

LETTERS TO THE EDITORS

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D-Enzyme: a Disproportionating Enzyme in Potato Juice

THE synthesis of amylose is catalysed by the enzyme phosphorylase, which effects a reversible transglucosylation reaction between glucose-1-phosphate and chains of α -1:4-linked glucose units. Hitherto this has been the only known plant enzyme capable of effecting the synthesis of α -1:4-glucosidic linkages. We now have to report the discovery of an enzyme in the potato which can effect the synthesis and degradation of (short) amylose-type chains by transglucosylation. The enzyme was detected in greatest amount in the alcohol-precipitated fraction of potato juice which also contains the greatest amounts of Q-enzyme. The latter enzyme catalyses the conversion of amylose into amylopectin, which involves the simultaneous splitting of α -1:4-links and synthesis of α -1:6-links (an irreversible transglucosylation)¹. The new enzyme manifested itself when a Q-enzyme preparation was allowed to act on the linear maltosaccharides produced by the partial acid hydrolysis of amylose². Two effects were noticed. First, iodine-staining material was synthesized from the achroic saccharides and, secondly, paper chromatograms of the digests revealed that the substrates had been disproportionated into products of higher and lower molecular weight, the latter including glucose. For this reason, we have provisionally named the new factor D-enzyme.

D-enzyme brings about rapid disproportionation of malto-triose, -tetraose, -pentaose, -hexaose and -heptaose; but action in the case of maltose is doubtful. Glucose itself is not a substrate. The greater the molecular weight of the maltosaccharide substrate, the greater is the final intensity of iodine stain. With maltohexaose the iodine colour changes through brown and red to purple-red, the intensity then remaining very nearly constant for prolonged periods of digestion. On addition of glucose to such a digest, however, the iodine-staining power disappears rapidly. The simplest explanation of these results would be that the action of D-enzyme is to effect the transfer of glucose units, either singly or severally, from one molecule of substrate (donor) to an acceptor molecule, which may be either a maltosaccharide or glucose. Furthermore, in view of the fact that the products stain with iodine, it would seem probable that the linkage synthesized is of the α -1:4-chain-forming type.

Proof of the unbranched character of the products was obtained by treatment of maltotetraose with D-enzyme and afterwards with salivary α -amylase. Charcoal fractionation of the hydrolysate yielded only glucose, maltose and maltotriose, and in amounts corresponding to 97 per cent of the maltotetraose taken. This result demonstrates that D-treated maltotetraose does not contain any substantial proportion of branched structures. Thus waxy maize starch, in which α -1:6- and α -1:4-links are present in a ratio of 1:23, is hydrolysed by α -amylase to yield maltose (41.8 per cent), maltotriose (28.4 per cent) and 29.8 per cent of limit dextrans containing both types of linkage³.

While it is clear that D-enzyme catalyses redistribution reactions among linear maltosaccharides, the

pattern of its action is still obscure. The most significant observation concerns the place of maltose in this scheme. As already mentioned, D-enzyme appears not to utilize maltose as a substrate and, moreover, maltose is not formed (except in traces and only after prolonged action) when D-enzyme acts on other maltosaccharides. Thus the lower molecular weight products from each maltosaccharide always contain in addition to glucose every lower linear maltosaccharide except maltose. Possible explanations of these effects are being considered, but further work is obviously necessary and is proceeding.

It seems evident that the role of glucose in causing removal of iodine-staining material (see above) is due to its functioning as an acceptor for the transferring action; it cannot act as a donor. In a parallel experiment, D-enzyme was allowed to act on maltohexaose, and glucose labelled with carbon-14 was then added. When the digest became achroic the products were fractionated on paper. Radioactivity was found to be distributed throughout the zones corresponding to the maltosaccharides.

Two bacterial enzymes are known which catalyse somewhat similar reactions. Amylomaltase from *E. coli*, which synthesizes amylose-like molecules from maltose⁴, is clearly different from D-enzyme. The Schardinger dextrinase action reported by Norberg and French⁵ does, however, bear a certain resemblance to that of D-enzyme. The *in vivo* function of D-enzyme can, at the moment, be a matter for conjecture only; but it may either provide 'primers' for phosphorylase synthetic action, or itself catalyse the synthesis of amylose. The latter possibility carries with it the implication that phosphorylase function may be confined to the degradation of starch.

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² Whelan, W. J., Bailey, J. M., and Roberts, P. J. P., *J. Chem. Soc.*, 1293 (1953).

³ Whelan, W. J., and Roberts, P. J. P., *Nature*, **170**, 748 (1952).

⁴ Monod, J., and Torriani, A., *Ann. Inst. Pasteur*, **78**, 65 (1950).

⁵ Norberg, E., and French, D., *J. Amer. Chem. Soc.*, **72**, 1202, 1746 (1950).

Cortisone and the Metabolic Response to Injury

THE pattern of the metabolic response of man to injury (for example, fracture of a long bone), in particular its effect on protein catabolism, has been under investigation for some time by one of us¹ as this phenomenon is of basic importance to our understanding of protein metabolism in general. The reaction is characterized in man by a marked increase in the urinary excretion of nitrogen and sulphur, which reaches a peak from the fourth to the eighth day after the injury and then slowly declines. There is also a loss of phosphorus and potassium. This phenomenon has been confirmed by many workers and in other forms of injury². Cuthbertson, McGirr