Specificity of Oxidation of Linoleic Acid Homologs by Plant Lipoxygenases

I. R. Chechetkin[1]*, E. V. Osipova[1], N. B. Tarasova[1], F. K. Mukhitova[1], M. Hamberg[2], Y. V. Gogolev[1], and A. N. Grechkin[1]

[1]Kazan Institute of Biochemistry and Biophysics, Kazan Scientific Center, Russian Academy of Sciences, ul. Lobachevskogo 2/31, 420111 Kazan, Russia; fax: (843) 292-7347; E-mail: chechyotkin@mail.knc.ru
[2]Department of Medical Biochemistry and Biophysics, Division of Physiological Chemistry II, Karolinska Institutet, SE-171 77 Stockholm, Sweden; fax: 46-8736-0439; E-mail: mats.hamberg@mbb.ki.se

Received January 22, 2009
Revision received February 27, 2009

Abstract—The lipoxygenase-catalyzed oxidation of linoleic acid homologs was studied. While the linoleic acid oxidation by maize 9-lipoxygenase (9-LO) specifically produced (9*S*)-hydroperoxide, the dioxygenation of (11*Z*,14*Z*)-eicosadienoic (20:2) and (13*Z*,16*Z*)-docosadienoic (22:2) acids by the same enzyme lacked regio- and stereospecificity. The oxidation of 20:2 and 22:2 by 9-LO afforded low yields of racemic 11-, 12-, 14-, and 15-hydroperoxides or 13- and 17-hydroperoxides, respectively. Soybean 13-lipoxygenase-1 (13-LO) specifically oxidized 20:2, 22:2, and linoleate into (ω6*S*)-hydroperoxides. Dioxygenation of (9*Z*,12*Z*)-hexadecadienoic acid (16:2) by both 9-LO and 13-LO occurred specifically, affording (9*S*)- and (13*S*)-hydroperoxides, respectively. The data are consistent with the "pocket theory of lipoxygenase catalysis" (i.e. with the penetration of a substrate into the active center with the methyl end first). Our findings also demonstrate that the distance between carboxyl group and double bonds substantially determines the positioning of substrates within the active site.

DOI: 10.1134/S0006297909080069

Key words: lipoxygenase, enzyme–substrate interaction, polyenoic fatty acid, oxylipin