Phospholipases A₂ are lipid degrading enzymes which catalyze the reaction

\[ \text{PLA}_2\text{Ca}^{2+} \rightarrow \text{H}_2\text{O} + \text{PLA}_2\text{Ca}^{2+} \]

with \( \text{Ca}^{2+} \) as an essential cofactor bound to the enzyme.

The postulated reaction mechanism is similar to that of the serine proteinases, with an Asp-His couple as proton donor and the nucleophilic serine-OH replaced by a water molecule bound to the essential \( \text{Ca}^{2+} \)-ion in PLA₂ (Dijkstra et al., Nature 289,604). The extracellular enzymes of this type (e.g. pancreatic and venom PLA₂'s) have molecular weights of about 15000 and their amino acid sequences are highly homologous. Their specific activity with aggregated substrates is much higher than with monomeric substrates. The structures of bovine and porcine pancreatic PLA₂ were determined at 1.7 \( \AA \) and 2.6 \( \AA \) resolution, respectively (Dijkstra et al., J. Mol. Biol. 147,97 and Dijkstra et al., J. Mol. Biol. 168,163). There are a total of 21 amino acid differences, which hardly affect the secondary structure. However, the single change of a Val in the bovine into a Phe in the porcine enzyme at position 43 completely alters the conformation of the chain between residues 58 and 70, resulting in the disappearance of a small \( \alpha \)-helix. Such a change would not have been predicted by any of the current methods. The concommitant loss of rigidity in this part of the structure may be compensated for by a second, low affinity \( \text{Ca}^{2+} \)-binding site (Glu71+Glu92) in porcine PLA₂ which is not present in the bovine enzyme (Asn71). These structural differences can, at least in part, account for the observation that porcine PLA₂ binds to micelles better than bovine PLA₂, while their affinities for monomeric substrates are similar, which can be attributed to the almost identical active sites.

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