and ribose 5-phosphate.

K. Isomerization of ribose 5-phosphate gives ribulose 5-phosphate.

L. Epimerization of C-3 of xylulose 5-phosphate gives ribulose 5-phosphate.

M. Phosphorylation of C-1 of ribulose 5-phosphate in the presence of ATP gives ribulose 1,5-bisphosphate, thus completing the reductive pentose phosphate cycle.

ENZYME (SYNONYM) KEY

Reductive Pentose Phosphate Cycle (Photosynthesis)

2.7.1.19 = phosphoribulokinase

3.1.3.11 = hexosebisphosphatase (heptosebisphosphatase)

4.1.1.39 = ribulosebisphosphate carboxylase

4.1.2.13 = fructosebisphosphate aldolase

2.2.1.1 = transketolase

2.7.2.3 = phosphoglycerate kinase

5.1.3.1 = ribulosephosphate 3-epimerase

5.3.1.1. = triosephosphate isomerase

5.3.1.6 = ribosephosphate isomerase

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Figure: The Reductive Pentose Phosphate Cycle of Photosynthesis

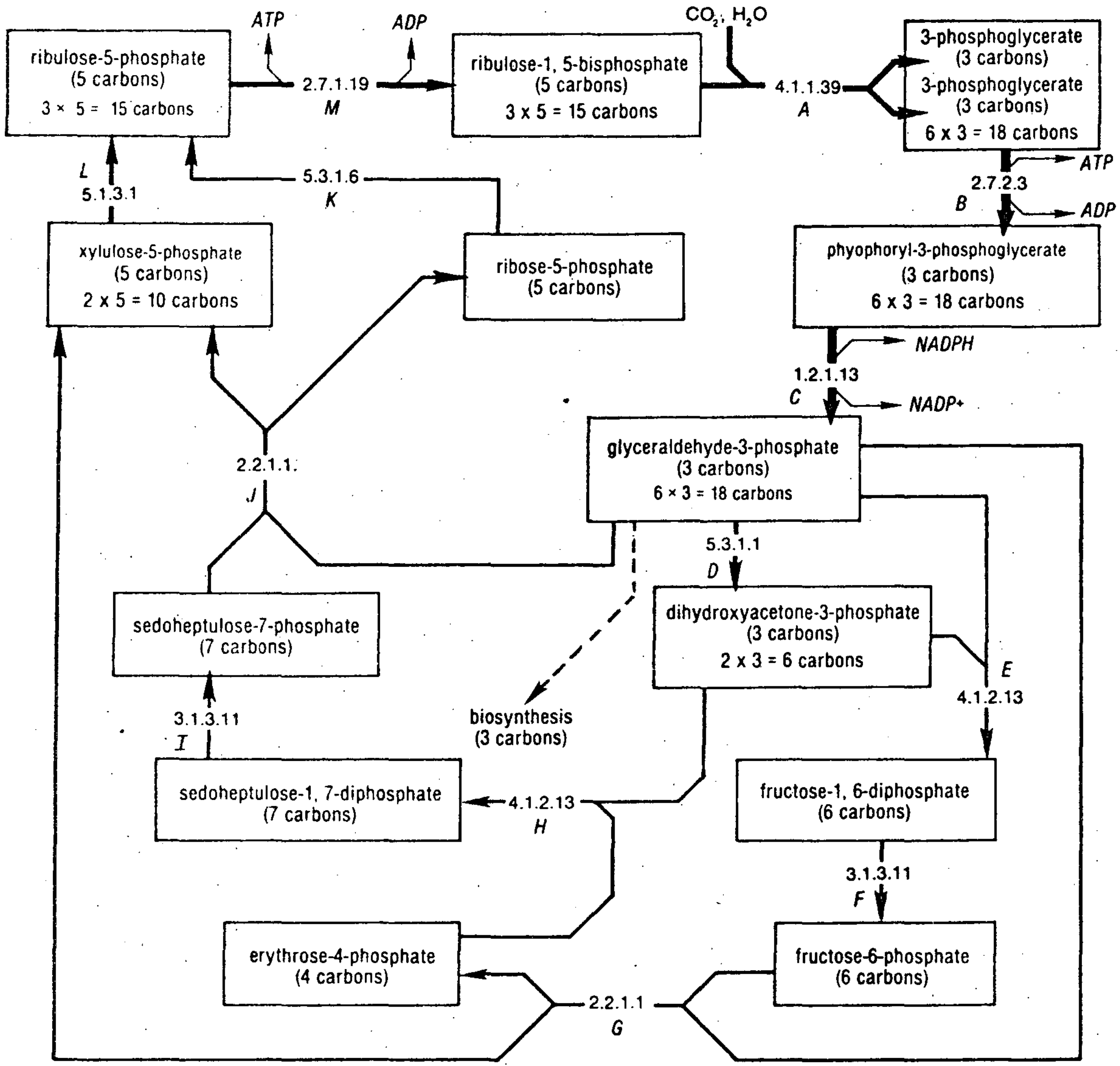

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Fig. 1

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