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* configured hydroperoxides [9]. (ii) Alternatively, chemical
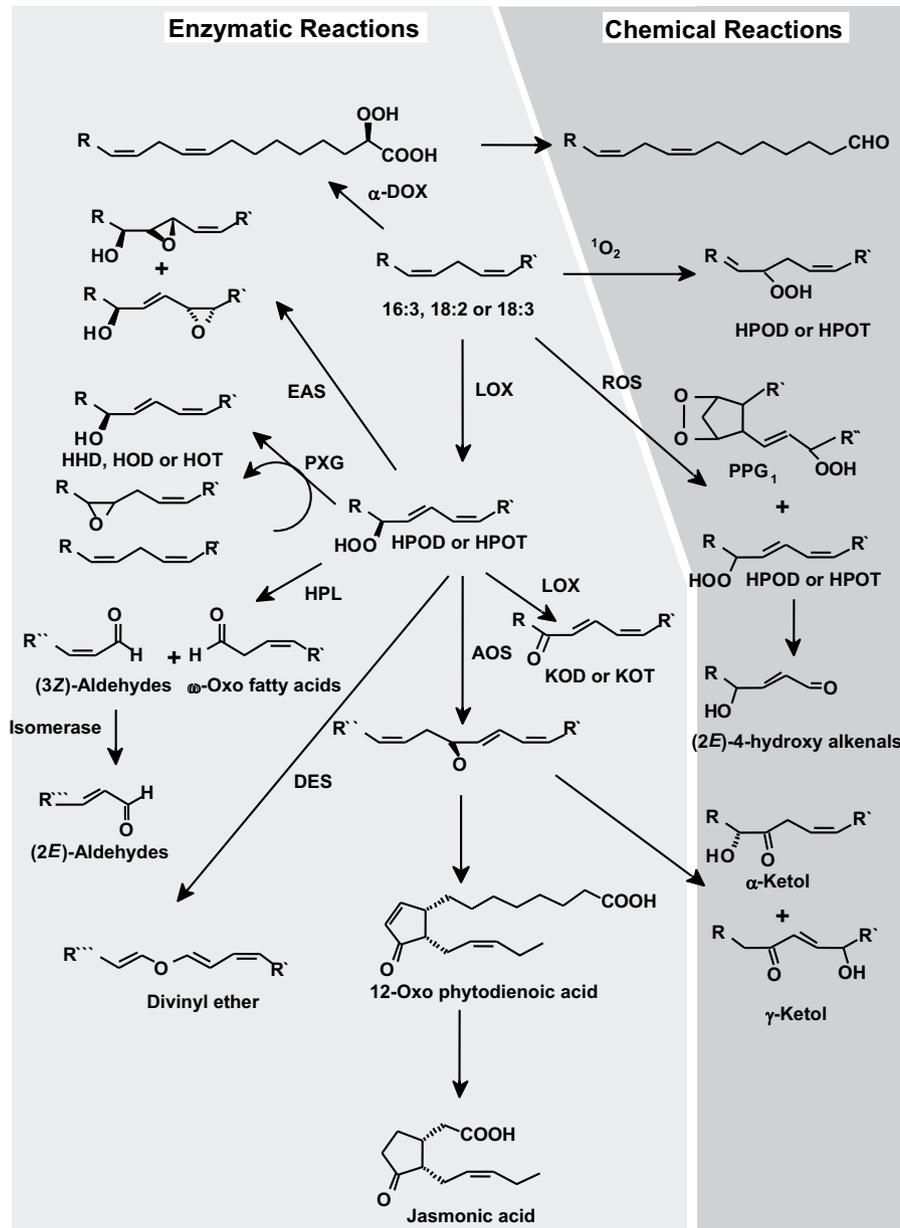
Fig. 1. Overview of oxylipin biosynthesis. The formation of oxylipins starts with the conversion of polyunsaturated fatty acids (PUFAs) containing a (1Z,4Z)-pentadiene system, such as linoleic acid or α-linolenic acid. Initial conversion of PUFAs by lipoxygenase (LOX) or 2-dioxygenase (α-DOX) generates 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. Poly-unsaturated 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

exogenous application of different cyclopentenone phytoprostanes has been demonstrated to induce plant defence responses [15,16]. It is important to note that significant amounts of oxylipins derived from non-enzymatic or chemical oxidation are found in plant tissues, and that some of the same substances can also be generated enzymatically by the LOX pathway [6]. Basal levels of products derived from non-enzymatic peroxidation are generally in the same range or even above those of the products of enzymatic peroxidation [3].

2. Different guises of oxylipins in plant cells

2.1. Non-esterified or free oxylipins

Numerous studies indicate that oxylipins can occur in different appearances in plant cells. The simplest situation is presented by free oxylipins that have been reported from various plant systems. In addition to free oxylipins that can associate with soluble compartments, such as the cytosol, the stroma of plastids or the peroxisomal matrix [21–24], oxylipins have been found to be esterified with a number of other molecules in the cell.

2.2. Esterified oxylipins

2.2.1. Arabidopsides
Considering their origin from PUFAs, it is not surprising that oxylipins, such as 12-oxo phytodienoic acid (OPDA) or dinor-OPDA (dn-OPDA) occur esterified to complex lipids [25–32]. Reported derivatives of the plastidial galactolipids, mono and digalacto-syldiacylglycerol (MGDG and DGDG) that contain OPDA and/or dn-OPDA instead of fatty acyl moieties are collectively called Arabidopsides. Depending on the distribution of OPDA at either or both sn-1 and sn-2 positions, several Arabidopsides can be distinguished (named Arabidopsides A-G), and new Arabidopside species are still being discovered [33]. The formation of OPDA-containing galactolipids after wounding or elicitation may be caused by the rapid incorporation of newly synthesized OPDA into plastidial lipids. In support of this possibility, OPDA and dn-OPDA appear to be preferentially associated with galactolipids. The only OPDA molecule so far reported to occur in the phospholipid fraction is OPDA esterified to the sn-1 position of phosphatidylglycerol with trans-hexadecenoic acid at the sn-2 position; this phospholipid is also restricted to plastids [29]. So far it is unclear whether oxylipins bound in plastidial lipids are a storage-form of signaling molecules that are readily-releasable upon stress. Recent evidence indicates that detectable amounts of Arabidopsides are found only in a selected number of species of the genus *Arabidopsis* [32], suggesting that Arabidopside pools in most plants may be very small, or that the lipids represent a particular adaptation found only in certain species.

2.2.2. Other oxylipin-esters and conjugates
Oxylipins can be bound to phospholipids, neutral lipids, sulphate, glutathione, ethanolamine, carbohydrates or amino acids in the form of esters or conjugates. The divinyl ether fatty acid colneleic acid can be found esterified to phospholipids, and keto, hydroxy, as well as hydroperoxy derivatives of either LA or α-LeA are detectable in the neutral lipids and phospholipids of cucumber and sunflower seedlings [34,35]. However, the most prominent example is JA, which can occur as a methyl ester (MeJA), be bound in glycosyl esters, form amide-conjugates with various amino acids [36] or is hydroxylated at the ω- or (ω − 1)-end of its side chain that is then further sulphated [37]. Recently, the conjugate of JA and isoleucine (JA–Ile) has been implicated as a biologically active form of JA which interacts with a JA-receptor [38–40]. Glutathionylation

is another modification, found for instance with OPDA and (2*E*)-hexenal [41].

3. Key enzymes for oxylipin biosynthesis in plants

In order to elucidate the physiological relevance of different oxylipin species and to investigate the functional interdependencies between oxylipins and other signaling pathways, the biosynthetic enzymes must be considered. The following paragraphs summarize information available on key enzymes of oxylipin metabolism in plants (Fig. 1).

3.1. Acyl-lipid hydrolases or phospholipases

Over the last 15 years numerous reports have been published that describe attempts to alter oxylipin biosynthesis by overexpression of either one of the enzymes involved in their biosynthesis [42,43]. From these data it is evident that oxylipin biosynthesis takes place upon external stimulation, and that it is mainly driven by the availability of either of its substrates, roughanic acid, LA or α-LeA [37]. In this context it is relevant that the plastidial phospholipases, DAD1 and DGL, appear to have a role in oxylipin signaling in *Arabidopsis*, as evident from studies on *dad1* and *dgl* mutants [44–46]. In addition, another group of acyl-lipid hydrolases from the patatin family seems to be involved in supplying the oxylipin biosynthetic pathway with substrates [47]. However, despite of these examples, enzymes involved in providing the LOX pathway with free PUFAs are as yet not well defined and more research is needed here.

3.2. Lipoxygenases

LOXs catalyze the regio- and stereo-specific dioxygenation of PUFAs containing a (1Z,4Z)-pentadiene system, e.g., LA, α-LeA, or roughanic acid. Plant LOXs are classified with respect to their positional specificity of LA oxygenation, which can occur either at carbon atom 9 (9-LOX) or at C-13 (13-LOX) of the hydrocarbon backbone in case of a fatty acid with 18 carbon atoms [9]. The different specificities result in the formation of two groups of compounds, the (9S)-hydroperoxy and the (13S)-hydroperoxy derivatives of PUFAs [48]. Recently a (9R)-hydroperoxide forming LOX has been described from cyanobacteria [49,50]. Genomic analysis of different plant species indicates that genes encoding LOXs are present as multigene families in all cases, for instance with six members in *Arabidopsis* or at least 14 in potato (*Solanum tuberosum*) [48]. Different LOX-isoforms occur in the cytosol, the stroma, the vacuole or associated with different membranes [51]. In *Arabidopsis* LOX-activity is mainly associated with the plastidial envelope of leaf chloroplasts and with the plastidial stroma [52–54]. It is possible that LOX-isoforms with different subcellular localization provide different pools of hydroperoxy PUFAs that are substrates for alternative pathways of further conversion and may have different effects on physiology [48]. Whereas plant and animal LOXs have traditionally been considered to oxygenate mainly free PUFAs, a number of studies provide evidence that plant and animal LOXs are capable of oxygenating also ester lipid substrates, such as fatty acids bound to phospholipids or galactolipids [55,56], triacylglycerols [35,57,58] or cholesterol esters [59,60].

3.3. CYP74-enzymes

A number of key enzymes of oxylipin metabolism are representatives of an atypical family of cytochrome P450 monooxygenases, the CYP74-enzymes. AOS, HPL and DES are all CYP74-enzymes and, in contrast to other P450 enzymes, do not

require molecular oxygen nor NAD(P)H-dependent cytochrome P450-reductase as cofactors [61–67]. Carbon-oxygen bonds formed by CYP74-enzymes use acyl-hydroperoxides as both substrate and oxygen donor.

3.3.1. AOS

AOS transforms fatty acid hydroperoxides into unstable allylic fatty acid epoxides [68] and is a key enzyme of the octadecanoid pathway leading to JA biosynthesis (Fig. 2). All AOSs purified from plants are membrane-associated. Whereas a single *AOS* gene has been described for *Arabidopsis* [67], flax (*Linum usitatissimum* L.) [69], guayule (*Parthenium argentatum*) [70], and barrel medic (*Medicago truncatula*) [71], two AOSs have been found thus far in tomato (*Solanum lycopersicum*) and barley (*Hordeum vulgare*) [4], and three AOSs have been described for potato [65]. Recently the structures of AOS from guayule and *Arabidopsis* have been solved and will provide further insight into the reaction mechanism of these enzymes [72,73].

3.3.2. HPL

HPL catalyzes the cleavage of fatty acid hydroperoxides into ω-oxo fatty acids and (3Z)-alkenals, generating a group of C_6 volatiles referred to as green leaf volatiles (GLVs) that include (2E)-hexenal, (2E)-hexenol, (3Z)-hexenal, hexanal, and hexanol [7], depending on the available substrate, thereby decreasing the pools of fatty acid hydroperoxides available for alternative production of jasmonates. HPL-derived C_6 volatiles previously reported [74] have been suggested to have roles in signaling during plant defence processes [75,76]. The role of these oxylipins as signals in defence against sucking insect pests has been demonstrated for instance for GLVs generated by 13-HPL by antisense-mediated depletion of this specific 13-HPL in transgenic potato plants [77]. Furthermore the decrease in the toxic HPL-derived volatiles increased the performance of aphids [78]. Single cDNA-clones for HPLs have been isolated from a number of plants, including *Arabidopsis* [79], corn (*Zea mays*) (patent WO00/22145), barley [62], guava (*Psidium guajava*) [80], bell pepper (*Capsicum annuum*) [81], melon (*Citrullus lanatus*) [82], potato [83], and tomato [84,85]. Several reports described the

Fig. 2. Subcellular compartmentation of jasmonate biosynthesis. The formation of octadecanoid oxylipins including jasmonate (JA) starts with the lipase-mediated release of α-linolenic acid (α-LeA) from membrane lipids. Lipoxygenases (LOXs, 1) transform the fatty acid into the 13-hydroperoxy α-linolenic acid (13-HPOT). Allene oxide synthase (AOS, 2) converts 13-HPOT to an instable intermediate, 12,13-epoxy-9,11,15-octadecatrienoic acid (12,13-EOT), which is the substrate for allene oxide cyclase (3), yielding 12-oxo phytodienoic acid (OPDA). OPDA is exported from the plastid by an unknown mechanism, and imported into peroxisomes by the ABC-transporter, COMATOSE1 (CTS1, 4). In the peroxisome, OPDA is activated by OPDA:CoA-ligase and reduced by OPDA-reductase 3 (OPR3, 5) to 3-oxo-2-(2-pentenyl)-cyclo-pentane-1-octanoic acid (OPC-8:0), which is transformed to JA by three rounds of β-oxidation (6). JA is exported to the cytosol by an unknown mechanism (7) where it can be conjugated to isoleucine (Ile) by jasmonate:amino acid transferase (8), forming the biologically active JA–Ile.

localization of AOS and HPL in chloroplasts of leaves [52,83,86]. A plastidial location is implied by the fact that many CYP74-cDNAs encode plastidial transit peptides [65]. 13-HPL was localized in the outer envelope, and 13-AOS was found within the inner envelope of tomato mesophyll chloroplasts [86]. The 13-HPL is constitutively expressed in leaves and during floral development of potato plants, preferentially forming (3Z)-hexenal and (3Z)-hexenol [77]. A deletion in the coding region of the CYP74B2 gene in the *Arabidopsis* Columbia-0 ecotype effectively results in the absence of HPL in this ecotype and limits production of GLVs. Detailed biochemical studies have confirmed the absence of functional HPL activity in the *Arabidopsis* Col-0 ecotype, indicating that HPL activity is dispensable for normal growth and development and not replaced by an alternate enzyme capable of cleaving 13-hydroperoxy LA [87]. In cucumber (*Cucumis sativus*) increases of C_9 aldehydes with wounding have been reported [88].

3.3.3. DES

DES catalyzes the conversion of fatty acid hydroperoxides into divinyl ether fatty acids. DES cDNAs have been isolated from tomato [61], tobacco (*Nicotiana tabacum*) [89], and potato [90]. Whereas the tomato, tobacco and potato enzymes are highly specific for 9-hydroperoxides, another enzyme from garlic (*Allium sativum*) has a preference for 13-hydroperoxide substrates (13-DES) [91]. For DES-derived oxylipins, first hints for a role in defence against plant pathogens such as *Phytophthora infestans* were provided by the detection of increased levels of the conjugated fatty acids, colneleic acid and colnelenic acid, and upon infection of potato and tobacco [89,92–94]. Transgenic lines overexpressing DES are available, but have not been characterized in detail thus far [91].

The evolutionary origin of oxylipin production is closely related to that of CYP74-enzymes. CYP74-enzymes have radiated from ancestral enzymes to exhibit a range of specific activities and, thus, remarkable catalytic plasticity. The observation of multifunctional enzymes indicates that the structural backbone of CYP74-enzymes can support a number of alternative conversions of fatty acid hydroperoxide substrates. For instance, the tomato CYP74C3 not only acts as an allene oxide synthase but can also catalyze allene oxide cyclization or hydrolysis [95]. Based on X-ray crystallography data it has also been demonstrated that few amino acid changes are required to transform an AOS enzyme into an HPL or vice versa, highlighting close structural relations [73]. The involvement in particular of AOS and HPL in the production of jasmonates and GLVs, respectively, suggests that the evolution of these signaling factors may have arisen as a consequence of only small genetic variations. Using bioinformatics tools and biochemical data, it has been proposed that enzymes required for oxylipin biosynthesis were already present in the last common ancestors of plants and animals, but that they were lost in metazoan lineages with only few exceptions [73].
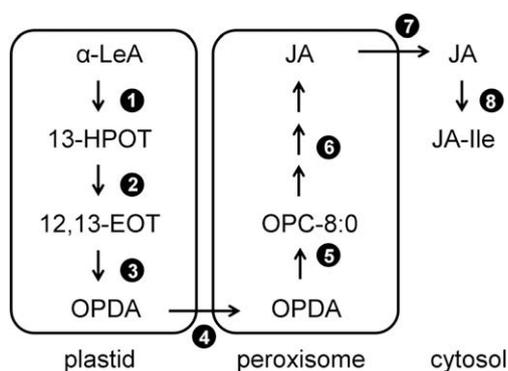
3.4. Dioxygenases

α-DOX catalyzes the conversion of PUFAs to the corresponding 2-hydroperoxy fatty acids, yielding an alternative source of fatty acid hydroperoxides to that presented by LOXs [96]. In *Arabidopsis*, two isoforms of α-DOX have been reported. Studies on the cellular signals mediating the activation of α-DOX1 in *Arabidopsis* revealed that gene expression is induced by pathogens, salicylic acid, intracellular superoxide or singlet oxygen and nitric oxide, three signaling molecules mediating cell death [97,98]. The accumulation of α-DOX2 transcripts was enhanced in leaves subjected to artificial senescence by leaf detachment [99]. So far, α-DOX proteins are not well characterized except the one from rice [100].

3.5. Other enzymes of JA biosynthesis

The octadecanoid pathway employs a number of enzymes that further convert AOS-products into biologically active oxylipins within the plastid and furtheron in the peroxisome (Fig. 2). Allene oxides (allylic epoxides) provided by AOS can either cyclise chemically to cyclopentenones [101,102] or in case of the allene oxide that derives from 13-hydroperoxy α-LeA by enzymatic conversion by allene oxide cyclase (AOC, EC 5.3.99.7), yielding chiral OPDA [103,104] (Fig. 1). Studies by several groups have demonstrated that the biosynthesis of JA involves enzymatic reactions occurring in at least three different compartments (Fig. 2): the conversion of LA to OPDA in the plastid [67,105], the reduction of OPDA to 12-oxo phytoenoic acid (OPC-8) [106–109] and subsequent β-oxidation (i.e., conversion of OPC-8:0 to JA) in peroxisomes [24], and conjugation to amino acids in the cytosol [36].

Although no information is available on the export of OPDA from chloroplasts, recent reports indicate that OPDA is subsequently transported into peroxisomes via the ABC-transporter PXA1/CTS/PED3 also acting in fatty acid import [110] and is activated by a peroxisomal OPDA:CoA-ligase [23,111]. Subsequent reduction of OPDA by OPDA-reductase isoform 3 (OPR3) [112,113] may take place on the OPDA-CoA ester, rather than on free OPDA. In consistence with this observation it has been shown that OPC-8 and OPC-6 can be activated by 4CL-like acyl-CoA-ligases [23,111], suggesting two parallel pathways of activation/conversion in JA biosynthesis. The final steps in JA biosynthesis would require the consecutive action of acyl-CoA oxidases (ACXs, EC 1.3.3.6), a multifunctional protein (AIM1/MFP2, EC 1.1.1.35) with enoyl-CoA hydrolase and β-hydroxyacyl-CoA dehydrogenase activity, and a 3-ketoacyl-CoA thiolase (KAT, EC 2.3.1.16) [114]. A role for ACX1 and KAT2 in wound-induced JA biosynthesis of *Arabidopsis* was suggested based on increased gene expression upon wounding and JA application as well as by a reduction in wound-induced JA formation in corresponding antisense-plants [115]. Expression of enzymes acting in the octadecanoid pathway, including DAD1, LOX2, AOS, AOC, and OPR3, is inducible at least in *Arabidopsis* and tomato by JA, wounding, and pathogen challenge [44,103,116–119], suggesting feed-forward activation to regulate JA biosynthesis. Stress-induced accumulation of JA, likely formed by pre-existing enzymes of the octadecanoid pathway, precedes the induction of genes encoding JA biosynthetic enzymes. Whereas enzymes for JA biosynthesis are generally abundant in leaves of *Arabidopsis*, it has been demonstrated that JA accumulates only after the plants are challenged by biotic or abiotic stresses [37]. To explain this apparent discrepancy, it has been proposed that enzymes and substrates are sequestered, and that rapid substrate-release upon stress may initiate JA formation as discussed above. An alternative explanation is presented by the observation that enzymes of the octadecanoid pathway are post-translationally modified in a stress-inducible manner [103], a field clearly requiring more experimental attention in the future.

4. Conclusions

Cellular functions for oxylipins emerge to be as diverse as the appearances of oxylipins themselves. The biosynthesis of oxylipins is highly dynamic and occurs in both a constitutive mode and as a consequence of various stresses. Oxylipin signals are involved in numerous signaling processes and are, thus, integral components of the plant signaling network. Whereas the biosynthesis, perception and physiological role of, e.g., OPDA or JA are well defined, the relevance of other oxylipins for plant function is only recently becoming apparent. The latest technological advances in the field of oxylipin analysis open the field for non-targeted metabolomic approaches, which may provide further insights into the contributions of little-known oxylipin species in plant function and development.

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