

Paper V, Gr-I.

Metabolism of Carbohydrate: glycogenesis  
Part II

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Contd. from Part I -

4. Transfer of glucose from UDP-glucose to glycogen primer:- In this step, glucose moiety of UDP-glucose is transferred to an already existing glycogen primer molecule. This primer is present as a conjugate to a protein molecule named glycogenin, a polypeptide of 332 amino acids. Carbon-1 of the first glucose of the glycogen primer forms a covalent bond with -OH of tyrosine of the protein glycogenin. The enzyme, glycogen synthase, brings about cleavage of the phosphoester bond between C-1 of glucose and  $\alpha$ -P-O<sub>4</sub> of UDP and leaves glucose with oxonium ion as intermediate. This immediately reacts with -OH of the C-4 of terminal glucose of glycogen primer forming  $\alpha$  (1-4) glycoside bond. Glycogenin acts as a self-glycosylating enzyme and brings about its own glycosylation by

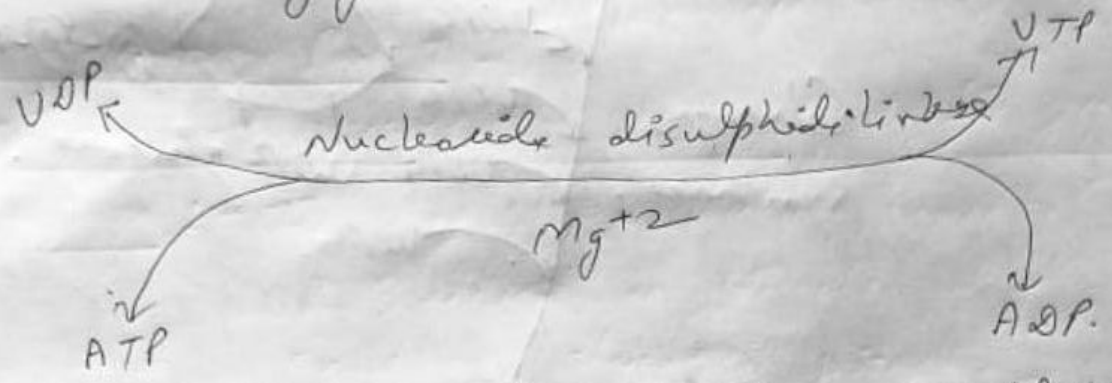
(Pg. 2)

introducing glucose from UDP-glucose to -OH of its own tyrosine. The free energy change of the reaction is highly negative ( $\Delta G^\circ = -13.3 \text{ kJ per mol}$ ). UDP liberated is converted back to UTP by the enzyme nucleoside diphosphate kinase, which brings about transfer of energy-rich phosphate from ATP to UDP.

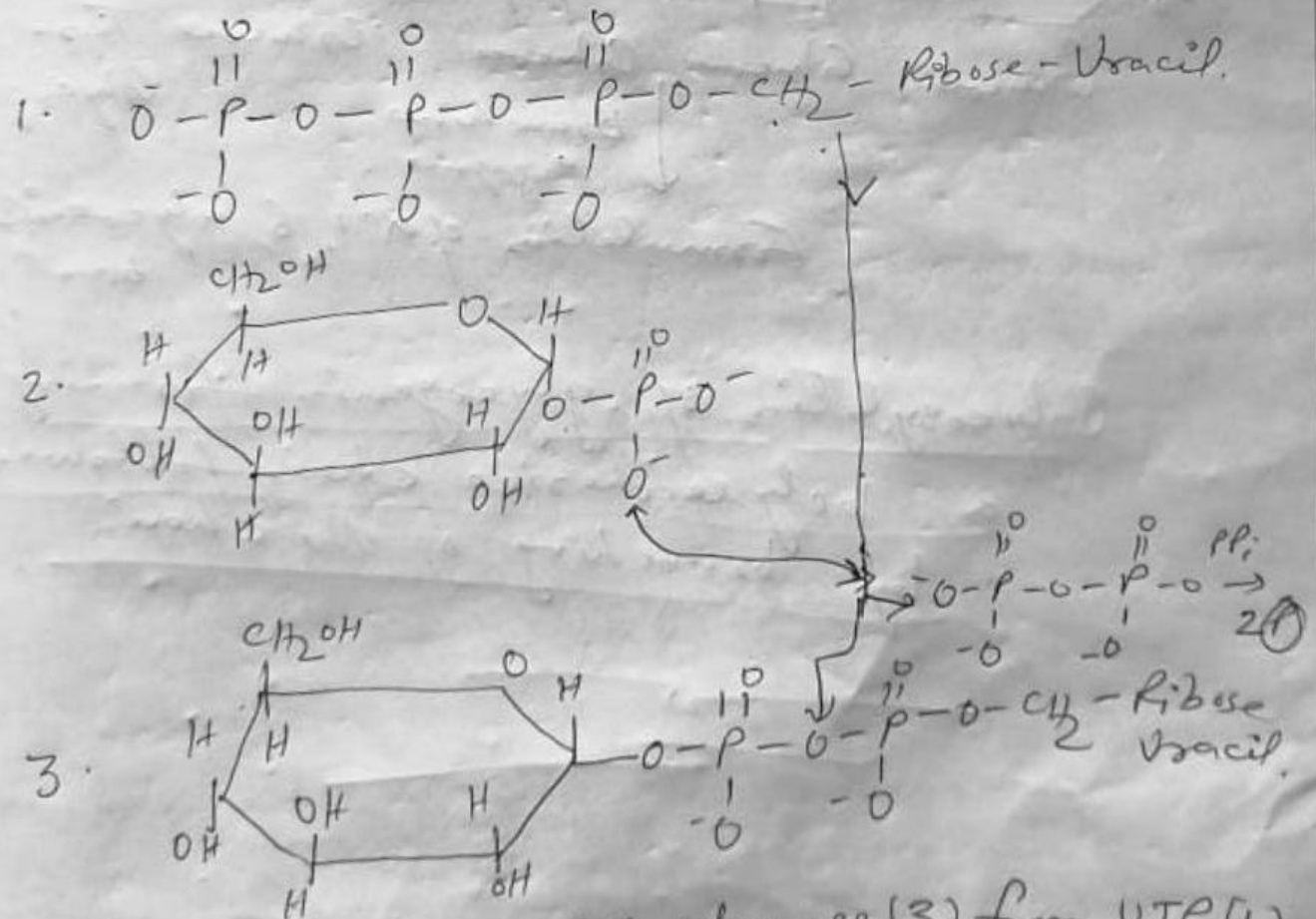
Similarly, fresh UDP-glucose molecules are generated through reactions 1-3 and the glucose unit are transferred to the non-reducing end of the glycogen primer, one after other and the glycogen goes on increasing its linear length by addition of glucose units by  $1 \rightarrow 4$  glycosidic bonds.

⑤ Branching of the linear polymer: After repeated actions of different enzymes in succession, through step 1 to step 4, different branches of glycogen primer increase linearly away from its glycogenin. Once a linear chain has elongated by 11 glucose residues. Another enzyme, a branching enzyme, amylo (1,4  $\rightarrow$  1,6) transglycosylase brings about transfer of an oligosaccharide piece of 6 to 7 glucose units from the growing chain to an adjacent chain by forming a branch point of  $\alpha$ -1,6 glycosidic

bond between Carbons-6 of the adjacent chain and Carbons-1 of the oligosaccharide piece. This branch point is mostly away by at least four glucose units from the nearest branch point. This branch point is formed of oligosaccharide and the growing chain continues to grow further and further by addition of new glucose units by  $\alpha-1 \rightarrow 4$  glycoside bonds.

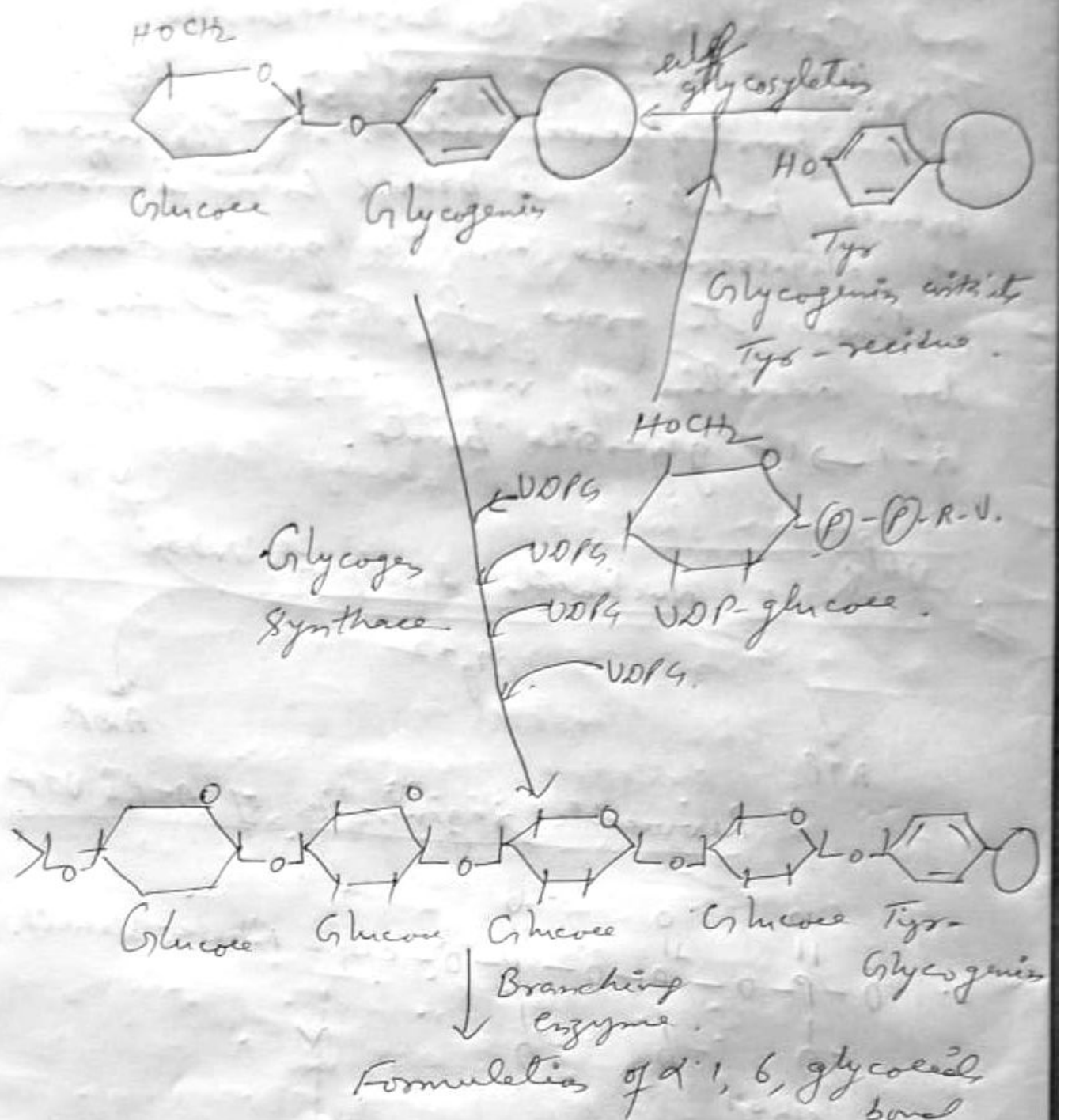


Reversible regeneration of ATP & UTP



Formation of UDP-glucose (3) from UTP (1) & glucose-1-P<sub>2</sub> (2).





Glycosylation of glycogenin forming a polysaccharide chain followed by branching of the chain.

