

TWO NOVEL LIPOXYGENASE SUBSTRATES: SYNTHESIS AND CATALYSIS

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The last decade has seen fascinating developments regarding the chemistry of soybean lipoxygenase, type I (SBLO-I). The enzyme has been found to catalyze reactions of monounsaturated fatty acids, producing β -unsaturated enones. This reaction proceeds by way of a hydroperoxide intermediate, suggesting a mechanism similar to its natural reaction with pentadiene systems. The existence of the hydroperoxide was confirmed by substrate reactions in the presence of reducing agents, capturing the intermediate as a chiral allylic alcohol. The production of two distinct alcohol structures suggests a regiospecific rearrangement mediated by the Sn(II) reducing agent. Future SBLO-I studies will be aided greatly by synthetic analogs of natural substrates. We have synthesized two such substrates and carried out SBLO-I catalyzed reactions. One substrate is analogous to 12-Z-octadecenoic acid. The other incorporates a conjugated diene system. Both substrates represent a new chapter in the study of lipoxygenase chemistry.