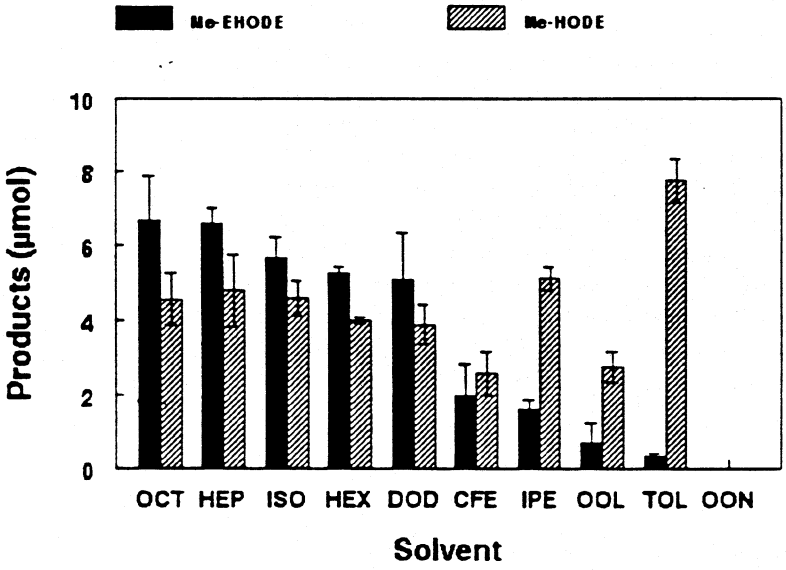
Fatty Epoxy Alcohol Production from Fatty Hydroperoxide Using Oat (*Avena sativa*) Seed Peroxygenase in Organic Solvent

Introduction

The enzyme peroxygenase catalyzes the heterolytic cleavage of a peroxygen bond to transfer oxygen to an oxidizable functional group such as a carbon-carbon double bond (Blée, 1996). In this instance the product is an epoxide. Thus oleic acid is converted to its 9,10-epoxide, and linoleic acid to the 9,10- and 12,13-epoxides by peroxygenase (Hamberg and Hamberg, 1996, 1990; Hamberg and Fahlstadius, 1992; Blée *et al.*, 1993). Studies with soybean and broad bean show that only *cis*-unsaturated double bonds are substrates of peroxygenase (Hamberg and Fahlstadius, 1992; Blée *et al.*, 1993). Peroxygenase can also catalyze internal epoxidation. Thus when peroxygenases from soybean and broad bean are presented with a hydroperoxide of linoleic acid (13(*S*)-hydroperoxy-9(*Z*),11(*E*)-octadecadienoic acid, HPODE), the product is 9,10-epoxy-13(*S*)-hydroxy-11(*E*)-octadecenoic acid (EHODE) (Hamberg and Hamberg, 1990; Blée *et al.*, 1993). Oat seed peroxygenase catalyzes the epoxidation of oleic acid using hydrogen peroxide as the oxygen donor (Hamberg and Hamberg, 1996). It also converts linoleic acid to a number of other oxygenated derivatives. In this study, the methyl ester of HPODE (Me-HPODE) was presented to oat seed peroxygenase in organic solvents, and the structure of the major epoxidized product was determined.

Results and Discussion

Structure of the epoxy alcohol produced by oat seed microsomes. Two major products resulted from the action of oat seed microsomes on Me-HPODE. One product was identified as methyl


Me-EHODE
Me-HODE
Products (μmol)
10
8
6
4
2
0
OCT HEP ISO HEX DOD CFE IPE OOL TOL OON
Solvent

Conclusion

This research has confirmed the presence of the enzyme peroxygenase in oat seeds by demonstrating that the hydroperoxide of methyl linoleate (Me-HPODE) can be directly converted to oxygenated products. As with other peroxygenase enzymes studied previously, the oat seed peroxygenase is capable of transferring oxygen only to a *cis* double bond. It was demonstrated that oat seed peroxygenase has full catalytic activity in hydrocarbon solvents. This finding may increase the utility of this enzyme in the synthesis of highly oxygenated lipids f