

Plant Oxylipins: an Emerging Advance to Study their Role in Plant Defence Against Diseases incited by Various Plant Pathogens

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ABSTRACT: To meet the needs of the world's population, which is constantly expanding, food security is a significant concern. Crop loss due to diseases is a major concern to overcome this global food security challenge. Plants can develop local or systemic immunity induced by pathogens or certain chemical products known as oxylipins. Plant Oxylipins (POs) are a group of extremely complex and diverse compounds that are produced as a result of oxidation of lipids. Unsaturated fatty acids might first be oxidized by enzymatic or chemical processes. A wide range of alternate processes further convert hydroperoxy fatty acids into a huge number of different oxylipin classes. The presence of oxylipins in complex lipids as esters or as free fatty acid derivatives broadens their structural diversity even more. All biological systems experience lipid peroxidation, which manifests in processes that are controlled during development and in reaction to environmental changes. The oxylipins that are produced may play a variety of biological roles. The POs, such as reactive oxygen species and electrophile species, stimulate defence related gene expression based on their chemical composition. Plants' growth, development, and responses to their environment are all regulated by the oxylipin jasmonate (JA), particularly their defense mechanisms against necrotrophic plant pathogens. The oxylipins that are produced can have a variety of biological purposes, some of which involve signalling. Comprehensive analytical tests are available to determine the oxylipin profiles of plant tissues in order to clarify the functions of oxylipins in a specific biological system. Overall phytooxylipins has a great potential to be used as biocontrol agents, however more research should be done regarding the mechanisms underlying these multifaceted compounds.

Keywords: Plant oxylipins, Biosynthesis, Jasmonic acid, Plant Defence, Lipid peroxidation.

INTRODUCTION

Oxylipins are important compounds in plants, serving important developmental and defensive activities. This class of compounds comprises hydroperoxides, keto acids, hydroxides, oxoacids, divinyl ethers and aldehydes, all formed by oxidation of unsaturated fatty acids (Mosblech *et al.*, 2009). Oxylipins are found in all species in free, esterified or galactolipids, or combined with other compounds (e.g., methyl groups, isoleucine) (Wasternack and Feussner 2018). The precursors of oxylipin production differ by organism, as do the enzymes that oxidise them. Because aerobic biological systems undergo autooxidation, oxylipins (e.g., phytoprostanes) are also synthesized nonenzymatically in the presence of singlet oxygen or ROS (Griffiths, 2015). In 2001, a first oxidised galactolipid was completely described in *Arabidopsis thaliana* (L.) Heynh (Stelmach *et al.*, 2001). Oxylipins are synthesized when oxygenases add oxygen to polyunsaturated fatty acids (PUFAs) and sometimes

monounsaturated fatty acids. Plants have evolved several methods to restrict invasion and growth of possible microbial diseases, both locally (local defence) and in distant tissues (systemic acquired resistance or SAR). Recent findings show that independent receptors of microbial compounds and self-structures can activate diverse plant defences. Thus, the perception of conserved microbial molecules (MAMPs) by pattern recognition receptors (PPRs) triggers MAMP-triggered immunity to stop pathogen invasion. Later, R-gene products recognise specific effector molecules released into the plant cell by invading pathogens, triggering a stronger defence response. Effector-triggered immunity (ETI) is often accompanied by HR and SAR (Zhang and Zhou 2010). Plants have specialised receptors to recognise endogenous signals generated by damaged host structures (DAMPs). Salicylic acid (SA), jasmonic acid (JA), and ethylene (ET) activate plant immunity through known signalling mechanisms (Glazebrook, 2005). Recent progress has showed that hormonal pathways must interact and be coordinated to fine-tune

plant defence against pathogens. Pathogens have evolved methods to regulate hormone synthesis and signalling in order to circumvent plant defensive mechanisms and redirect host metabolism for the purpose of microbial growth and sustenance. This adds another layer of complexity to the situation (Grant and Jones 2009).

Biosynthesis and roles of Oxylipins. Biosynthesis of oxylipins starts when enzymes called lipases break down fatty acids from membrane lipids like phospholipids, MGDGs, and DGDGs. To name a few, linoleic acid (LEA), linoleic acid (LA), and hexadecatrienoic acid (HTA) are all plant substrates for lipoxygenases (LOX), which are enzymes that catalyse the insertion of oxygen into fatty acid chains. These unsaturated fatty acids are also susceptible to oxidation when they are exposed to α -dioxygenases (DOX) (Wang *et al.*, 2018). Enzymes 9- and 13-LOX are regioselective, meaning that they catalyse the oxidation of fatty acids into fatty acid hydroperoxides in a manner that is determined by the oxidation site. Following the oxidation of LA and HTA by 13-LOX, the hydroperoxides 13-HPOT and 11-hydroperoxyhexadecatrienoic acid (11-HPHT) are formed as a result (Griffiths, 2015). These hydroperoxides are substrates for the enzyme allene oxide synthase (AOS), which converts them into unstable allene oxides. After that, those molecules undergo a cyclization process, either naturally or with the help of enzymes, which results in the formation of OPDA and dnOPDA, respectively. To this date, two distinct routes leading from (dn)OPDA to the synthesis of JA have been mapped out (Wasternack and Hause 2013). OPDA and dnOPDA can both be reduced by OPDA reductase 3, also known as OPR3. The products that are generated from this reduction can subsequently be converted into JA through either three or two cycles of β -oxidation, respectively (Ahmad *et al.*, 2016). In the plant species *A. thaliana*, researchers have just recently uncovered a surprising JA synthesis pathway that does not require OPR3. It is possible for OPDA and dnOPDA to access the peroxisome, where they would then undergo either three or two rounds of β -oxidation, respectively. After leaving the peroxisome, the product that was generated undergoes a reduction in the cytoplasm by OPDA reductase 2 (OPR2), which results in the formation of JA (Chini *et al.*, 2018). JA is a member of a family of oxylipins known as jasmonates. This family of oxylipins includes oxylipins that are created enzymatically as a result of the transformation of LA and HTA acid into JA and its derivatives, such as JA-isoleucine (JA-Ile). It has been shown that JA derivatives and some of their precursors have the ability to alter gene expression, which can result in significant changes in both developmental and defence processes. For instance, they play a role in the process of plant defence, the growth of flowers, the ageing of leaves, and the germination of seeds (Ahmad *et al.*, 2016).

The Jasmonates have been the subject of substantial research, and their biological functions were just recently evaluated (Wasternack and Feussner 2018). This enzyme cleaves the C12-C13 link and creates (3Z)-hexenal and (9Z)-traumatol from 13-HPOT, while it produces (3Z)-hexenal and (7Z)-dinortraumatol from 11-HPHT (Nakashima *et al.*, 2013). It was recently discovered that the first products of HPL are hemiacetals, which are unstable molecules that quickly change into aldehydes and oxoacids (Mukhtarova *et al.*, 2018). In addition to producing oxidised derivatives known as divinyl ethers, the sequential action of LOX and divinyl ether synthase (DES) on fatty acids, primarily LEA and LA, results in the formation of fatty acids (Stumpe *et al.*, 2008). The colneleic and colnelenic acids are formed from the 9-hydroperoxides of LEA and LA, respectively, and are considered to be among these substances. The 13-hydroperoxides of LEA and LA, in turn, give rise to the production of etheroleic and etherolenic acids, respectively. Different metabolic pathways allow the hydroperoxide fatty acids to be converted into a wide variety of other chemicals, including epoxides, epox alcohols, ketols, hydroxy fatty acids, and aldehydes, amongst others (Hamberg, 1998) (Table 1). Oxylipins can be divided into two categories, depending on how they were made: reactive electrophile oxylipins (RES-oxylipins), also known as reactive carbonyl species (RCS), and non-reactive oxylipins (Findling *et al.*, 2018). Specific to the, -unsaturated carbonyl moiety, which is frequently present as a component of a cyclopentenone ring, reactive electrophiles have structural similarities. This structure enables them to interact with free thiol groups by Michael addition, controlling the amount of glutathione and the activity of proteins (Knieper *et al.*, 2022).

Cytochrome-P450-dependent mono-oxygenases. Cytochrome-P450-dependent mono-oxygenases are responsible for the oxidation of fatty acids by a single oxygen atom. These mono-oxygenases are also responsible for catalysing in-chain and -hydroxylations of saturated and unsaturated C10 to C18 fatty acids. The recent cloning of fatty-acid hydroxylases from a variety of plant species has shown that these oxidases have different substrate specificities and regulatory patterns than one another (Kahn *et al.*, 2000). It is believed that these enzymes have a role in reducing the potentially deleterious consequences of free-fatty-acid accumulation that might be caused by lipases in the early responses to stressful conditions. This could be the case because lipases are one of the enzymes that could cause this accumulation. On the other hand, very little is known about the roles that these enzymes play in biological processes. Among them, CYP94A1 and CYP86A8 are thought to be involved in the biosynthesis of cutin and in the possible formation of fatty-acid-derived signals, although experimental evidence of such roles is still required (Wellesen *et al.*, 2001).

Table 1: Effective Antimicrobial Free Pos.

Bacteria	Plant Oxylipins									
	u-5(Z)-Etherolenic acid	(G)-cis-12,13-Epoxy-9(Z)-octadecenoic acid	(G)-threo-12,13-Dihydroxy-9(Z)-octadecenoic acid	11(S),12(S)-Epoxy-13(S)-hydroxy-9(Z),15(Z)-octadecadienoate	13(S)-Hydroperoxy-9(Z),11(E),15(Z)-octadecatrienoic acid (13-HPOT)	13(S)-Hydroperoxy-9(Z),11(E)-octadecadienoic acid (13-HPOT)	Colneleic acid	9(S)-Hydroperoxy-10(E),12(Z),15(Z)-octadecatrienoic acid (9-HPOT)	9(S)-Hydroperoxy-10(E),12(Z)-octadecadienoic acid (9-HPOT)	2(E)-Nonenal
Bacteria										
PC	-	-	-	-	-	-	-	-	-	x
P.S	++++	-	-	++	-	+	++++	-	+	++++
Xc	-	-	-	-	-	-	-	-	-	++++
Fungi										
Ab	+++	++	++	x	++	-	-	-	-	++++
Bc	-	-	-	+	++++	-	-	+++	++	++++
Ch	+	+++	+++	-	++++	++++	++++	++++	++++	++++
Fo	-	-	-	-	+	-	+	-	-	x
Lm	++	-	+++	x	++	-	x	-	x	++++
Oomycetes										
Pi	+	-	-	+	-	-	x	-	-	++++
Pp	-	+++	-	-	++++	++++	x	++++	++++	++++

Pectobacterium carotovorum (Pc), *Pseudomonas syringae* (Ps), and *Xanthomonas campestris* (Xc), *Alternaria brassicae* (Ab), *Botrytis cinerea* (Bc), *Cladosporium herbarum* (Ch), *Fusarium oxysporum* (Fo), *Leptosphaeria maculans* (Lm), *Phytophthora infestans* (Pi) and *Phytophthora parasitica* (Pp). +++++, very highly effective; +++, highly effective; ++, moderately effective; +, effective; —, not effective; x, not tested.

Cyclo-oxygenase-like activity. Specific -oxidizing systems are responsible for catalysing the hydroxylation of the carbon to the carboxylic group in fatty acids rather than cytochrome P450s, which are the enzymes that would normally complete the reaction. An oxygenase known as PIOX (pathogen-induced oxygenase) is responsible for the oxidation of unsaturated C18 fatty acids to their corresponding 2(R)-hydroperoxide. This oxygenase was initially discovered in tobacco leaves that had been treated with harpin, which is a bacterial elicitor (Hamberg *et al.*, 1999). PIOX and cyclo-oxygenase both have similar amino acid sequences. Cyclo-oxygenase is the enzyme that catalyses the committed step in the conversion of arachidonic acid to cyclized eicosanoids. PIOX and cyclo-oxygenase share some amino acid sequence identity. Pea -dioxygenase appears to be a bifunctional enzyme, similar to cyclo-oxygenase in this regard (Saffert *et al.*, 2000). In higher plants, fatty acid -hydroperoxides are rapidly reduced into their corresponding alcohols by a reductase. This reaction is in competition with the spontaneous decarboxylation of fatty acid -hydroperoxides into aldehydes containing an odd number of carbons. When it was shown that crude extracts from the leaves of pumpkin, tomato, and rice predominantly synthesised noraldehydes and noracids after feeding pathogen-infected plants with linoleic acid, a link between defence responses and the occurrence of such lipid derivatives was hypothesised. This link was supported by the observation that this crude extract synthesised noraldehydes and noracids (Kato *et al.*, 1994). In addition, the expression of PIOX can be triggered not just by harpin but also by wounding, treatment with jasmonic acid, or even during interactions between plants and insects (Hermsmeier *et al.*, 2001). These pieces of evidence point to a potential involvement for -oxidizing systems in plant defence; however, the precise activities of noraldehydes and 2-hydroxy acids have not been uncovered as of yet.

LOX pathway. LOXs are enzymes that speed up the process of inserting molecular oxygen into fatty acids that have the necessary 1, 4-pentadienyl functionality. For instance, the position 9 or 13 of linole(n)ic acids

(C18:2 and C18:3) are oxidised to yield hydroperoxyoctadecadi(tri)enoic acids. This occurs in the case of linole(n)ic acids. According to Kühn *et al.* 1991, the products of this reaction are capable of undergoing additional transformations at the hands of the same LOXs. For instance, they may be dehydrated to produce ketodienoic fatty acids. However, fatty acid hydroperoxides are primarily substrates for other enzyme systems, and it is the so-called 'LOX pathway' that is responsible for the transformation of these highly reactive molecules into a sequence of oxylipins. The recent cloning of some of these enzymes has shown that they represent a novel family of unique cytochrome P450s known as CYP74. These cytochrome P450s are distinct from the traditional P450s in that they react solely with fatty acid hydroperoxides rather than with molecular oxygen and reductants. Recent spectroscopic studies have indicated that at least two of them share common structural characteristics, and the amino acid sequences of CYP74 members exhibit a significant degree of homology, notably inside the heme catalytic site (Psylinakis *et al.*, 2001).

Esterified oxylipins. *Arabidopsis thaliana* (L.) Heynh was the first plant that had an oxidised galactolipid entirely described in the year 2001 (Stelmach *et al.*, 2001). Since then, a large variety of esterified oxylipins from the same species have been reported. Esterified oxylipins have only been described more recently outside of the *Brassicaceae* family, which raises the question of how wide spread their occurrence is and what biological functions they serve. Despite the fact that a great number of studies have suggested that these compounds might play key roles in the processes of plant defence and growth, their specific biological activities continue to be unknown. Although the existence of plant esterified oxylipins has been known for a considerable amount of time, it has only been during the past two decades that their structures have been properly defined. Only the oxylipin sections of the molecules are often studied following methanolysis or some other procedure that liberates the free oxylipin fatty acid. This is because prior analytical technologies made it very difficult to fully characterise mixtures that

were formed of oxidised complex lipids. In most cases, the whole of the structure was not determined (Fauconnier *et al.*, 2008). Potato cultivars were demonstrated to create distinct profiles of esterified oxylipins when they were exposed to fungal infection in the year 2008. These profiles included colnelic and colnelenic acids, as well as 9-hydroxylinolenic acid (9-HOT) and 13-HOT (Fauconnier *et al.*, 2008). It was demonstrated by Miersch *et al.* (2004) that tomato flower parts contain significant quantities of various esterified oxylipins include HOTs, hydroxylinoleic acids (HOD), ketolinolenic acids (KOT), ketolinoleic acids (KOD), and hydroperoxylinoleic acids (HPODs) (Miersch *et al.*, 2004). Lastly the treatment of tomatoes with avirulent rhizobacterium *Pseudomonas putida* BTP1 causes accumulation of esterified 13-HPOD, 13-hydroperoxylinolenic acid (13-HPOT), 13-HOT and 13-HOD, which are then liberated as free chemicals with *Botrytis cinerea* infection (Mariutto *et al.*, 2014). More recently, the analysis of complex lipid mixtures has become less problematic due to the development of advanced analytical methods such as high-performance liquid chromatography (HPLC)-tandem mass spectrometry (MS/MS) and direct infusion MS/MS (Vu *et al.*, 2012). Despite this, a large number of esterified oxylipins have been described, which has led to a better comprehension of the biosynthetic routes and roles associated with these Oxylipins (Goebel and Feussner 2009). In the case of linolipins, a recent study showed that their production in flax leaves can be induced by 24-epibrassinolide (EPB) (Fedina *et al.*, 2017), a plant steroid hormone implicated in plant stress responses (Lee *et al.*, 2018). Linolipin production following Pectobacterium atrosepticum infection of leaves pretreated with EPB was greatly increased compared to non-treated leaves, suggesting an hormonal regulation of esterified oxylipin production during plant bacterial infection (Fedina *et al.*, 2017).

Functions of esterified Oxylipins. It has been proposed that plant esterified oxylipins are not only employed as a pool of free oxylipins, but that the entire molecule itself might have a direct role to play in the process. Notably, *in vitro* experiments demonstrated that some of them had the ability to inhibit the growth of pathogens, such as arabidopside E with *P. syringae*; however, at the same concentration, MGDG and free OPDA did not have a significant effect (Andersson *et al.*, 2006). Additionally, arabidopsides E and G both inhibit the growth of *B. cinerea in vitro* (Kourtchenko *et al.*, 2007), and arabidopside A possesses direct antifungal activities that are effective against *Alternaria brassicicola*, *Leptosphaeria maculans*, and *Sclerotinia sclerotiorum* (Pedras and To 2017). Arabidopsides A, B, D, and F have the ability to restrict cress root growth. This suggests that plant esterified oxylipins may also play a role in plant development (Hisamatsu *et al.*, 2005). There is evidence that arabidopsides have a role in senescence due to the accumulation of these compounds in *A. thaliana* mutants that exhibit early leaf senescence (Hu *et al.*, 2018). In the same manner, arabidopsides A, B, C, D, and F have an impact on the leaves of *Avena sativa* L., cv. zenshin that promotes senescence. When compared at the same concentration, Parveen *et al.*,

the effect of oxidised DGDGs on inducing senescence is significantly stronger than that of oxidised MGDGs. In fact, oxidised DGDGs are capable of inducing senescence in a manner that is analogous to that of JA, OPDA, and methyl jasmonate, which is a well-known senescence promotor (Shigemori *et al.*, 2011). In addition to this, it has been demonstrated that an OPDA-containing MGDG that was isolated from *I. tricolour* possesses stomatal opening properties in *Commelina communis* L. (Ohashi *et al.*, 2005). The results of all of these investigations point to the possibility of a direct participation of esterified oxylipins in the stress responses and developmental processes of plants. It is possible that some arabidopsides exist in stereoisomer mixtures and that different enantiomers possess different biological activities. This is supported by the fact that arabidopside D was found to be a racemic blend of two enantiomers (Hisamatsu *et al.*, 2005). In addition, arabidopside D was reported to be a mixture of two enantiomers. It has not yet been possible to complete the synthesis of arabidopsides, and the process of esterified oxylipin extraction and purification is still difficult due to the low molecule yields that are achieved. This creates a barrier for the conduct of some biological research, such as the prevention of the growth of plant pathogens, the investigation of the interactions between arabidopsides and plant membrane lipids, and the investigation of the biological activities of various stereoisomers. As was indicated earlier, the formation of oxidised galactolipids in *A. thaliana* most likely takes place in the thylakoid membranes as a result of the oxidation of MGDG and DGDG. According to Kelly *et al.* (2016), lipids of the latter are a key component of photosystems I and II of the light harvesting complex II and are therefore necessary for the process of photosynthesis and the growth of plants. *A. thaliana* mutants that are unable to produce DGDG have a decreased capacity for photosynthesis as well as a changed chloroplast shape, which suggests that lipid integrity is necessary for the proper functioning of the chloroplasts (Lin *et al.*, 2016). It's possible that the creation of arabidopside in these membranes, particularly in response to stress, changes the characteristics of the membrane. Due to the fact that the photosynthetic capacity of chloroplasts carrying arabidopsides has not been investigated as of yet, this gives an interesting opportunity for future research.

Biosynthesis and subcellular localization of esterified oxylipins. There are two primary hypotheses that are being presented to explain the biosynthesis of esterified oxylipins. In the first place, it has been hypothesised that free oxylipins might be synthesised from free fatty acids, and then, they could be esterified into complex lipids. Alternately, fatty acids that have been esterified into complex lipids have the potential to be converted directly into oxylipins (Chechetkin *et al.*, 2009). In general, it is believed that LOX enzymes, which are responsible for the initial step in the transformation of fatty acids into oxylipins, only employ free fatty acids and do not use esterified substrates (Babenko *et al.*, 2017). However, it has been shown that certain LOX can utilise esterified substrates

in vitro. These esterified substrates include phospholipids and galactolipids among others (Meyer *et al.*, 2013). It was demonstrated that LOX1 had the ability to oxidise MGDG (Nakashima *et al.*, 2011). The production of arabidopside due to the fact that arabidopsides are oxidised into MGDG and DGDG, it was initially proposed that these chemicals were formed as a result of the oxidation of plant chloroplast membrane galactolipids (Stelmach *et al.* 2001). The free (dn) OPDA might then be swiftly esterified into chloroplastic MGDG and DGDG, or the unsaturated fatty acids in MGDG and DGDG could be directly converted into (dn) OPDA by the action of LOX, AOS, and AOC. Both of these processes are possible. Notably, the second idea received backing from the finding in 2012 that galactolipid fatty acid chains can be directly oxidised. This was a significant piece of evidence. There was no production of ¹⁸O-labeled arabidopsides from *A. thaliana* leaves that had been cultured in water that had been labelled with ¹⁸O before the leaves were injured. This experiment demonstrated that esterified fatty acids do not undergo the processes of hydrolysis, oxidation, and re-esterification. Additionally, arabidopsides are created rapidly in totally disturbed cells, even in the absence of free fatty acid synthesis; this lends support to the notion that arabidopsides are produced by a mechanism that involves esterification of fatty acids (Nilsson *et al.*, 2012). The oxygenation of fatty acids by LOX is the first step in the formation of OPDA. There are a total of six LOX isoforms in the *A. thaliana* genome, four of which are 13-LOX (LOX2, LOX3, LOX4, LOX6) and two of which are 9-LOX (LOX1, LOX5) (Wasternack and Hause 2013). It is interesting that LOX2 is extensively implicated in the synthesis of (dn)OPDA-containing esterified oxylipin, because the production of arabidopsides A, B, and C in wounded plants is drastically reduced in *Arabidopsis lox2-1* mutants in comparison to wild type plants (Zoeller *et al.*, 2012). It has been hypothesised that this enzyme competes with AOS for esterified fatty acid hydroperoxides. This hypothesis is based on the fact that an increase in HPL expression results in a decrease in the accumulation of arabidopside (Nilsson *et al.*, 2016). These findings are in line with the observation that the wild type strain of *A. thaliana* Columbia 0 produces a substantial amount of arabidopsides despite the absence of any functional HPL expression (Chehab *et al.*, 2008). Finally, given that (dn) OPDA esterified in galactolipids and formed after freeze-thawing in *A. thaliana* are only present as S, S stereoisomers, it was proposed that allene oxide cyclization does not occur spontaneously but rather enzymatically by the action of AOC. This suggests that freeze-thawing triggers the activation of LOX2, AOS, and AOC that are likely already synthesised. Nevertheless, *A. thaliana* possesses four different isoforms of the AOC gene, and it is unknown which one of these isoforms, if any, is responsible for this metamorphosis (Nilsson *et al.*, 2016). There have also been reports of MGDGs that have one oxidised chain and are acylated on the galactose 60 hydroxyl groups. Examples of these include arabidopsides E and G. (Kourtchenko *et al.*, 2007). Rapid production of non-

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acylated (dn) OPDA in *A. thaliana*, containing MGDG and DGDG, occurs in response to stress. Production reaches its peak after approximately 5 minutes. After that, the concentration of those molecules drops, and oxidised acyl MGDGs are generated; they reach their peak approximately 30 minutes after the stress has been applied (Vu *et al.*, 2014). Actually, (dn) OPDA esterified in galactolipids is transferred to the galactose moiety of other MGDGs by acylated galactolipid associated phospholipase 1 (AGAP1), generating OPDA-acylated MGDG. A deletion of the AGAP1 gene in *A. thaliana* results in the inability of the mutants to synthesise either oxidised or non-oxidized acyl MGDGs (Nilsson *et al.*, 2015).

Host–pathogen communication of oxylipins. Host–pathogen recognition relies upon an elaborate multi-molecular communication. In this context, oxylipins—oxidized fatty acids (FAs)—produced in several phyla can regulate numerous events associated with physiological and pathological processes (Fernandes and Ghag 2022). Oxylipins share significant structural and functional similarities across different mammal, plant, fungal, and bacterial taxa, including part of their biosynthetic pathway, structure, function, and modifications. Oxylipins are signalling molecules that play a role in the control of immunity and development in plants. The oxylipins in plants with the best characterization are called jasmonates; these include jasmonic acid (JA), 12-oxo-phytodienoic acid (12-OPDA), and JA derivatives such as methyl jasmonate and JA-isoleucine. Pathogen infection and pest wounding are the best-studied environmental triggers in this context (Gorman *et al.*, 2021). JA and its derivatives act as defence regulators, influencing the reproductive and pathogenetic processes during the interaction with both beneficial and pathogenic microorganisms (Shaban *et al.*, 2021). Oxylipins regulate quorum sensing, among other things, in bacteria and fungi. According to Martinez *et al.* (2019), the "oxylipin regulation system" in fungi and bacteria can use host oxylipins to increase pathogenicity (e.g., toxin production is increased or the organism enters the biofilm stage) and change the rate of reproduction in host tissues by sporulation (Scarpari *et al.*, 2014). The defence mechanisms of plants are impacted by bacterial oxylipins. These characteristics provide validity to Niu and colleagues' (Niu *et al.*, 2020) theory that oxylipins may function as "words" in the lipid common language in host-pathogen communication with a paracrine action. Since both actors will create the same molecules at the same time, it is difficult to distinguish between those produced by the host and those by the pathogen. Oxylipins play a relevant ecological role for the producers (i.e., plants, fungi, and bacteria) and their interspecific interactions (Beccaccioli *et al.*, 2021). In plant–pathogen interactions, plants (the host) produce oxylipins to systemically signal pathogen attack, mounting an efficient defense system and interfering with pathogen growth and reproduction (Scarpari *et al.*, 2014).

Effectiveness of oxylipins as Signalling Molecules in Plant Defence Mechanisms. Plant oxylipin signatures are affected by the type of stressor, the plant species being stressed, the organ or organs that are affected,

and the lifestyle of the pathogen (Wasternack and Feussner 2018). For example, tobacco (*Nicotiana tabacum*) leaves that have been infected by the hemibiotroph *Pseudomonas syringae* accumulate high levels of α -dioxygenase (α -DOX) and 9-lipoxygenase (LOX) products (Hamberg *et al.*, 2003). In contrast, certain potato cultivars that have been infected by *Phytophthora infestans* and tomato (Jones *et al.*, 2006). The presence of phytooxylipins and reinforced epidermal walls in the tolerant cultivar suggesting a mechanism for disease tolerance against *Phytophthora sojae* in soyabean, when compared with susceptible cultivar. The pathogen-associated molecular pattern (PAMP)-triggered immunity (PTI), which functions as a basal resistance, is the first phase of the immune response. After then, infections will release effectors that will prevent PTI from working. Effectors are recognised, and as a result, effector-triggered immunity results in significantly increased disease resistance (ETI). Systemic acquired resistance (SAR), also known as broad-spectrum resistance, has now been activated, and this will keep the plant on high alert and ready to defend itself against new threats for the next few weeks to months (Zhang *et al.*, 2018). Elicitors are another way that SAR can be activated. The scientific literature is replete with articles on oxylipins' roles as signalling molecules in plant defence mechanisms, and numerous research offer evidence for a robust relationship between phytohormones (Koo, 2018). Because they are so quick to accumulate in injured plants, JA and its derivatives, which are known as jasmonates, are the LOX-derived metabolites that have been studied the most (Howe, 2018). JA plays an important part in the process of systemic wound signalling. It is possible for methyl-JA to be emitted as a volatile organic chemical in plants in order for them to communicate with one another, either within their own species or with other species (Yan and Xie 2015).

Biocidal properties of oxylipins. The biocidal effects of Plant Oxylipins (Pos) may be due to a number of potentially deadly mechanisms, including membrane pore development, membrane destabilisation, denaturation of protein or nucleic acid, or oxidative bursts. In vitro tests significantly demonstrated that 2(E)-hexenal possesses the highest efficiency among POs, with an activity similar to that of a detergent that causes severe damage to membranes and cell walls (Ma *et al.*, 2017). This kind of behaviour is often seen in reactive electrophile organisms (RES). By analogy with ROS, the term RES was given to molecules that contain an α,β -unsaturated carbonyl group and that accumulate in diseased and damaged plant tissues. This was done in order to differentiate them from ROS. In modern times, this word is also used for molecules such as FA ketodienes, ketotrienes, and OPDA. This is because alternative chemical configurations can give molecules electrophilic characteristics (Farmer and Mueller, 2013). It has been shown that RES in plants that have been infected by a pathogen will both increase the production of genes involved in defence and directly change proteins (Farmer and Mueller 2013). For instance, Muller *et al.* (2017) found that OPDA was shown to bind cyclophilin 20-3 (CYP20-3), which is a

binding protein that modulates stress-responsive cellular redox homeostasis. It is widely known that an excessive amount of electrophilic molecules produced by a cell can interfere with normal cellular functioning and, in the long run, lead to the death of the cell. This is true regardless of the defence mechanism employed by the cell (Farmer and Davoine 2007).

In terms of its chemical structure, the PO family is quite versatile, and it contains a large number of geometric isomers. According to Graner *et al.* (2003), various biological effects can be produced by isomers of the same oxylipin structure but with different regioisomers. Changes made to the hydroxy or epoxy groups of the corresponding oxylipins can have a significant impact on the biological activity of those oxylipins. Even HPOD and HPOT, which are only differentiated from one another structurally by a single double bond, display strikingly dissimilar antibacterial activities. On the other hand, it was not evident what the difference was between the 9- and 13-forms in terms of the suppression of the growth of pathogens; nonetheless, linolenic acid (LnA) products appear to be more efficient than LA products (Prost *et al.*, 2005). In addition, epimerization is a straightforward process that controls hormone action. It does this by changing the active form of bioactive (+)-7-iso-jasmonoyl-L-isoleucine into its inactive counterpart, JA-Ile (Fonseca *et al.*, 2009).

Are Membranes Active Actors or Passive Filters in PO Biocidal Activity? It is still unclear how POs contact and interact with plant cells or pathogens after being released into cellular compartments, despite the fact that hundreds of studies have investigated PO biosynthesis. Recent research has shown that HPOs are able to interact with biomimetic plant plasma membranes (PM) in a lipid-dependent manner. This interaction takes place when the HPOs affect the lateral organisation of the domains (Deleu *et al.*, 2019). It would appear that the chemical structure and, more specifically, the conformation of HPOs are involved, which points to the existence of a structure–activity link. These findings prompt the question of where the antibacterial properties of POs come from and whether or not and how POs interact with the infectious agent PM. Because of their amphiphilic character, HPOs are able to interact with PM lipids, which may be another factor that contributes to their central involvement in plant defence. Other amphiphilic compounds, such as lipopeptides, have been shown to have direct biocidal activity. This property of their appears to be directly linked to their capacity to interact with the lipid component of biological membranes and, as a result, to affect membrane characteristics (Sarwar *et al.*, 2018). It has been observed that biomimetic membranes are sensitive to lipopeptides in a manner that is reliant on the lipid composition as well as the organisation of the lipids, which confirms the critical role that lipids play in these interactions (Henry *et al.*, 2011). By similarity with chemical structure and amphiphilic qualities, we can expect the same behaviour for HPOs along with other POs that interact with bacterial or fungal membranes. This is because amphiphilic properties allow molecules to interact with both hydrophobic and

hydrophilic surfaces. It is clear that the organisation and dynamics of the PM ensure clear communication, which in turn governs important physiological processes. Both the composition and the organisation of the PM are incredibly complicated, and the PM has a strong asymmetrical distribution. However, despite the obvious fact that lipids continue to play a significant role as key regulators, the mechanisms by which lipids are built in the PM are still the subject of ongoing research (Gronnier *et al.*, 2018). In both plants and mammals, lipids have frequently been suggested to play a role in the regulation of reproductive development, secondary metabolism, and the growth of pathogens (Siebers *et al.*, 2016), as well as in the attenuation of stress responses, immune signalling, and inflammatory processes (Okazaki and Saito 2014). Emerging lines of evidence suggested that the functions of FA were connected to alterations in the lipid content of membranes and the regulation of fluidity (Walley *et al.*, 2013). Because the only thing that sets HPOs apart from each other is the presence of an extra highly reactive hydroperoxide function, it is safe to presume that their behaviours are analogous to one another. More research needs to be done in order to discover which lipid patterns are typical of infectious diseases caused by pathogens and which ones are unique to each of those diseases. It is possible that monocotyledons and dicotyledons interact differently with their membranes in different ways. This is due to the fact that the lipid compositions of different plant species are exceedingly diverse. In addition, the participation of membrane receptors, whether proteic or not, has not been ruled out as a possibility. Recent research has uncovered oxylipin plant transporters, such as the AtJAT1/AtABCG16 transporter in arabidopsis. This transporter demonstrates an unexpected dual localization in both the nuclear envelope and the PM of the plant (Li *et al.*, 2017). It does this by managing both the cellular efflux of jasmonate and the nuclear import of jasmonate-ile, which is how it controls the cytoplasmic and nuclear partitioning of jasmonate phytohormones. For this reason, the upkeep of a critical level of nuclear JA-Ile concentration is absolutely necessary in order to activate JA signalling. In the meantime, fresh research has shown that GLUCOSINOLATE TRANSPORTER-1 (GTR1) is another transporter in arabidopsis that is responsible for JA and JA-Ile transfer (Ishimaru *et al.*, 2017). These investigations shed insight on new mechanisms for the control of hormone signalling, and it is possible that many additional transporters will be identified in the years to come.

Role of jasmonic acid during programmed cell death and defence. Jasmonic acid (JA) has special roles in plant defence and developmental processes. Pioneering research from Zenk's lab has demonstrated that a number of fungal infections and elicitors enhance JA accumulation in cell cultures of *Petroselinum hortense*,

Eschscholtzia californica, *Rauwolfia canescens*, and *Glycine max* (Muller *et al.*, 1993). It's interesting to note that JA also builds up when plants are exposed to UV light or high temperatures (Herde *et al.*, 1996), highlighting the crucial function that JA plays in the suppression of both biotic and abiotic signaling. Recent studies have demonstrated that JA is produced in response to singlet oxygen as well. Reactive oxygen species (ROS), which are produced during oxygenic photosynthesis, include singlet oxygen as one of its major forms (Muhlenbock *et al.*, 2008). Singlet oxygen harms the plant in the same way as other kinds of ROS. Higher plants have evolved defenses against ROS so that, under normal growth conditions, equilibrium between ROS generation and scavenging is reached (Foyer and Noctor 2000). Additionally, Chl's biosynthetic pathway is strictly regulated (Mock *et al.*, 1998). Chl production stops at the stage of protochlorophyllide (Pchl_{id}), the first precursor of chlorophyllide, when angiosperms grow in dark environments (Chl_{id}). Pchl_{id} is transformed to Chl_{id} and the block in the production of 5-aminolevulinic acid only after illumination. Numerous genes with varied responses to singlet oxygen have been found through transcriptome analysis (op den *et al.*, 2004). Singlet oxygen decreased the expression of genes for photosynthetic proteins (op den *et al.*, 2004). BONZAI (BON) 1, BON1-ASSOCIATED PROTEIN (BAP) 1, EDS 1, and genes encoding enzymes involved in the production of ethylene and JA, two essential components of stress signaling in higher plants, are among the genes that were increased by singlet oxygen (Kendrick and Chang 2008). JASMONATE RESISTANT 1 (JAR1) conjugates JA with isoleucine to form jasmonoyl-isoleucine (JA-Ile), which binds to the coreceptor complex consisting of the F-box protein coronatine-insensitive 1 (COI1) and a repressor jasmonate-ZIM domain (JAZ) protein. The recognition of JA-Ile frees important transcriptional regulators like MYC2 from JAZ repression, which eventually triggers defence responses such the manufacture of specialised metabolites (Nguyen *et al.*, 2022). While JA-Ile is the most common and effective bioactive form of JA, other JA conjugates, mostly with hydrophobic amino acids, have been discovered (Delfin *et al.*, 2022).

Methods for the Determination of Oxylipins. Among the various analytical tools used for the determination of oxylipins, tandem MS/MS instruments have recently become the most popular, due to their high sensitivity when analyzing the levels of these compounds in biological samples (Gabbs *et al.*, 2015). UHPLC, on the other hand, provides the highest resolution, speed and sensitivity in oxylipin analyses. The development of this type of instrumentation significantly facilitates operation, speeds up the analysis, and also ensures better selectivity and sensitivity, as well as lower detection limits (Table 2).

Table 2: Methods for the analysis of general lipid peroxidation and oxylipin profiles.

Method		Analytes	Equipment	References
Indirect	Thiobarbituric acid-reactive-substances (TBARS) assay	Malondialdehyde	Spectrometer (+/- HPLC)	Hodges <i>et al.</i> (1999)
Evaluation of lipid peroxidation	Aldehyde assay	4-Hydroxy alkenals	HPLC/DAD or MS; GC/MS	Esterbauer and Zollner (1989)
	Thermal decomposition	Volatile alkanes (ethane and n-pentane)	GC	Degousee <i>et al.</i> (1995)
	FOX2 assay	Lipid hydroperoxides	Spectrometer	Griffiths <i>et al.</i> (2000)
	Autoluminescence imaging	Spontaneous photon emission	(Cooled) charge-coupled device cameras	Havaux <i>et al.</i> (2006)
Identification and quantification of oxylipins	Oxylipin profiling/ "oxylipin signature"	Oxylipins	HPLC/DAD and GC/MS	Stumpe <i>et al.</i> (2005)
	Profiling of volatile organic compounds (VOCs)	VOCs	VPE arrangement, GC/negative CI-MS	Müller <i>et al.</i> (2006)
	Identification of Arabidopsides	Arabidopsides	ESI-MS(/MS) and NMR	Andersson <i>et al.</i> (2006)
	Non-targeted metabolite profiling	Jasmonates and Arabidopsides	UPLC/TOF-MS (pseudo-MS/MS)	Glauser <i>et al.</i> (2008a,b)

CONCLUSION AND FUTURE SCOPE

Plant polyenoic fatty acids, whose traditional functions were limited to the modification of membrane structures and functions and to serve as energy storage forms, are now widely regarded as lipid bioregulators that mediate cell responses to extracellular signals after their release from membranes and oxidative transformation into oxylipins. These oxygenated fatty acids, which are mostly derived from linole(n)ic acids, have important roles in plant defence systems, particularly as components of defence barriers (like cutin), as toxins (antifungal and antibacterial compounds), or as signal transduction mediators (e.g. jasmonates). Interactions between plants and pathogens set off a complicated chain of events that involve specific receptors, signaling pathways, changes in extracellular pH and membrane potentials, activation of several phosphorylase and kinase cascades, and eventually result in various defence responses. During plant-pathogen interactions, lipid metabolic pathways and plant lipids are critical, and several modifications in membrane lipids are known to take place at the infection site. In addition, lipids and their by-products are released from membranes and serve as signal molecules to activate plant defense responses. Oxylipin biosynthesis is extremely dynamic, occurring both naturally and in response to various stresses. Therefore, much more research is required to comprehend the diversity of oxylipins originating from plants, their unique functions in physiological processes, and the mechanisms of oxylipins' early signaling. It is worthwhile to investigate the potential of these metabolites as biotic stress defence agents as well as their function in enhancing plant tolerance and resistance mechanisms. In order to better understand how oxylipins operate during plant-pathogen interactions and in biotically stressful environments, focused metabolomics and lipidomics investigations are important.

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