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Review

# Oxylipins: Structurally diverse metabolites from fatty acid oxidation

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ABSTRACT

Oxylipins are lipophilic signaling molecules derived from the oxidation of polyunsaturated fatty acids. Initial fatty acid oxidation occurs mainly by the enzymatic or chemical formation of fatty acid hydroperoxides. An array of alternative reactions further converting fatty acid hydroperoxides gives rise to a multitude of oxylipin classes, many with reported signaling functions in plants. Oxylipins include the phytohormone, jasmonic acid, and a number of other molecules including hydroxy-, oxo- or keto-fatty acids or volatile aldehydes that may perform various biological roles as second messengers, messengers in inter-organismic signaling, or even as bactericidal agents. The structural diversity of oxylipins is further increased by esterification of the compounds in plastidial glycolipids, for instance the Arabidopsides, or by conjugation of oxylipins to amino acids or other metabolites. The enzymes involved in oxylipin metabolism are diverse and comprise a multitude of examples with interesting and unusual catalytic properties. In addition, the interplay of different subcellular compartments during oxylipin biosynthesis suggests complex mechanisms of regulation that are not well understood. This review aims at giving an overview of plant oxylipins and the multitude of enzymes responsible for their biosynthesis.
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## 1. Oxylipins are a diverse class of metabolites derived from fatty acids

Plant oxylipins are a diverse class of lipid metabolites that derive from the oxidation of unsaturated fatty acids. Oxylipins formed in plants include fatty acid hydroperoxides, hydroxy-, oxo-, or keto-fatty acids, divinyl ethers, volatile aldehydes, or the plant hormone JA [1]. The first committed step of oxylipin biosynthesis is the formation of fatty acid hydroperoxides, which can occur by enzymatic processes [2] or by chemical (auto)oxidation [3].

### 1.1. Enzymatically formed oxylipins

Reactive hydroperoxides of the abundant fatty acids: linoleic acid (LA, 18:2: where *x*:*y* is a fatty acid containing *x* carbons and *y* double bonds), α-linolenic acid (α-LeA, 18:3) or roughanic acid (16:3) are formed predominantly by lipoxygenases (LOXs, EC 1.13.11.12) [4] or can also be formed by α-dioxygenase (α-DOX) [5]. Subsequent conversion of hydroperoxides can occur by various alternative pathways, including those initiated by allene oxide synthase (AOS, EC 4.2.1.92), divinyl ether synthase (DES), hydroperoxide lyases (HPL), peroxygenases (PXG), or epoxy alcohol synthase (EAS), as indicated in Fig. 1. The resulting oxygenated derivatives include the phytohormone, jasmonic acid (JA), as well as oxylipins with characteristic reactive epoxide, α,β-unsaturated carbonyl, or aldehyde functionalities. For a more detailed view of the chemical characteristics of various oxylipins, the reader is referred to more specialized reviews on the topic [1,6–8]. To pay tribute to the complexity of oxylipin metabolism, key enzymes of the main pathways for oxylipin biosynthesis will be discussed in more detail in a separate section below.

### 1.2. Oxylipins formed chemically

In parallel to enzymatic conversion, which leads to the formation of pure oxylipin enantiomers, oxidative stress and formation of reactive oxygen species can lead to chemical membrane lipid peroxidation [3]. Whether compounds are formed enzymatically or non-enzymatically can be decided mainly by two ways: (i) In case of fatty acid hydroperoxides based on a higher abundance of one or the other enantiomer, or the observation of a racemic mixture, respectively, since LOXs catalyze either the formation of *S* or *R* configurated hydroperoxides [9]. (ii) Alternatively, chemical

*Abbreviations:* ACXs, acyl-CoA oxidases; AOS, allene oxide synthase; DES, divinyl ether synthase; dn-OPDA, dinor-OPDA; α-DOX, α-dioxygenase; EAS, epoxy alcohol synthase; GLVs, green leaf volatiles; HPL, hydroperoxide lyase; JA, jasmonic acid; JA–Ile, jasmonic acid isoleucine conjugate; KAT, 3-ketoacyl-CoA thiolase; LA, linoleic acid; α-LeA, α-linolenic acid; LOX, lipoxygenase; MeJA, jasmonic acid methyl ester; MFP, multifunctional protein; OPC-8, 12-oxo phytoenoic acid; OPDA, 12-oxo phytodienoic acid; PXG, peroxygenase; PUFA, polyunsaturated fatty acid.

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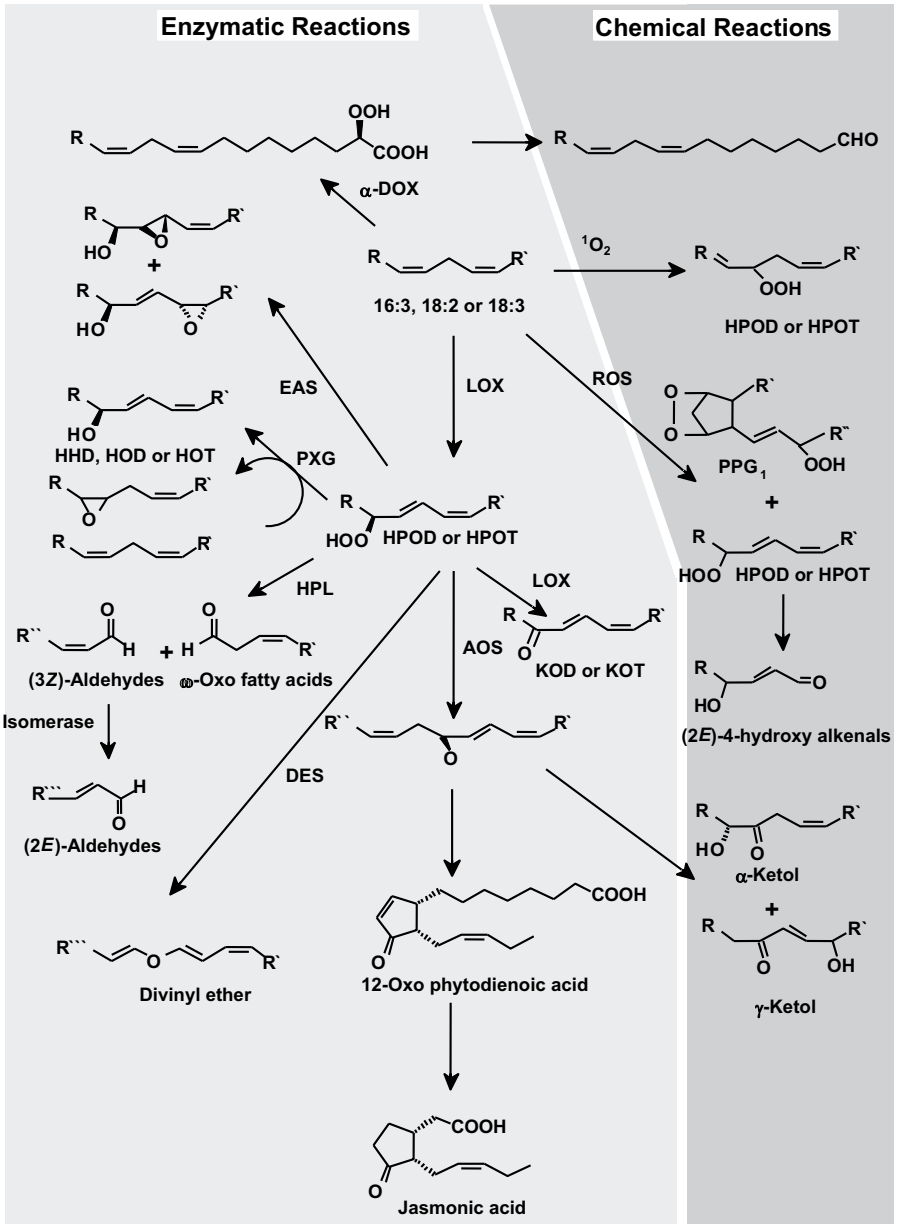


**Fig. 1.** Overview of oxylipin biosynthesis. The formation of oxylipins starts with the conversion of polyunsaturated fatty acids (PUFAs) containing a (1*Z*,4*Z*)-pentadiene system, such as linoleic acid or α-linolenic acid. Initial conversion of PUFAs by lipoxygenase (LOX) or 2-dioxygenase (α-DOX) generates fatty acid hydroperoxides that are substrates for alternative metabolic pathways defined by the key enzymes indicated. AOS, allene oxide synthase; AOC, allene oxide cyclase; DES, divinyl ether synthase; EAS, epoxy alcohol synthase; HPL, hydroperoxide lyase; PXG, peroxygenase. PUFAs can also be non-enzymatically converted into fatty acid hydroperoxides and hydroxy fatty acids. Allene oxides formed by AOS can spontaneously cyclise to form cyclopentenones, or hydrolyze into α-ketols and β-ketols. Non-enzymatic reactions are shaded in dark grey (right), enzymatic reactions in light grey (left).

oxidation may lead to different positional isomers of hydroxy fatty acids and LOXs insert molecular oxygen only at C-9 or C-13 of LA or α-LeA, respectively, whereas reactive oxygen species can lead to formation of hydroxides at C-10 and C-12 in case of LA and in addition at C-15 and C-16 in case of α-LeA [10–12] (Fig. 1). The most abundant fatty acids, LA and α-LeA, are particularly prone to undergo oxidation by free radicals, yielding racemic mixtures of peroxy fatty acid radicals [3]. Such radicals can start a chain of oxidative reactions leading to the formation and accumulation of racemic free or esterified fatty acid hydroperoxides. Polyunsaturated fatty acid (PUFA) hydroperoxides and peroxy radicals with more than two double bonds can be further oxidized in the process, generating bicyclic endoperoxy hydroperoxides with short half-lives such as the phytoprostane PPG$_1$ [3]. Other sequences of spontaneous reactions create phytoprostanes, which are similar in structure to isoprostanes in animals. The levels of phytoprostanes esterified in the membranes of some plant species are generally an order of magnitude higher than those of free phytoprostanes [13,14], and overall levels of phytoprostanes increase after exposure to oxidative stresses, such as peroxide or heavy-metal treatment, or after pathogen challenge [13–16]. Many oxidized lipids generated during oxidative stress serve as ligands for protein lipidation have profound effects on gene expression patterns and, therefore, may represent mediators of oxidant injury. Well-characterized products of peroxy radical chemistry include di- and trihydroxy fatty acids, epoxy alcohols, ketodienes, ketotrienes and alkenals [17]. While in animals major oxylipins involved in protein lipidation are 4-hydroxy-2-alkenals such as 4-hydroxy nonenal [18], in plants phytoprostanes and keto fatty acids seem to be the major players [19]. Phytoprostanes have been found in plants as well [20], and

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