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Opinion Article

Chemistry and Metabolism of Ribonuleotide Reductases

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DESCRIPTION

Ribonucleotide Reductase (RNR), also known as Ribonucleoside Diphosphate Reductase (rNDP), is an enzyme that catalyzes the development of deoxyribonucleotides from ribonucleotides. It catalyzes this formation by eliminating the 2'-hydroxyl group of the ribose ring of nucleoside diphosphates. This reduction yields deoxyribonucleotides. Deoxyribonucleotides in turn are castoff in the synthesis of DNA. The reaction catalyzed by RNR is firmly conserved in all living organisms. Furthermore, RNR plays an acute role in regulating the total rate of DNA synthesis so that DNA to cell mass is maintained at a constant ratio during cell division and DNA repair. A somewhat unusual feature of the RNR enzyme is that it catalyzes a reaction that profits *via* a free radical mechanism of action. The substrates for RNR are ADP, GDP, CDP and UDP. DTDP (Deoxythymidine Diphosphate) is produced by another enzyme (thymidylate kinase) from dTMP (deoxythymidine monophosphate).

Ribonucleotide Reductases are allocated into three classes. Class I RNR enzymes are made from large alpha subunit and small beta subunits which associate to form an active heterodimeric tetramer. By reducing NDPs to 2'-dNDPs, the enzyme catalyses the *de novo* synthesis of deoxyribonucleotides (dNTPs), which are precursors to DNA synthesis and vital for cell proliferation. Class II RNRs yield a 5'-deoxyadenosyl radical by homolytic cleavage of the C-Co bond in adenosylcobalamin. In addition, Class III RNRs contain a stable glycyl radical. The Class I beta subunit usually comprises a di-metal centre and a stable tyrosyl radical. In humans, the beta subunit depends on on a di-iron cofactor. In *E. coli*, the tyrosyl radical is located at position 122 (Y122) on condition that the stable radical for the Class I RNR2 subunits. The tyrosyl radical is deeply buried inside the protein in a hydrophobic environment, positioned close to the iron centre that is used in the stabilization of a tyrosyl radical. The structure of two μ-oxo-linked irons is ruled by ligands that serve as iron binding sites: four carboxylates [aspartate (D146), glutamate (E177, E240, and E274)] and two histidines (H180 and H277). Association happens between the C-terminus of RNR2 and the C-terminus of RNR1. Enzymatic activity is reliant on association of the RNR1 and RNR2 subunits. The active site consists of the active dithiol groups from the RNR1 as well as the deferred center and the tyrosyl radical from the RNR2 subunit.

CONCLUSION

Other residues of RNR2, such as aspartate (D273), tryptophan (W48), and tyrosine (Y356) further stabilize the active-site tyrosyl radical thus permitting electron transfer. These residues aid in the transfer of the radical electron from tyrosine (Y122) of RNR2 to cysteine (C439) of RNR1. The electron transfer originates on RNR2 tyrosine (Y122) and continues in RNR2 to tryptophan (W48), which is separated from RNR1 tyrosine (Y731) by 2.5 nanometres. Electron transfer from RNR2 to RNR1 occurs *via* tyrosine (Y356 to Y731) and continues on through tyrosine (Y730) to cysteine (C439) in the active site. Site-directed mutations of the RNR primary structure specify that all residues cited above contribute in the long distance transfer of the free radical to the active site.

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