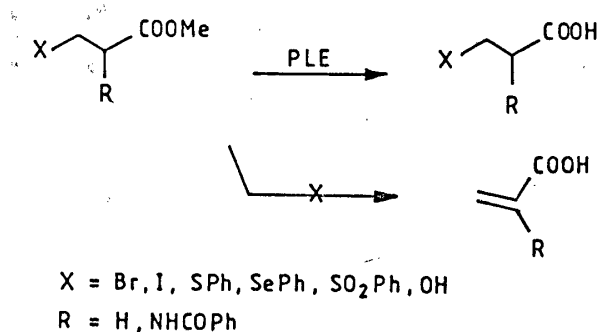


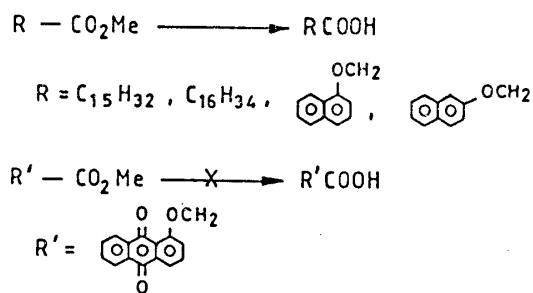
ABSTRACT

The hydrolase enzyme, Pig Liver Esterase (PLE) has been utilised to effect various transformations which were, otherwise difficult to achieve by chemical reagents. All the PLE-catalysed transformations described here, proceeded with a high degree of selectivity. Base-promoted hydrolysis of esters attached with good leaving groups at the β -position led to elimination accompanying hydrolysis. PLE, working in the vicinity of neutral pH, smoothly catalysed the hydrolysis of such types of esters without any elimination or stereochemical scrambling.

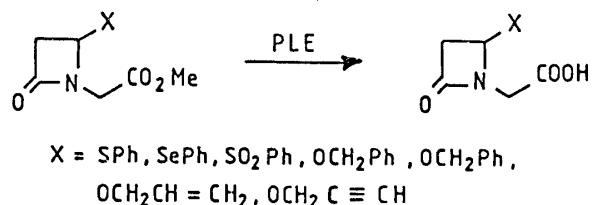


The catalytic activity of PLE has been extended to the hydrolysis of long chain fatty esters. At the same time, it has been demonstrated that anthracene-based esters with a smaller dimension than long chain fatty esters, are not substrates for PLE. A comparatively smaller naphthalene-based

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β -lactams substituted with a 2-furyl or 2-thienyl group at C-4 have been prepared in scalemic form (50% ee) via the hydrolysis of the corresponding 3-carboxyesters with PLE, followed by decarboxylation. No enantioselectivity was observed with a phenyl or a p-methoxy phenyl group present at C-4. A related enzyme Pig Pancreatic Lipase (PPL) failed to produce any enantioselectivity in all the cases.

ABSTRACT

This dissertation entitled “ **Enantiospecific Synthesis of Cyclopentanoid Natural Products from L-Glutamic Acid**” describes part of a long term program operating in these laboratories devoted to the application of α -amino acids as chiral templates in natural products synthesis. Of all the members of the chiral pool, amino acids, due to their versatility as well as commercial availability, have been the most extensively used for the synthesis of chiral, enantiomerically pure carbo- and heterocycles. The interest in the preparation of chiral compounds in enantiomerically pure form has greatly increased lately due to several factors: the enantiospecificity shown by most biological systems in their responses to drugs, odorants, etc., the regulatory pressure on the pharmaceutical industry to market chiral drugs as single enantiomers, and the strong desire for synthetic efficiency. In fact, even the agrochemical industry is now paying increasing attention to chirality and in particular to the resolution or synthesis of single enantiomers where pesticidal activity is found to be specifically associated with one isomer form. This dissertation is divided in two parts. Part I describes an enantiospecific route to jasmonoid natural products, (+)-methyl epijasmonate, (-)-methyl cucurbate and (+)-cucurbitic acid from L-glutamic acid. The key step here is a 5-(3,4) ene cyclization of a functionalized 1,6-diene, which sets up three chiral centers with a high degree of diastereoselectivity. Part II has been subdivided into two sections. Section A describes the preparation of an advanced intermediate for the synthesis of a fungitoxic sesquiterpene, (-)-chokol A from L-glutamic acid where the pivotal step is 5-(3,4) ene cyclization of a doubly activated 1, 6-diene. Section B describes the development of LiClO_4 -doped silica gel as a new and efficient catalyst for ene cyclization of doubly activated 1, 6-dienes, some of which are prone to side reactions including polymerization under standard conditions.

Keywords: *Ene, Enantiopurity, Chiral, Lithium Perchlorate.*