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Review

Mechanisms of Plant Natural Immunity and the Role of Selected Oxylipins as Molecular Mediators in Plant Protection

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Abstract: Weed resistance to herbicides should be minimized, as this can lead to serious limitations in the food security for people around the world. The aim of the research was to summarize the latest research on the reactions of plants to pesticides, including herbicides, in order to assess the possibility of using jasmonates and brassinosteroids to stimulate the natural, induced systemic immunity of plants, as well as outline the possibility of the interaction of oxylipins with ethylene, salicylates and other compounds. Multiple types of resistance correspond to developed mechanisms of resistance to more than one herbicide, and this resistance has been induced by selection processes. Activation of the mechanisms of systemic immunity depends on the reception of extracellular signals, and their transduction between individual cells of the plant organism. Jasmonic acid (JA), as well as its methyl ester (MeJA), ethylene (ET), salicylic acid (SA) and methyl salicylate (MeSA), are key plant growth regulators that play a fundamental role in this process. JA and ET activate the mechanisms of induced systemic immunity (ISR), while SA determines the acquired systemic immunity (SAR). JA, MeJA and OPDA belong to the family of oxylipins, which are derivatives of linolenic acid (CLA), and are a group of active signaling molecules that are involved in the regulation of many physiological processes, including those that are related to herbicide resistance. Understanding the signaling mechanism in oxylipins, and mainly brassicosteroids (BRs) and jasmonates (Jas), would allow a better understanding of how immune responses are triggered in plants.

Keywords: brassinosteroids; crop management techniques; high temperature stress; phytohormone effects; jasmonates; stress response mechanism

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1. Introduction

The over-reliance on herbicides to reduce weed infestation in crops has led to the rapid evolution of herbicide-resistant (HR) weeds. Increased awareness of herbicide resistance, and the adoption by farmers of a variety of weed control tactics, are essential in HR weed management. It should include best management practices, in order to prevent HR weeds from evolving and spreading [1]. Since the late 1950s, when the first cases of weed resistance to herbicides (HR) were observed, more than 500 unique cases have been reported in non-cultivated land, and more than 100 cases in various crops, in more than 70 countries, in more than 260 species that weaken the effectiveness of more than 160 herbicides, or in more than 100 cases in 20 locations of their operation (APS). With the current high rate of growth in the number of weed species, especially glyphosate-resistant, main field crops with herbicide resistance, HR weeds now occupy a significant part of the global crop area [1,2]. Hence, research is now directed at protecting herbicide-tolerant weed crops through biochemical, genetic and crop control strategies.

Oxylipins are biologically active molecules that are formed in all aerobic organisms enzymatically, or as a result of the action of free radicals and reactive oxygen species. They are very important lipid mediators that are made of polyunsaturated fatty acids (PUFA), such as the following: arachidonic acid (ARA), eicosapentaenoic acid (EPA), docosahexaenoic acid (DHA), linoleic acid (LA) and also α-linolenic acid (ALA) [2,3], in reactions that are catalyzed by cyclooxygenase (COX), cytochrome P450 (CYP 450), lipoxygenase (LOX), and also through non-enzymatic oxidation pathways [4,5]. The use of herbicides in arable crops triggers the phenomenon of selection. The susceptible plants are killed, while the herbicide-resistant plants can survive, and reproduce without competition from herbicide-sensitive plants [6]. If the herbicide is used continuously, resistant plants successfully reproduce and become dominant in the population. Consequently, the evolution of herbicide resistance will increase in the population. After the herbicides enter the plant, they are transported to the site of activity. This transport can take place both in inanimate tissues (apoplast, e.g., cell walls, xylem) or living tissues (symplast, e.g., cellular plasmolemma) [5,7].

Current research has focused mainly on the biosynthesis of the plant JA signaling molecule, and its role in the regulation of developmental and conservational processes [8,9]. Recent genetic studies indicate that the metabolic precursors of jasmonate are active as signals in themselves, and that their synthesis and perception are critical to the induced systemic defense response [10]. The biological importance of oxylipins in plants is comparable to the eicosanoid family of lipid mediators in animals [11,12]. Oxylipins belong to the family of oxidized natural products that are formed from fatty acids, in processes involving the steps of oxygen-dependent oxidation [13–15]. The bioactive acetylene oxylipins C17 and C18 usually contribute to the anti-inflammatory, cytotoxic and potential anti-cancer properties of herbaceous plants. Oxylipins are widely distributed in plants of the *Apiaceae*, *Araliaceae* and *Asteraceae* families, and induce cell cycle arrest and/or cancer cell apoptosis in vitro; moreover, they have a chemopreventive effect on cancer development in vivo. Bioactive acetylene oxylipins C17 and C18 are a group of promising compounds that lead to the development of pesticides of plant origin [9,14,15].

Oxylipins are involved in a variety of biological processes, but most of all, they are important in the regulation of metabolism in plants. The ability of oxylipins to act as a molecular mediator is due to their association with peroxisome proliferator-activated receptors (PPAR), docosahexaenoic acid (DHA), linoleic acid (LA) and ALA [1–3], in reactions that are catalyzed by cyclooxygenase (COX), cytochrome P450 (CYP 450), lipoxygenase (LOX), as well as via non-enzymatic oxidation pathways [4,5] and G protein-coupled receptors (GPCRs) [16,17]. The enormous heterogeneity of oxylipins, their presence in low concentrations, as well as the appearance of many structurally similar forms of oxylipins, make their qualitative and quantitative determination difficult as a result of the low sensitivity of traditional assay methods. It is important to reduce oxidation, photodegradation, or thermal degradation of oxylipins during the determination and handling of samples [17].

The value of oxylipins for plant organisms is comparable to the value of eicosanoids in animals and humans. Oxylipins are involved in the regulation of inflammation, cell adhesion, migration and proliferation, angiogenesis and other hormonal regulations, being the so-called "local hormones" [16]. Shipelin and Sidorova [18] hypothesized that the molecular structure of oxylipins allows them to be positioned as adaptogens, and justifies the use of plants as potential sources of oxylipins in plant protection. The aim of the study is to provide an analytical review of publications that have characterized the adaptogenic potential and sources of oxylipins (plant, cyanobacterial and algae). Numerous publications from recent years mention the growing interest in oxylipins in plants, cyanobacteria and algae. In just mushrooms and higher plants alone, about 150 oxylipins and their derivatives have been discovered. Among the plant sources of oxylipins, of particular interest are the following: Peruvian poppy root (*Lepidium meyenii*), white briony (*Bryonia alba* L.), licorice (*Glycyrrhiza glabra*), and blackcurrant seed oil (*Ribes nigrum*). Some of the macroalgae are able to synthesize various oxylipins via enzymatic or non-enzymatic means, including anti-inflammatory leukotrienes, prostaglandins and resolvins [18,19].

There are approximately 67,000 species of weeds, pathogens and invertebrates in the world that pose a great challenge to agriculture. Together, these organisms cause 40% of global food losses [20], despite the use of plant protection products. Weeds are considered to be the best known and harmful crop reducers [21]. Potential losses caused by weeds are estimated at 34%, and they are significantly higher than those caused by invertebrates [18%] or pathogens [16%] [10,22]. Losses caused by agricultural pests in developing countries account for 40–50%, and are much greater compared with 25–30% of the losses in developed countries [20]. These losses are predicted to increase further in the coming future, due to the globalization of trade, agricultural intensification and climate change [23]. Weeds are, therefore, the most important biotic factor that influences plant production. Preventing crop losses that are caused by weeds is crucial to maintaining global food security [20–23]. In the case of herbicide-resistant weeds that are found in cereals, eighteen cases of herbicide-resistant bracts in eleven different countries have been reported in Europe, with the majority of cases from the Czech Republic, Germany and Poland [24,25]. Biotypes are resistant to inhibitors of acetolactate synthase (ALS), photosystem II and acetyl coenzyme-A carboxylase (ACCase), and exhibit single-, cross- and multiple resistance. Weed-resistant biotypes have been proven to be better adapted to changing and difficult environmental conditions. Therefore, their population increases rapidly in successive growing seasons. In Poland, biotypes of weed resistance to ALS inhibitors, mainly chlorsulfuron and iodosulfuron, are extremely common, especially in the northern, western and central part of the country [24–27]. Currently, 514 unique cases of herbicide secondary resistance [species × site of action] have been reported worldwide, in the case 267 plant species [154 dicots and 113 monocots]. Thus far, weed resistance to 165 different herbicides has been observed, including twenty-three of the twenty-six known sites of herbicide action. Herbicide-resistant weeds have been reported in ninety-seven crops, in seventy-two countries [12,19,28].

Landing page resistance can occur as a result of changes in the biochemical sites of the action of one herbicide. Inappropriate resistance occurs through mechanisms that reduce the number of herbicide molecules and reach their target site [29]. In major field crops, synthetic herbicides are used to control weeds worldwide. Cross-resistance can occur with herbicides from the same or different herbicide families, and with the same or different sites of action. Multiple resistance refers to the evolved mechanisms of resistance to more than one herbicide (e.g., resistance to inhibitors (ALS) and (ACC), and this resistance has resulted from separate selection processes). Currently, weed resistance has been transferred to 161 different herbicides, covering twenty-three of the twenty-six known herbicide sites [19,20,28–36].

We can protect crops that are associated with herbicide tolerant weeds through biochemical, genetic and crop control strategies. The "European Green Deal" forces producers to change their approaches to plant protection; hence, this paper emphasizes the importance and advantages of enhancing the natural resistance of plants to pests, with particular emphasis on the importance of oxylipins in plant protection. Hence, the aim of this paper was to summarize the latest research on the reaction of plants to pesticides, including herbicides, in order to assess the possibility of using jasmonates and brassinosteroids to stimulate the natural, induced systemic immunity of plants, as well as investigate the possibility of the interaction of oxylipins with ethylene, salicylates and other compounds.

2. Methodology

In order to demonstrate the importance of bioactive compounds of the oxylipin type [PO], and to fully assess the entire context, a quantitative analysis of the rich scientific literature was carried out, indicating a great interest in these compounds due to their very beneficial properties and protective effects. The search for this group of bioactive compounds and their relationships with plant health and productivity was carried out using the Scopus database. The Scopus online database [37] was used to search for bibliometric data, using the TITLE-ABS-KEY [bioactive compounds and plant protection] search. All

of the publications that mentioned these words or their derivatives in the title, abstracts or keywords, were then identified in the search strategy [38]. The functions of the Scopus internet platform under the name 'Analysis' and 'Create a citation report' were used for key analyses. Complete records and cited references were exported to VOSviewer for additional processing. Then, the terms that were used in the titles of papers, abstracts of publications and keywords were analyzed using VOSviewer [38]. As a result of the search, one hundred and twenty publications from the period between 1990 and 2022 were considered.

3. Building the Natural Resistance of Plants

Plants have excellent strategies that use many constitutive or induced anatomical, molecular and biochemical defense mechanisms (Figure 1).

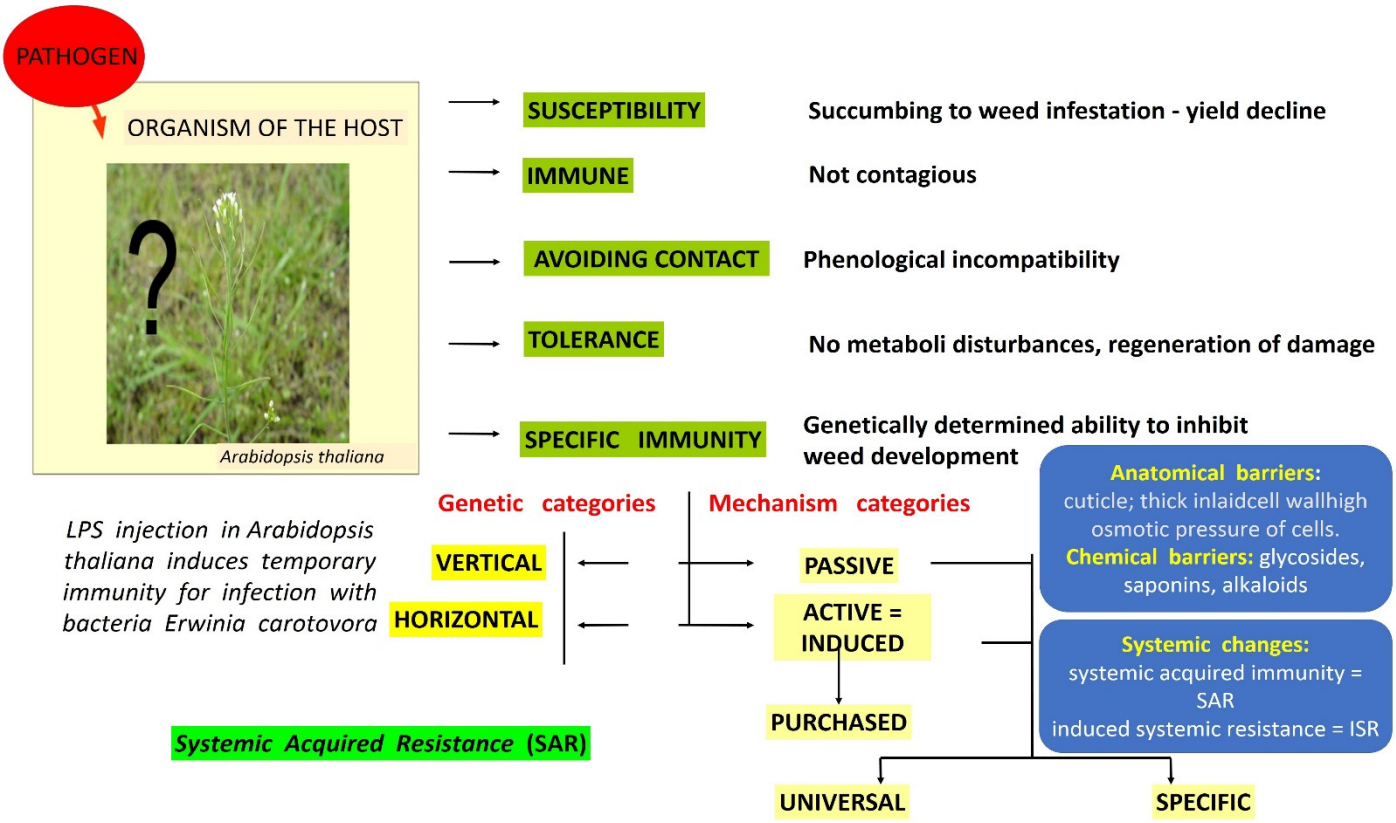


Figure 1. Plant resistance to biotic and abiotic factors. Source: own.

Induced immune responses are triggered in response to a direct, sudden attack by a pathogen, injury or contact with a trigger molecule, or elicitor. They are a signal for the mobilization of the defense system in the whole plant, and the appearance of so-called systemic resistance. There is systemic induced resistance (ISR—induced system resistance) that is triggered by contact with non-pathogenic organisms or synthetic elicitors, and systemic acquired resistance (SAR—system acquired resistance), as a result of prior contact with the pathogen. However, as a result of the emergence of new data, this division is being systematically modified. Higher plants do not have specialized, mobile immune cells or antibodies; however, they are able to effectively defend themselves against the attack of pathogens, since in the case of plants, almost every cell triggers an effective defense response as a result of the effective functioning of the immune system. Constitutive defense mechanisms protect the entire plant passively, through the following: physical barriers, such as the cell wall and the cytoskeleton; waxes (composition) on the surface of the plant; and secondary metabolites that are produced constitutively, e.g., saponins (Figure 2).

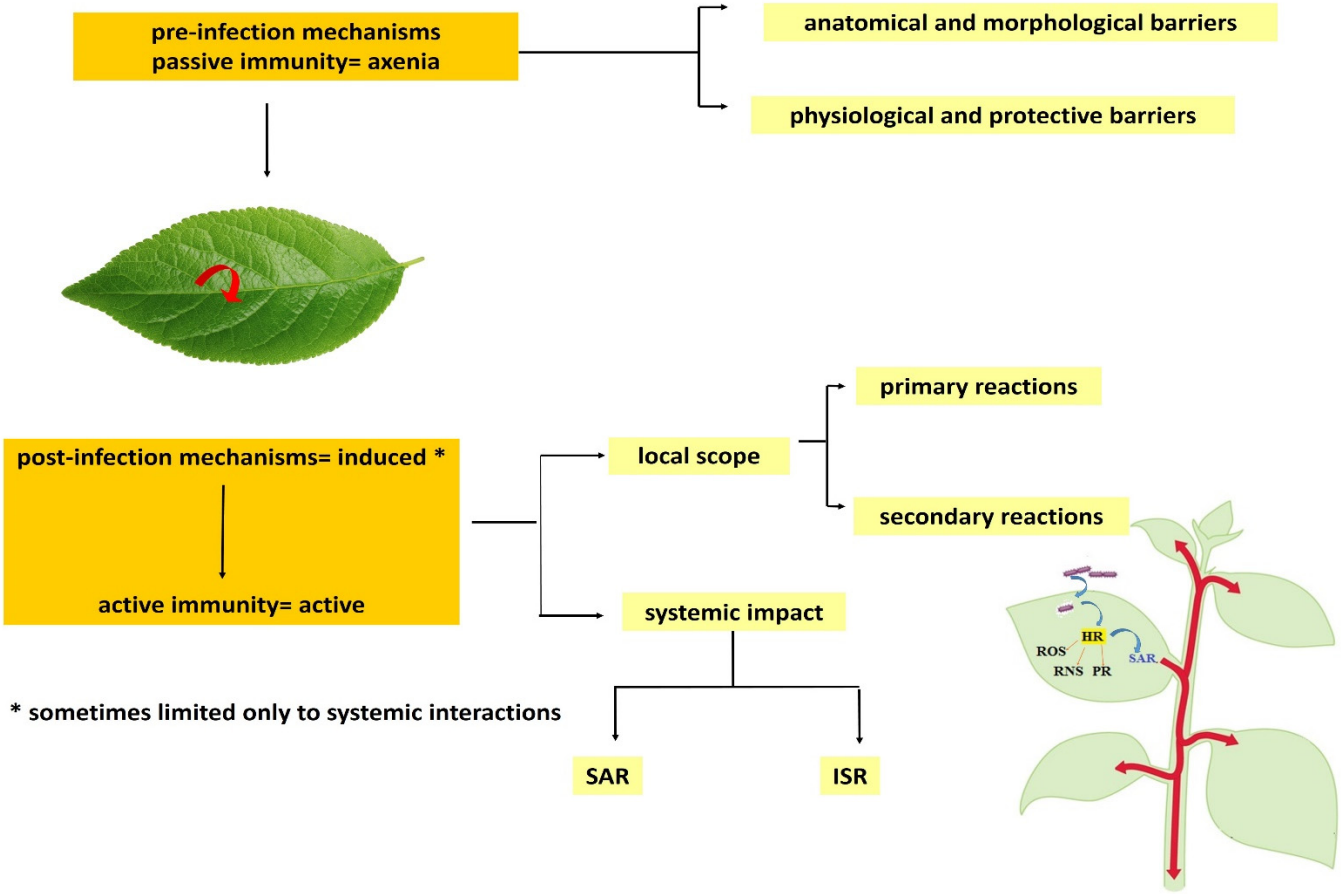


Figure 2. Induced and active immunity. Source: own.

One of the models that describes the immune system of plants is the zigzag model presented by Jones and Dangle, which concerns two levels of resistance. Induced defense mechanisms defend the plant against both host and non-host pathogens, and are induced by the appearance of attendant signals that are related to the presence of pathogenic organism-elicitors [28,39]. This model was the first to demonstrate the complex interplay between plants and their pathogens, and is extremely useful.

Jons and Dangle's [39] zigzag model shows the successive steps in plant-pathogen interaction. First, it presents pathogen-related molecular patterns (PAMPs). They are recognized by plant transmembrane PRR receptors, which allow for the emergence of molecular pattern-induced immunity (PTI); finally, the activation of a defense reaction occurs. In the next phase, the infectious pathogen provides effectors that either interfere with PTI, or enhance the nutrition and spread of the pathogen, ultimately leading to the development of sensitivity (ETS). Only in the third phase of this process can effectors become avirulence factors (avr), when the plant already has the appropriate resistance proteins (R). Recognition of the immune effector by the R protein activates a specific immune effector trigger (ETI), which leads to the development of a hypersensitivity reaction (HR). In the next phase, the pathogen may gain a new effector, e.g., in horizontal gene transfer, which may reduce an ETI. In response, selection may favor new plant R alleles whose products recognize the new effector, again leading to the activation of the ETI [28,39].

3.1. Resistance of Weeds to Herbicides

Weed herbicide resistance is arguably the most important research area in the field of weed science, which results from the excessive and one-way use of active substances in herbicides. As a consequence, individuals that contain resistance genes are selected from

the weed population, which results in the depletion of the genetic pool of agro-ecosystems, and in an increase in the costs of eliminating resistant weeds [2,24].

The use of herbicides in arable crops triggers the phenomenon of selection. Susceptible plants are killed, while herbicide-resistant plants can survive and reproduce without competition from herbicide-sensitive plants [6]. If the herbicide is used continuously, resistant plants successfully reproduce and become dominant in the population. After the herbicides enter the plant, they are transported to the site of activity. This transport can take place both in inanimate (apoplast, e.g., cell walls, xylem) or living tissues (symplast, e.g., cellular plasmalemma) [6,7]. The movement of herbicides can take place over short distances (activity in living cells close to entry), as well as over longer distances, through the vascular system of plants [17,40].

Herbicide resistance may result from several mechanisms, among which loss of target site sensitivity appears to be the most important. Weeds may be resistant to one specific herbicide, which is called simple or single resistance. Resistant biotypes may also have a mixed (cross) resistance to at least two herbicides, with the same mechanism of action, but with different chemical structures. However, our knowledge of specific DNA changes that confer resistance at non-target sites is still in the early stages [2,22]. Currently, there is also so-called multiple resistance, consisting of the insensitivity of a specific weed biotype to at least two herbicides from different chemical groups, and with different mechanisms of action.

Numerous resistance-conferring mutations in weeds have been identified from dozens of weed species, and now include nine herbicide target sites in chronological order, such as the following: D1 protein (atrazine), acetolactate synthase (chlorimuron), tubulin (trifluralin), acetyl CoA carboxylase (clethodim), 5-enolypyruvylshikimate-3-phosphate synthase (glyphosate), phytoene desaturase (fluridone), protoporphyrinogen, oxidase (glufosinate), and auxin receptor (2,4-D) [2,6,7,10,21,22]. Beckie [2] has provided the most recent update of the new mutations that have recently been identified for each of these nine targets. He believes that "new mutations" are those that trigger an amino acid change that has not been previously reported in any of the weed species. Although it has already been observed that gene duplication events confer resistance to groups 1 and 9 herbicides, the basic genetic mechanisms of resistance evolution lie outside the corresponding target coding region.

The International Herbicide-Resistant Weed Database [12] presents the numbers of species that are resistant to each site of action. As many species have developed resistance to more than one site of action, the sum total represents the unique cases of resistance, not the number of species. Thus far, over 514 species of weeds that are resistant to various active substances have been identified. Of these, 268 are dicotyledons, and 246 are monocotyledons. In the world, the greatest number of biotypes (as many as 170) show resistance to acetolactate synthetase (ALS) inhibitors. Herbicide-resistant weeds have been found in ninety-three crops in seventy-two countries [12,41–44]. There are biotypes of weeds that are known to have naturally developed resistance to triazine herbicides, by mutating the D1 protein gene [44]. This resistance can also be due to the rapid degradation or conjugation of herbicides. Glutathione-S-transferase and cytochrome P450 monooxygenase are the main enzymes that are involved in these processes [24,45].

In nature, we can encounter cross resistance, which occurs when there is resistance to two or more herbicides, with the same or different mode of action, resulting from the presence of a single immune mechanism (one genetic mutation). The mechanism of weed resistance to herbicides from the group of ALS inhibitors (according to the HRAC classification marked with the letter B) has been very well described [12,44–46]. The resistance of these substances to herbicides is most often associated with the Pro197 mutation. As a result, the amino acid proline, at position 197, can be replaced with a different group of amino acids. The most common, however, is the Pro197-Ser mutation in weed-resistant biotypes. Many researchers [44,47–50] proved that using sulfometron to control different biotypes of weeds that are resistant to ALS herbicides can be strictly determined, whether it is either mutational or non-mutational resistance.

Another type of resistance is multiple resistance, which is a resistance to herbicides from more than one chemical class to which a given population has been exposed [51]. It refers to a biotype of a weed or crop that has developed resistance mechanisms to more than one herbicide. This resistance arose as a result of separate selection processes. Multiple resistance has been reported for weed species such as the following: *L. rigidum*, *A. myosuroides*, *C. canadensis*, *A. palmeri* and *A. tuberculatus* [52–55]; in the case of spring barley and wheat, with active ingredients such as chlorpropham, chlorsulfuron, clomazone, diclofopmethyl, ethalfluralin, fluazifop butyl, imazapyr, metolachlor, metsulfuron-methyl, quisalophop-ethyl, sethoxydim, tralkoxydim, triallate, triasulfuron and trifluralin); multiple resistance was found in South Australia in as many as 6 sites of action: inhibition of acetyl-CoA carboxylase HRAC group 1 (Older version A), group 2 (older version B), inhibition of microtubule formation HRAC group 13 (older version F4); inhibition of microtubule formation 2HRAC group 3 (older K1); inhibition of microtubule organization HRAC group 23 (older version of K2); and inhibitors of the synthesis of very long-chain fatty acids HRAC group 15 (older version of K3 N) [12].

Synthetic auxins (HRAC O group) one, which mimic the naturally occurring plant hormone indole-3-acetic acid (IAA), have a wide range of use in the selective control of broadleaf weeds in grass crops. SAHs are divided into several subclasses which include the following: (1) phenoxycarboxylates, (2) benzoates, (3) pyridine carboxylates, (4) pyridyloxycarboxylates, (5) quinolone carboxylates, (6) pyrimidine carboxylates and (7) aryl picolinates. Each subclass has a distinct chemical structure. SAHs have been used since the introduction of 2,4-D (1945) until now, with the introduction of florpiraxifene-benzyl in 2018. In order to maintain the usefulness of SAH, it is essential to gain more knowledge about resistance mechanisms, and how selection and subsequent evolution have taken place in weed species that are resistant to SAH [54].

Mechanisms of synthetic resistance to auxin herbicides is well-known in weed species. *Papaver rhoeas* is the most common dicotyledonous weed species in winter cereals in Europe. This cross-pollinated species is difficult to control due to its high seed production, persistent seed banks and extended seed germination times. With the emergence and spread of herbicides, the resistance of *P. rhoeas* made it become an increasingly nuisance weed, especially in southern Europe. Phenoxy-carboxylate (2,4-D) and biotypes of this weed species that are resistant to MCPA and ALS inhibitors (tribenuron methyl) have been reported for 10 years in Spain, France and Greece. Few studies have been performed to reveal the mechanisms and genes that are involved in *P. rhoeas* resistance to SAH. The lack of 2,4-D translocation in resistant plants may contribute to their immune response. The production of ethylene in sensitive- and 2,4-D-treated plants was 4–8 times higher than in resistant plants [54]. According to Beckie [2], 2,4-D may not reach the nuclear protein receptor complex in resistant plants, which in turn causes the repression of auxin genes, some of which are responsible for ethylene production. Accumulation of ethylene in *P. rhoeas* cells can inhibit photosynthesis and produce H_2O_2, a reactive oxygen species, which leads to plant death.

In 2017–2020, the ConResi consortium that consisted of scientific institutes, agricultural and natural science universities and pharmaceutical companies, implemented a project on the following subject: "Strategy for counteracting weed resistance to herbicides as an important factor in ensuring sustainable development of the agroecosystem". The aim was to develop and implement a holistic strategy to reduce the risk of spreading herbicide-resistant weed biotypes, and to develop means to control them. Four species of weeds were investigated: (1) field foxtail (*Alopecurus myosuroides* Huds.), (2) grain broom (*Apera spica-venti* (L.) P. Beauv), (3) field poppy (*Papaver rhoeas* L.) and (4) cornflower (*Centaurea cyanus* L.). In total, over 2150 samples of seeds of the above-mentioned species of weeds from all over Poland were assessed, and were subjected to biological tests for sensitivity to the following herbicides: 2,4-D, chlortoluron, dicamba, fenoxaprop-P-ethyl, florasulam, iodosulfuron, pendimethalin, pinoxaden, piroxulam and tribenuron-methyl [28,56]. Resistant biotypes were found in each of the tested species, whereas monocotyledonous weeds, i.e., field grasshopper and grain

broom, turned out to be more resistant to herbicides than dicotyledonous weeds (field poppy and cornflower). Herbicide-resistant biotypes were subjected to molecular analyses, in order to determine the genetic basis of their resistance. Moreover, the environmental adaptations of resistant biotypes, as well as their competitiveness with winter wheat, were analyzed in a series of pot experiments that were carried out at various experimental stations and laboratories in Poland [26]. Synowiec et al. [23] demonstrated that the competitive effect of winter wheat on herbicide-susceptible or resistant bractbill biotypes is specific to local conditions. Under drought conditions, the biotype of bumblebee with multiple herbicide resistance turned out to be more competitive with winter wheat. In addition, the project included activities that enabled the implementation of research results into agricultural practice, particularly their dissemination among farmers [24,27].

An integral element of herbicide resistance management is the task of many authors [2,12,44,48,54] to periodically analyze the sensitivity of the population of weed species in the agro-region to commonly used herbicides. The analyses should provide information on inter- and intra-population variability in the effective dose (ED) required for 50 or 90%, as well as the reduction in biomass viability. Hence, an analysis of weed sensitivity to herbicides will help determine whether populations become less sensitive to the herbicide over time, and whether labeling rates need to be adjusted. Such studies are important in mitigating the quantitative (creeping) evolution of resistance, especially for key herbicides, such as glyphosate, and major problematic crossing weeds such as Lolium spp. [5,6]. Sublethal doses of the herbicide may even alter the metabolism, growth and survival of susceptible plant species that are highly selfish, such as *Avena fatua* L. (wild oats) [7].

Natural selection for herbicide-resistant weed genotypes can affect genetic variability or the genetic and physiological background that is variable, due to stress responses from exposure to sublethal herbicides. Stress-induced changes concern DNA mutations, epigenetic changes, transcription and protein modification, all of which can lead to herbicide resistance and pleiotropic effects [2,22]. The results of these studies are being developed, and provide great hope for their implementation, not only in Poland, but also in Europe. In light of the current status of weed resistance to herbicides in Poland, as well as the implementation of the Green Deal Directive in the European Union, research on this phenomenon is gaining importance, especially regarding the impact of biotypes that are resistant to the functioning of agrocenoses and natural biocenoses, and their economic impact. Adamczewski et al. [43] conducted research on weed resistance to herbicides in Poland. About 50% of the analyzed samples showed resistance to sulfonylurea herbicides. Resistance to acetyl-CoA carboxylase (ACCase) inhibitors was found in eighteen fields, and resistance to PSII inhibitors (isoproturon) was found in twelve fields. The resistance of *Alopecurus myosuroides* Huds. to herbicides was recorded in as many as twenty-six tested fields. In ten spring crops, they found that *Avena fatua* L. was resistant to acetyl-CoA carboxylase inhibitors. The resistance of *Centaurea cyanus* L. to tribenuron methyl was confirmed in twenty-three fields. *Matricaria inodora* L. and *Papaver rhoeas* L. proved to be resistant to methyl volcano in several fields of winter wheat. Moreover, three biotypes of *Chenopodium album* L. and two biotypes of *Amaranthus retroflexus* L. were resistant to metamitron. *Conyza canadensis* L., *Lolium* spp. showed resistance to glyphosate [13,42]. Empirical observations by Panozzo et al. [13] generally showed that there was a shift and decrease in susceptibility of Lolium spp. to glyphosate in Italy. This is likely due to the long-term use of glyphosate, and to the sublethal doses used. Therefore, it is necessary to determine the variability of response of *Lolium* spp. to glyphosate, and to identify the optimum field dose.

3.2. Resistance of Plants to Pesticides

Pesticide resistance is defined as the change in the sensitivity of a pest population to a pesticide, resulting in failure to control the pest when the pesticide is properly applied. Resistance can develop whenever the same or a similar pesticide with the same mode of action is used repeatedly. It is also believed that pests change or mutate to become

resistant. However, it is not a single pest (e.g., an insect, pathogen, or micro-organism) that changes, but the entire population which changes. When a pesticide is applied to a crop or treatment site, only a small fraction of the pest's population (e.g., one insect, one crop, or one in ten million weeds) can survive exposure to the pesticide, due to its genetic makeup. When surviving pests reproduce, some of their young inherit a genetic trait that confers resistance to the pesticide. These pests will not be damaged the next time a similar pesticide is used. If the same pesticide is used frequently, the percentage of the less susceptible will increase in the population. When a pesticide applicator recognizes that a once highly effective pesticide is not limiting or destroying the pest at the same rate, higher doses and more frequent applications become necessary, until a point is reached when the pesticide provides little or no control. Then, it can be considered that the population has become resistant [2,6]. With global warming and structural changes in agricultural production, epidemics of crop diseases are becoming more frequent, and it is possible that new types or variants of phytopathogens will emerge and evolve. As a result, the health of cultivated plants is under threat, and plant production is facing more frequent challenges. However, new methods for identifying and characterizing pathogens, in addition to better understanding of the mechanisms that govern plant-microbial interaction are critical to designing crop health management strategies, in order to minimize pathogen-related crop losses. Over the last two decades, tremendous progress has been made in deciphering the molecular mechanisms of plant resistance using model patho-systems. However, the disease resistance mechanisms of many crops remain poorly characterized, due to the genetic/genomic complexity of many crop species, and/or a poor understanding of their pathogens. However, next-generation DNA sequencing technologies have enabled the sequencing and characterization of the genomes of many crop species and their pathogens, which in recent times has greatly facilitated research into the mechanisms of crop–pathogen interactions. Such new knowledge should help to improve crop health and/or reduce pesticide use, and thus contribute to sustainable agriculture [2,6,22,25,40–42].

The pesticide detoxification system involves a three-phase process: Phase I—pesticide activation through hydrolysis, oxidation or reduction, induced by enzymes such as carboxylesterase, cytochrome P450 monooxygenases and peroxidase. Phase II—the activated pesticide is coupled with amino acids, glucose or glutathione; conjugation is catalyzed by the enzymes glutathione S-transferase and UDP-glycosyltransferase. In phase III, the conjugated pesticides are transferred to vacuoles/apoplasts, or bind to the cell wall/lignin [6,29,41]. In agricultural crops, the most common mode of herbicide tolerance is metabolism induced by changes by enzyme systems, such as cytochrome P450 (CYP) monooxygenases; glutathione S-transferases (GSTs); and glucosyl transferases (GTs). These enzymes, as well as cofactors such as reduced glutathione (GSH), are activated by certain chemicals called safeners [42]. Safeners are, in turn, used in conjunction with herbicides to tolerate crops such as *Triticum aestivum* L., *Oryza sativa* L. and *Zea mays* L. [42,43].

Immunity inducing factors are elicitors, i.e., compounds released when interacting with a potential pathogen, which, when recognized by the appropriate receptors, trigger a cascade of events that leads to the generation of plant resistance. Elicitors induce a defense response in the plant, through receptors that transmit a signal to the cell nucleus. It is a group of very diverse proteins that are synthesized by plants. Due to the similarities in their domain structure, they were divided into five classes. R proteins interact with the avirulence factors Avr, secreted by bacteria, fungi, and the Avr proteins of viruses. Most of the currently known R proteins are found in the cytosol, suggesting that they recognize intracellular Avr factors. The following was found in the genome of the model *Arabidopsis* plant: 149 genes that encode R proteins of the NB-LRR type, including the only known function-participation in defense reactions; 233 genes that code for LRK proteins; 110 genes that code for proteins of the RLP type [2,44]. Due to the type of triggered immunity, there are common elicitors and race-specific elicitors. Common elicitors (i.e., β-glucans, chitin, polypeptides, glycolipids) are produced by many pathogens, and interact with all cultivars of the affected host plant species. They are responsible for the liberation of so-called

racial-non-specific resistance (field, horizontal, partial). Race-specific elicitors (products of avr avirulence genes) are active only in variants that have a complementary resistance gene (R). They are the prerequisite for the occurrence of type resistance gen-na-gen, or race-specific (vertical, full) resistance. Rapid reactions that occur mainly in the periphery of the cell, which do not require gene expression, are a direct consequence of recognition of a pathogen/elicitor by a plant cell. They include the following: membrane depolarization, ion flux across the membrane (K^+ and Cl^- outflow and H^+ and Ca^{2+} inflow), and oxygen explosion. The 'gene to gene' hypothesis assumes that the recognition of the pathogen, and the activation of defense reactions, occurs only when the plant possesses the appropriate R resistance gene, and is attacked by micro-organisms that carry the corresponding avr avirulence gene. The pathogen with the avr gene is pathogenic to plants that do not have the appropriate R gene-no-defense response [2]. The main precursor in the synthesis of SA is phenylalanine. In the first stage, this amino acid is converted into trans-cinnamic acid with anti-auxin properties, by means of the PAL enzyme (ammonia-L-phenylalanine), in the process of non-oxidative deamination. This acid, depending on environmental conditions and under the influence of a specific isomerase, can be transformed into cis-cinnamic acid, which has auxin-like properties. Trans-cinnamic acid in the oxidation process turns into benzoic acid, which then undergoes hydroxylation to become salicylic acid. In turn, the hypothetical pathway leads to the transformation of trans-cinnamic acid into trans-coumaric acid, which is converted to cis-coumaric acid, which forms the basic coumarin skeleton [44]. The markers of the resistance reaction are phenylalanine ammoniaolase (PAL); chalcone isomerase (CHI); isoflavone reductase (IFR); cinnamate 4-hydroxylase; 4-coumaryl-CoA ligase; chalcone synthase (CHS); prenylotransferase [6]; pathogenesis-related proteins (PR), and pathogen-dependent stress associated with pathogenesis. The components of the signal chain in the immune reaction are PR proteins, which are mainly hydrolytic enzymes: β- (1,3) endoglucanases and chitinases, as well as peroxidases. The first to describe the PR of tobacco infected with mosaic virus was Ivanoski, who reported in 1892 that extracts from contaminated leaves were still contagious when filtered through a Chamberland filter candle. However, Ivanowski probably did not fully understand the meaning of his discovery. Beijerinck, in 1898, was the first to name "virus", the initiator of the tobacco mosaic. Thus, Ivanovski and Beijerinck made an unequal but decisive and complementary contribution to the discovery of viruses. The functions of PR proteins include creating a protective barrier against pathogens by separating them and collecting them at the site of infection; weakening the sensitivity of plants; showing antibacterial and antifungal activity in vitro (some antiviral). They are expressed as the result of a hypersensitivity reaction. Their expression depends on the intensity and type of attack. They can mediate plant resistance to the pathogen by overexpressing their genes in transgenic plants. The prevalence of antifungal proteins correlates with the prevalence of fungi that colonize plants, animals and humans (in the last decade there has been a drastic increase in fungal infections—about two hundred human fungal pathogens) [25,40,41,44].

When plants are infected, both plants and pathogens secrete protein-containing molecules that determine their interactions. While proteins secreted by the pathogen are involved in infection and pathogenicity, proteins secreted by plants play a key role in their resistance. Host–pathogen interaction is defined as the way in which microbes or viruses persist in the host organism at the molecular level, and then the cellular level, the organism level, and finally at the population level. The term is most often used to refer to pathogenic micro-organisms, although they may not cause disease in all intermediate hosts [44].

4. Oxylipin

Phytoxylipins (OPs) are metabolites that are produced in plants by the oxidative conversion of unsaturated fatty acids through many metabolic pathways. They usually act as signal particles, at very low concentrations. Examples of plant phytohormones include SA, ET, JA, auxin, ABA, brassinosteroid, gibberellic acid and cytokinin (Figure 2) [57]. OPs play a very important role in the plant immune response that is caused by biotic and

abiotic stress factors. As signaling molecules, SA, JA and ET influence the regulation of processes that are related to plant resistance. Moreover, ABA, auxins, as well as BRs and GA, are assigned certain functions in shaping immunity. Pathogenic infections stimulate plants to produce one or more types of hormones, depending on the type of pathogen. SA-supported signaling pathways participate in plant resistance against biotrophic and hemibiotrophic pathogens, while JA- and ET-dependent pathways participate in plant resistance against necrotic pathogens [39,57]. Some synthetic auxins, such as 2,4-D and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), are considered herbicides. Dicotyledons, such as dandelions, are more sensitive to auxins than monocots such as cereals, making them valuable herbicides. Biochemical analyses and a genetic approach have shown that oxidized derivatives are actively involved in plant defense mechanisms. During the last decade of the 21st century, interest in this field has focused on the biosynthesis of JA (a branch of the metabolism of C18 polyunsaturated fatty acids), and its relationship to other plant defense signaling pathways. Recently, however, antisense strategies revealed that oxylipins other than jasmonates are also essential for plant resistance to pathogens and herbicides [58–60].

4.1. 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 [5,61]. 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 [17,41,59].

4.2. Brassinosteroids

Brassinosteroids (BRs) are phytohormones that are a common group of plant steroid hormones. They occur in relatively low concentrations, and their content in plants depends on the species, tissue and development stage of the plants. Their presence was demonstrated in algae, bryophytes, ferns, gymnosperms and angiosperms. The richest sources of BRs are pollen grains and unripe seeds, while their content in shoots and leaves is much lower. BRs have also been identified in the roots of some plant species [29–32,62]. They show high biological activity, thanks to their influence on metabolism, as well as on plant growth and development. These phytohormones are attributed to numerous protective actions, especially in the case of plants that are exposed to biotic stress (e.g., viral, bacterial and fungal pathogens) and abiotic stress (e.g., thermal, water, salt and oxidative stress, oxygen deficiency or heavy metals). In conditions of low temperatures (0–3 °C), BRs increase plant resistance to cooling, and increases the survival of plants that are subjected to high temperatures, while stimulating the synthesis of heat shock proteins. BRs also contribute to the growth of the root mass, and to an increase in the sucrose content. They also stimulate the activity of sucrose synthetase under the influence of water stress. Under salt stress, these phytohormones accelerate the germination and development of seeds, and inhibit the degradation of photosynthetic pigments; moreover, they contribute to lowering the permeability of the cytoplasmic membranes to sodium ions. Under oxidative stress, BRs cause an increase in the activity of enzymatic antioxidants, and an increase in the content of ascorbic acid and carotenoids. BRs also reduce the accumulation of heavy metals by plants, and also contributes to increasing the production of photoheating [31,33,35]. Information on the exogenous use of plant hormones in the protection of plants against weeds is still limited. Salicylic acid (SA) is a natural plant hormone, and a signaling molecule, that increases plant tolerance by reducing the toxic effects of salinity on growth and yield. The exogenous use of phytohormones, such as SA, is considered to be the most effective molecular means in regulating plant growth, glycolysis and yield; in ion uptake and utilization; in stomata conductivity, in photosynthesis, transpiration; and in enzymatic and non-enzymatic tests synthesized under environmental stress [60]. The effectiveness of

exogenous SA application is mainly based on the plant species and the concentration used. Low concentrations of salicylic acid (less than 1 mM) are more effective in increasing plant growth than higher concentrations (greater than 1 M), which reduce the growth of many plant species [20,61]. The use of SA was found to increase tolerance to salinity stress, with a decrease in Na^+, Cl^-, and H_2O_2, and an increase in Ca^+ and K^+, within plants [21]. Salicylic acid can reduce ethylene biosynthesis, boron toxicity and lipid peroxidation, and protects plants against membrane damage, especially under conditions of drought and salinity stress [60]. Recently, many efforts have been made to find an effective approach to develop tolerance to abiotic stresses in plants, which ultimately develops plants that survive under stressful conditions. The exogenous use of plant phytohormones, especially SA, is the most promising strategy for increasing plant tolerance under salinity conditions [20,21,35,60]. Therefore, the current research focuses on the exogenous application of SA to mitigate the influence of abiotic and biotic factors on the growth and yield of crops, by reducing oxidative damage to crops that are rich in bioactive compounds.

Due to their high biological activity, BRs are important regulators of many processes in plants: they participate in the processes of transcription and translation. They show a stimulating effect on the growth of various plant organs (e.g., targeted cell elongation), increase the activity of enzymes that encode the synthesis of pectins and structural proteins of cell walls; proteoglycans and extensions activate the expressions of genes that encode cellulose synthase subunits, V-ATPaz [31,63].

BRs induce sprouting, and are also able to overcome the physiological blockage of germination, shown by gibberellin mutants. They also activate the process of cell proliferation, stimulating the expression of the CycD3 gene that encodes the D3 type cyclin responsible for cell transition from G1 to S. They are steroidal plant hormones that are involved in promoting plant growth and development. The effect of BRs on the photosynthesis process depends on the plant species, the stage of development at which the hormones were administered, and the concentration used [35]. In general, BRs significantly increase stomata capacity and transpiration. In studies conducted by Bajguz and Tretyn [30], plants that were treated with BRs showed an average two-fold higher content of chlorophylls a and b, non-reducing and reducing sugars and starch. Presumably, BRs have a stimulating effect on the increase in the leaf surface, and the assimilation of CO_2 in the Calvin–Benson cycle, which is attributed to the increased activity of the Rubisco enzyme [62]. BRs interact synergistically with other phytohormones, e.g., ET, JA or SA, which determine the acquisition of resistance to infection by plants [64]. ET, in interaction with auxins, affects the elongation growth of the stem. Rross et al. [65] observed a 40% reduction in auxins in pea seedlings, after application with various concentrations of etaphone (ET precursor), which resulted in an inhibition of shoot growth by 44%. The greater the dose of ET, the stronger the effect. The use of jasmonates [JA] in the studies by Monzón et al. [66] reduced the lengths of cortical cells as well as the cell production index in the sunflower root meristem, while ibuprofen only influenced cell elongation.

BRs regulate the activity of genes that are related to cell wall extension, and influence the activity of cell-wall-modifying enzymes, e.g., acetylesterase [62,67]. They also initiate cellulose biosynthesis in the cell walls of *A. thaliana* [L.] Heynh. infected with pathogens, and accelerate the activity of the antioxidant system [62,68–70]. BRs participate in the mechanisms of gene induction and signal transduction that are related to acquired and systemic immunity, and the synthesis of pathogenesis-related (PR) proteins. They occur in all parts of plants, including buds, fruits, seeds, leaves, shoots and roots [3,30,34]. The richest source of BRs are pollen grains and unripe seeds, in which these compounds are present in a concentration range from 1 to 100 ng g^{-1} of fresh weight. On the other hand, in shoots and leaves, a lower content is noted, within a range of 0.001–0.1 ng g^{-1} of fresh weight [30]. BRs influence the metabolism of plants, and by increasing their tolerance to a wide range of environmental stresses, such as low and high temperature, high soil salinity, this leads to an increase in crop yields [62,71].

BRs are also effective fungicides. The use of BRs in the cultivation of *Solanum tuberosum* resulted in a reduced frequency of infection with *Phytophthora infestans* Mont de Bary. This increase in plant resistance is probably related to the increased levels of AA and ET synthesis under the influence of BRs, and to the increased presence of phenolic and terpenic substances [72]. A similar phenomenon was found to occur in the case of Hordeum vulgare L. and *Cucumis sativus* L.; however, this was associated with increased activity of peroxidases and polyphenol oxides, which are involved in the metabolism of polyphenols [60,73]. ET, in interaction with auxins, also influences the elongation growth of the stem. Rross et al. [65] observed a 40% reduction of auxins in pea seedlings after application with various concentrations of etaphone (ET precursor), which resulted in an inhibition of shoot growth by 44%. The greater the dose of ET, the stronger the effect. A multi-study analysis by Qin et al. [63] showed that ET-regulated root development and elongation are auxin dependent, through alterations in auxin biosynthesis, transport, and signaling. It was also observed that auxin and ET act synergistically in controlling the growth of the primary root and hair, but antagonizing the formation of lateral roots. The two-phase effect on the growth of primary roots that depended on the concentration of abscisic acid [ABA], environmental conditions, development context, genotypes and plant species, was demonstrated by Qin et al. [63]. Usually, a low concentration of ABA stimulates the growth of primary roots, while a high concentration inhibits it.

4.3. Jasmonate-Defense Phytohormones

The jasmonates (JA) group is the best known and researched of the OPs; they are known as defense phytohormones, including JA and its derivatives such as MeJA, cis-jasmonoil (JA-C), jasmonoil, isoleucine (JA-Ile), jasmonoil ACC (JA -ACC), and several other metabolites. Plants produce volatile and non-volatile compounds, including phytohormones, which help them adapt to a changing environment [74,75]. Phytohormones play an important role in various physiological and developmental processes of plants, which determine the proper course of individual plant development phases. JA, JA-Me and MeJAs phytohormones are derivatives of fatty acid metabolism. The precursor of jasmonates is γ-linolenic acid, and its biosynthesis takes place in three subcellular structures: chloroplasts, peroxisomes and cytosol [76–79]. The biosynthesis of jasmonates has been described in detail in the literature [1,77,80–84]. The discovery of other elements of the JA signaling pathway, as well as the receptor of this hormone and its binding site, have made it possible to understand the mechanism of JA's action in the regulation of generative development in plants. The jasmonate receptor is the COI1 (coronatine insensitive1) protein [3,59,61,85–90]. JA signal perception takes place in the cell nucleus, and leads to the activation of the E3 ubiquitin ligase SCF-COI1 type (skpcullin-f-boxring box protein 1), and consequently to the proteolytic degradation of the transcription repressors, JAZ proteins (jasmonate zim-domain) [87,88,91]. Lowering the pool of these repressors enables the activation of transcription factors, and the expression of genes that are activated by jasmonates (Jas). After the plant reaches the state of competence, internal and environmental factors induce developmental changes (induction), resulting in the transformation of vegetative meristems into generative ones (evocation, initiation), and flowers are then produced (differentiation, morphogenesis). In *A. thaliana*, genes that are related to generative induction have been identified and characterized; four main pathways of flowering induction have been distinguished: photoperiod, vernalizing, autonomic and endocrine. They modulate the expression of integrator genes [60].

Research on the occurrence and physiological role of JA in plants was undertaken after it was demonstrated that jasmonic acid methyl ester [JA-Me] strongly accelerates the aging of Avena fatua leaves in the dark [chlorophyll degradation]. JA-Me was first detected in the essential oil of *Jasminum grandiflora* in 1962, and in 1967 it was found in the essential oil of rosemary (*Rosmarinus officinalis* L.) [87]. In 1971, jasmonic acid [JA] was detected in the filtrates of the fungus *Lasiodiplodia theobromae* (Griff et Maubl. [syn. *Botryodiplodia theobromae* Pat.]). This was the first time that it was found to inhibit plant growth [3,76].

The occurrence of JA and JA-Se has been demonstrated in many different systematic groups of higher plants, including in ferns, mosses, fungi and algae. These compounds are present in plants in very small amounts, from 0.1 mg to 5 mg per kg of fresh tissue weight. JA and its derivatives can occur in plants in combination with various amino acids, including with isoleucine, leucine, valine and tyrosine [81]. CLA is the primary precursor of [+]-7-iso-jasmonic acid (syn. [+]-2-epi-jasmonic acid) biosynthesis in plant tissues, which is transformed into (-)-jasmonic acid. JA and its derivatives have a structure that is similar to that of animal and human hormones, prostaglandins, compounds which are also found in plants, and have a certain physiological effect in the plant organism [68,78,81,87,92].

In the case of *Fusarium oxysporum* ssp. *matthiolae,* as many as twenty-one different compounds from the jasmonate group have been identified. Jasmonate biosynthesis in plants is modified by abiotic stress factors [mechanical damage, osmotic stress, detoxic stress, heavy metal salts—Cu^{++}, Cd^{++}, touch factors (in the case of *Bryonia dioica*) and biotic factors [81,87]. On the basis of much data, it has been proved that JA and JA-Me play a very important role in the immune responses of plants, by inducing the expressions of many defense proteins and secondary metabolites [24–26]. Defense proteins induced in plants by jasmonates include, for example, proteinase inhibitors, proteins related to pathogenesis-osmotines, thionines, peroxidase, β-1,3-glucanase, lipoxygenase and other compounds [14,78]. Jasmonates induce or stimulate the production of many secondary metabolites (various phytoalexins, flavonoids, sesquiterpenoids, glucosinolates, lignins) by inducing the expression of enzyme proteins that are involved in the biosynthesis of secondary metabolites (e.g., -methylglutaryl CoA and others) [19,76,81] from the cultures of *Pseudomonas syringae* cv. *atropurpurea* [70,81,90,91].

JA biosynthesis occurs through the reaction of 13-lipoxygenase [13-LOX] with polyunsaturated fatty acids, which are rich in lipids in plant membranes, to form 13-hydroperoxides. They are catalyzed by the synthase of allene-13-oxide [13-AOS] of the CYP74 family, and are then converted into 12-oxo-phytodienoic acid [OPDA] and JA in subsequent reactions of allene oxide cyclase, OPDA reductase and β-oxidation processes [19]. The main bioactive jasmonate in vascular plants is the JA-isoleucine conjugate [JA-Ile] [19,87].

Jasmonates, mainly JA and JA-Me, inhibit the growth of plants or their organs by disrupting the activity of both primary and secondary meristems, thereby inhibiting cell growth in the elongation zone. This is related to the disrupted hormone balance caused by jasmonates in plants, which in turn translates into various metabolic processes. JA, beginning from a concentration of 10 mg dm^{-3}, inhibits, for example, the germination of Camellia sinensis L. pollen grains; at a concentration of 100 mg dm^{-3}, it causes complete inhibition of the germination of this species [3]. Germination of many species of seeds, including weeds, is inhibited by JA and JA-Me, including deaf oat seeds [59], *Xanthium pennsylvanicum* [92], *Amaranthus caudatus* and others [32]. There are, however, examples of plant species in which JA or JA-Me stimulates germination, including *Acer tataricum* and *Pseudotsuga menziesii* [36].

JA mainly inhibits the growth of hypocotyl and seedling roots in lettuce, in *A. thaliana* roots [36], and in shoots of *Beta vulgaris* L. var. *saccharifera* [93]. Jasmonates are also involved in the regulation of many other physiological processes in plants by interacting with other plant hormones. JA and JA-Me stimulate processes such as aging in leaves (degradation of chlorophyll), leaf fall-off and the falling off of other organs, fruit ripening, curling of Bryonia dioica tendrils, formation of a secondary cut off layer in *Bryophyllum calycinum*, and the opening of flower buds in *Oryza sativa*. JA-Me inhibits the growth and flowering of *Chenopodium rubrum* [38]. JA stimulates the formation of secondary laticides in the case of *Hevea brasiliensis*, and JA-Me stimulates the formation of gums and resins in many species, e.g., tulips, in the stems and fruits of plum, peach, apricot and other fruit trees [36,60,94].

In many cases, jasmonates can find practical use. For example, treatment of a JA-Me consumable radish after leaf cutting, by soaking or by gaseous exposure, inhibits leaf killing and root growth [95]. Similarly, these compounds inhibit the seeds of some weed species [85].

JA-Me induces or stimulates the production of ET in many organs of various plant species. This hormone influences the biosynthesis of ET by regulating the activity of 1-aminocyclopropane-1-carboxylic acid synthase and oxidase [ACC]. JA-Me strongly stimulates the production of ET in tomatoes at various stages of maturation, and in apples at the preclimbic stage, where it stimulates the biosynthesis of ACC and its conversion to ET [11,96]. JA-Me strongly induces the aging of dendrobium and petunia flowers; the rate of aging was proportional to the concentration of this hormone. JA-Me induces ACC biosynthesis and ET production. The JA-Me-induced aging in petunia flowers was completely reversible by aminooxy acetic acid—an ACC synthase inhibitor, and silver thiosulfate [STS]—an inhibitor of ET action, which proves that JA-Me accelerates flower aging through increased ET production [60,97].

It has been known for quite a long time that mechanical damage is one of the factors that stimulates the production of ET in various organs and tissues of plants, through increased ACC production and ACC oxidase activity [7,8]. It is assumed that increased biosynthesis of this acid in damaged tissues and organs of plants stimulates the biosynthesis of ET, which, however, requires confirmation in research [97].

Moreover, the infection of plants by pathogens, mainly fungi, increases the production of ET in tissues [96], which is caused by mechanical damage to tissues by hyphae (increased JA production), and additionally by the presence of JA or JA-Me in the pathogen.

Jasmonates also regulate many biochemical processes, e.g., the biosynthesis of carotenoids, anthocyanins and other secondary metabolites [11,57]. Many secondary metabolites play a key role in the defense responses of plants against pathogens and herbicides [3].

JA acts as a signal for elicitor activity and phytoalexin accumulation, as well as other immune responses that occur during infection by pathogens [24–26]. Elicitation of cell suspensions of various plant species with yeast cell wall fragments, JA and JA-Me stimulate the production of various specific secondary metabolites. Some induced secondary metabolites have therapeutic properties, e.g., Taxol, alkannins, shikonins, xanthones, which are of great importance in the pharmaceutical industry, and in the production of herbicides for protection against weeds [11,57]. Treatment of plant seedlings, including weeds, induces the biosynthesis of secondary metabolites, e.g., alkaloids, such as in the case of *Catharanthus roseus* and *Cinchona ledgeriana* [80].

Jasmonates interact with ET in the regulation of various metabolic processes, in such following ways: (a) synergistically (e.g., expression of genes for proteinase inhibitors, osmotic, defensin); (b) in inhibiting processes that are induced by jasmonates (e.g., biosynthesis of nicotine, vegetative storage proteins, lectins); and (c) in inhibiting ET-induced processes (e.g., ET-induced apical bending). JA-Me can also act as a regulator within the cell, in addition to being an intercellular transduction signal and a messenger of information between plants [81]. Saniewski and Urbanek [76] suggested that endogenous jasmonates are the messenger of information between the stress signal and the stress response, being mainly involved in the induction of gene expression and biosynthesis of specific proteins and secondary metabolites [78,80]. These substances, when interacting with other plant hormones, auxins, ET and cytokinins, play an essential role in regulating morphogenetic processes in plants that are related to cell division and growth. JA and JA-Me are most concentrated in meristematic tissues and young leaves, as are auxins. It has already been shown that some processes that are induced by jasmonates are inhibited by auxins, and vice versa, certain processes stimulated by auxins are reduced by jasmonates [3,78,81]. It should be emphasized that both auxin and jasmonates stimulate the biosynthesis of ET, so it is likely that in meristematic tissues there are interactions between jasmonates, auxin and ET in the regulation of many metabolic processes.

Stress Factors and Jasmonate Biosynthesis in Plants

Jasmonates affect plant growth and development, tolerance to biotic and abiotic stresses, formation of storage organs, reproductive processes, root elongation, fruit ripening and aging [82,83]. Moreover, jasmonates are involved in the development of inflorescences

and flowers [84,85], and in the formation of secondary metabolites [88]. Analysis of the jasmonates signaling pathway (Jas) was assessed in dicotyledonous plant species such as *Arabidopsis* (*A. thaliana*), tomato (*Lycopersicum lycopersicum*), tobacco (*Nicotiana tabacum*) and monocotyledons such as barley (*Hordeum vulgare*), maize (*Zea mays*) and rice (*Oryza sativa*). Some stress factors, such as drought, increase the biosynthesis of jasmonates, especially JA. Thus far, the exogenous use of JAs has been studied on various plant species under conditions of abiotic stress, in particular, under conditions of salinity, drought and low or too high air temperature [83,98–101]. According to Ahmad et al. [1], it is effective in improving the stress tolerance of plants. However, its range of effectiveness depends entirely on the type and species of plant, or on the concentration of the solution. The regulation of JA synthesis is disturbed, both in stressed and non-stressed cells or plant tissues, which is related to metabolic reactions, including signal transduction. Although protein kinases are important components of JA signaling, and biosynthesis pathways, nitric oxide, ROS, calcium, ABA, ethylene and salicylic acid are also very important modifiers for plant growth and development during JA signal transduction and synthesis [100,101].

One of the main stressors is mechanical damage to plant organs or tissues. Mechanical damage is one of the factors that stimulates the production of ET in various organs and tissues of plants, due to the increased production of 1-aminocyclopropane-1-carboxylic acid (ACC). As a result of mechanical damage, there is an increased biosynthesis of JA or JA-Me in various plant organs (Table 1).

Table 1. JA biosynthesis as a result of mechanical damage.

Species	Organ	Source
Bryonia dioica	leaves	[1,2]
Avena sativa	leaves	[1,79,98]
Lycopersicon esculentum	leaves	[44,78]
Solanum tuberosum	tubers	[99,102–104]
Glycine max	hypocotyl	[2,17,105,106]
Nicotiana sylvestris	roots and shoots	[2,92]
Petunia hybrida	flower crown	[53,76]

The JA signal activates a group of factors that are responsible for the transcriptional up-regulation of defense genes [87]. The response of plants to stress is to activate the accumulation of secondary metabolites such as alkaloids and terpenoids [68]. Scala et al. [78] pooled newly generated *Catharanthus roseus* transcriptomic data, in order to identify new members. The transcription factors, BIS and ORCA, regulate specific genes that are involved in the synthesis of these alkaloids.

Although JA signaling strongly induces defense responses, it is tightly controlled in order not to impede plant growth during defense [10]. In order to prevent over-induction of defense, the active form of JA is rapidly converted into inactive forms by hydroxylation and/or other metabolic processes [106]. Acosta and Farmer [1] reported on a novel translational regulation of normal JA responses, which was found by analyzing the cytochrome P450 *Arabidopsis* double mutant, CYP94B1 and CYP94B3, which convert active JA-Ile into 12OH-JA-Ile. Chechetkin et al. [107] proved that rice seedlings follow an unprecedented allene oxide synthase pathway, by targeting hitherto unknown oxylipins 1–3. These products, (4Z) -2-pentyl-4-tridecene-1,13-diic acid (1), (2″Z) -2- (2′-octenyl) -decane-1,10-dioic acid ′2) and (2′Z, 5′Z′) -2′- (2′, 5′-octadienyl) -decane-1,10-dioic acid (3), of the Favorskii type, have a carboxyl function on the side of the chain. Compounds **1–3** are the newly discovered major oxylipins, along with the α-ketoles. Products 1–3 are biosynthesized from (9Z, 11E, 13S) -13-hydroperoxy-9,11-octadecadiene acid, (9S, 10E, 12Z) -9-hydroperoxy-10.12-octadecadiene acid (9-HPOD) and (9S, 10E, 12Z, 15Z) -9-hydroperoxy-10,12,15-octadecatriene acid, respectively, via allenic oxides and cyclopropenones. The

results of the studies by Chechetkin et al. [107] indicated that the conversion of allene oxide to cyclopropenone is controlled by soluble cyclase. Short-lived cyclopropenones are hydrolyzed to oxylipins 1–3, which have been collectively given the name "graminoids".

5. Interactions between JA, BR, ET and ABA

JA, BR, ethylene and ABA are the main phytohormones that can synergistically or antagonistically mediate biotic and abiotic stresses [108,109]. Jasmonic acid has been observed to antagonize ethylene in the regulation of HT stress [39]. *Arabidopsis* mutants, showing JA biosynthesis or JA signaling, are sensitive to heat stress, while the ethylene2-1 (ein2-1), insensitive to ethylene mutant thermotolerance as an EIN2-mediated pathway, negatively regulates thermotolerance [39,110]. On the other hand, JA has been observed to induce ethylene biosynthesis by increasing the activity of ethylene-producing enzymes in tomatoes [13]. It has been proposed that the JA-ET interaction is mainly mediated by the ET-activated transcription factor EIN3, and its close homologue EIN3-Like1 (EIL1) [84,111]. A possible antagonism between BRs and ET was speculated by Scala et al. [78], as confirmed by three observations: (1) the PTSGMS rice line with higher BR content (24-EBL and 28-HBL) under HT stress during anthesis showed lower ACC content in the bars; (2) the contents of 24-EBL and 28-HBL were significantly and positively correlated, while the content of ACC was negatively correlated with the content of AsA and the activity of catalase in the bars of the PTSGMS line; and (3) the application of 24-EBL or 28-HBL to the panicles of the PTSGMS line was significantly reduced, while the use of brassinazole (an inhibitor of BR biosynthesis) significantly increased the ACC content in flower pistils. However, there is still no direct evidence of an interaction between BRs and ET.

The synergistic effect of JA and ABA under the influence of HT stress was confirmed by the fact that foliar spraying with JA increases the ABA content in plant cells, thereby stimulating stomata closure and preserving water content [57]. However, antagonism between JA and ABA was observed in rice's response to nematode attack, and to salt stress [85]. An antagonistic interaction between BRs and ABA has also been suggested in the plant response to HT stress [57]. It has been observed that high endogenous levels of ABA can suppress the heat stress responses of BRs in *A. thaliana*, and the application of BRs to ABA-deficient mutants showed marked effects due to the higher accumulation of HSP [69].

There is speculation that ABA may minimize the role of BRs in heat stress, and that this interaction may involve decreased expressions of BZR genes in, e.g., maize [109]. BRs can play a large role in maintaining the ABA-ABA glucosylester balance to mitigate the effects of high and low temperatures on barley. These results indicate that BRs can interact with ABA, not only antagonistically, but also synergistically, in the plant response to HT stress [84,97]. An antagonistic interaction between JA and BRs on plant growth regulation has been demonstrated [91]. For example, it was observed that the use of MeJA substantially inhibits the expression of genes that are involved in BR biosynthesis, lowers the level of endogenous BRs, and activates JA-dependent innate resistance of rice to root nematodes [69]. The PTSGMS rice line with higher BR content also showed higher JA or MeJA content under HT stress, and these were significantly correlated [91]. It was speculated that there may be a synergistic relationship between JA and BRs in regulating rice's response to HT stress. However, more convincing evidence is necessary to support this hypothesis.

The antagonistic interaction between JA and SA is responsible for HT stress in signaling pathways [69,79,81]. BRs antagonize SA to regulate HT stress, as evidenced by the fact that endogenous SA content in *A. thaliana* was reduced when plants were treated with BRs under HT stress [81]. It has been argued that JA and BRs can increase both basal thermal tolerance and acclimation to heat stress, while SA has no function in acclimation to heat stress [79,81,107].

6. Plant Reactions to Injuries

In response to injury or attack by herbivores, the leaves and roots of higher plants release volatile organic compounds, the so-called VOCs [82,102,112]. VOCs, as shown by the studies of many authors [62,112], repel herbivores and/or attract organisms in higher trophic levels [112]. It has even been suggested that they also take part in direct and indirect plant protection [60]. Many field and laboratory studies have shown that VOCs that are emitted by undamaged shoots of monocotyledonous and dicotyledonous plant species can induce physiological and/or molecular and morphological changes [1,60] in undamaged neighboring plants. Moreover, it has been shown that volatile substances that have been emitted by mechanically damaged plants, or as a result of grazing from herbivores, are able to prepare plants (recipients) for a faster and more effective response to subsequent mechanical stress or herbivore attack [9,112]. However, root VOCs in such plant–plant interactions remain poorly documented, mainly due to technical difficulties related to research; it has been shown that it is possible to analyze VOCs, emitted in low concentrations by the roots of monocotyledonous plant species, without having to replant them or separate the roots from the soil environment before harvesting [19,112]. However, further VOC analyses are needed to improve identification and enable quantification of VOC emissions under stress-free conditions. They are based on mass spectrum data, and will be further validated using pure chemical standards. Further research is underway on the role of volatile root constituents in interspecific interactions between plants, using monocotyledon species as a biological model. There are also ongoing experiments that are investigating potential morphological, physiological and molecular changes in plants exposed to VOCs from the roots of monocotyledons [112].

7. Signaling via Oxylipins

Plant oxylipins (OPs) are a heterogeneous group of compounds that can play various roles in a plant defense strategy. Some of them have widespread antimicrobial activity [16,18,81]; other OPs are signaling molecules that are capable of eliciting a defense response, both locally and systemically. Some OPs can act as antimicrobial agents, influencing the growth, development and spread of pathogens. These signaling and antimicrobial responses indicate that these two different biological activities may be related in some way [19,60,62].

7.1. Oxylipins Produced by AOS

Jasmonates produce many defense responses, both directly (e.g., defense proteins, small molecules, and alkaloids) and indirectly (e.g., volatile compounds, non-floral nectar). The defense proteins include protease inhibitors that block proteases, leucine aminopeptidases and threonine deaminase (TD). This compound is involved in the initial stage of isoleucine biosynthesis, and may act as an anti-nutritional protein [18,81,113].

7.2. Plant Volatiles as Their Weapon against Herbivores and Pathogens

Plants in the entire agro-ecosystem cannot avoid pathogenic micro-organisms and pests. As a consequence, plants "arm themselves" with molecular weapons against their attackers. All plant defense responses rely on a complex signaling network, in which the hormones JA, SA, and ET interact with hosts, pests and pathogens. Leaf volatile compounds (GLV), C6 carbon particles, are very quickly emitted by herbaceous plants. They play a key role in plant protection. These volatile substances directly trigger plant defense responses. GLV, thanks to the cross-talk with phytohormones (mainly JA), can influence the defense reaction of plants against pathogens. These GLVs consist of C6 compounds, including alcohols, aldehydes and esters, and their name derives from their smell, which is reminiscent of the smell of freshly cut grass [9,60]. They are produced by herbaceous plants, and their increased release may be caused by abiotic and biotic factors (pathogens or herbivores). GLVs are also involved in inducing plant defenses, and inducing so-called "priming", that is, a state that prepares the plant for an extended response to an attack by herbivores or a pathogen [60]. Due to the fact that GLVs are involved in

many forms of plant adaptation to their environment, they are defined as multi-member molecules that arose as a result of disturbances in the plant protection system, helping plants survive in a hostile environment. Their particular physiological importance is important, as they play an essential role in plant defense responses. When *Nicotiana tabacum* is infected with Pseudomonas syringae var. syringae, it emits, e.g., E-2-hexenal [70,92]. Usually, GLV secretion begins 18–20 h after infection, while the number of bacteria is increasing exponentially, which takes about three days [62]. Pseudomonas syringae multiplies in the apoplast, and is a hemibiotrophic organism [60]. GLV has antimicrobial activity [60,80]. This applies to C6 aldehydes, of which E-2-hexenal has the highest antimicrobial activity, due to its reactive and electrophilic α, β-unsaturated carbonyl group [60]. It is very beneficial for the plant to produce GLV immediately after being injured, in order to reduce infection and rapidly inhibit bacterial growth [62]. Data on the antimicrobial activity of GLV are based on in vitro studies. For example, lima bean leaves release E-2-hexenal and Z-3-hexenol in concentrations that allow rapid inhibition of bacterial growth in vitro [36,70]. Thus far, the role of HPL, a key enzyme in GLV biosynthesis, on plant-bacterial interaction, has been investigated. It was also shown that HPL exerts a beneficial effect on the growth of the pathogen *P. syringae* DC3000 (DC3000) by inducing higher JA levels in infected *Arabidopsis*, as compared to HPL-free plants [28]. Initial treatment with E-2-hexenal contributes to an increase in the bacterial population, and the end result is dependent on coronatin and a transcription factor that integrates both JA and ET signaling pathways [28]. Pseudomonas makes good use of the antagonistic effects of JA on *Arabidopsis* SA-dependent defense mechanisms through the synthesis of coronatine, which mimics JA-Ile, the active form of JA [68–70]. An alternative hypothesis is that Pseudomonas benefits from inducing HPL by exploiting its effect on the JA pathway. However, this must be confirmed by further research.

Inner "Communications" of the Kingdom of Oxylipin

POs have been found to be involved in plant–plant and plant–pathogen interactions. More recently, research into lipid-mediated communication [9,107] has shown that organisms commonly use the oxylipin pathways as a means of communication, in order to obtain biological responses. Fungal oxylipins (FO) modify the responses of both plant and mammalian hosts, and herbicides modify plant hosts [59,107,114,115]. It has been suggested that plants and fungi communicate using the "oxylipin language", mainly through quorum-sensing mechanisms [2,107]. Therefore, a clear response to the exogenous use of PUFA derivatives purified from interacting partners should be observed. C18: two products (e.g., 9 (S)-and 13 (S) -HPOD) or green leaf volatile compounds (GLV) of different plant species, confirm the hypothesis that FO and OP may be involved in quorum detection. Green leaf volatiles (GLV) are an important group of plant volatiles. They are made up of six carbon compounds (C6), including alcohols, aldehydes, and esters, and are released from almost every plant. Since prematurely developed sex inducers (psi) are similar to OPs, they can influence the physiological processes of fungi that mimic the action of FO [59], thus facilitating the cross-perception of these molecules [107]. Analyses of several genomes revealed the presence of a fungal GPCR (G protein-coupled receptor). GPCRs have been shown to be responsible for the perception of HPO. The fungal cells sense for molecular interactions between extracellular signals. Therefore, they should be considered as oxylipin receptors [2]. This supports the hypothesis that FO, along with all stimulus forms, can be seen by fungi through a cascade via GPCR.

Future research should focus on the structural foundations of GPCR-effector interactions, and on the signaling conformations that will provide the missing link to better understand the mechanistic underpinnings of GPCR activation and signaling.

7.3. OP Research

Although the role of OPs in plant defense signaling pathways has been described in the literature, direct interaction of OPs with pathogens is also possible. Research on the potential antimicrobial effects of OPs focused on the in vitro effects of OPs against

biotrophic, necrotrophic or hemibiotrophic pathogens. Oxylipins derived from the 9-LOX and α-DOX pathways are characterized by very strong antibacterial activity [5,17,53]. 9-Keto10 (E), 12 (Z), 15 (Z) -octadecatrienoic (9-KOT), as the main product of 9-LOX linoleic acid (LA), is very active against *P. syringae* (Pst) DC3000 [5,17,59,60,70,102]. The in vitro activity and stability of 50 OPs against thirteen agriculturally important pathogens (bacteria, fungi and oomycetes) were tested [18,21,116].

All pathogens were inhibited by one or more oxylipins (Table 2). OPs were even more effective in inhibiting the germination of weed seeds, and especially with a very high effectiveness of (ω-5-Z) -etherolenic, colneic and colnelenic acids [21,64,116]. It was assumed that divinyl-, keto- and hydroxy-FA and HPO exhibit a strong direct antimicrobial effect, while others, such as JA and some volatile aldehydes, have only been suggested in signaling. The described studies were performed in vitro, so it is not known whether oxylipins can also induce such defense mechanisms under field conditions. In nature, plants do not experience isolated stress, and the reactions are controlled by various OP pathways that can interact and inhibit each other [21]. OPs proved to be even more effective in inhibiting the germination of fungal spores, with a very high effectiveness of such acids as (ω-5-Z) -etherolenic acid, colnenic acid and colnelenic acid [21,104,117]. Divinyl-, keto- and hydroxy-FAs and HPO are believed to have very strong, direct antimicrobial activity, while others, such as JA and some volatile aldehydes, are merely suggested for signaling.

Table 2. List of effective non-antimicrobial OPs in in vitro tests.

OP [a]	Strain Bacteria [b]			Fungi								Oomycetes	
	Pc	Ps	Xc	Ab	Bc	Ch	Fo	Lm	Rsp	Ss	IV	Pi	Pp
ω-5(Z)-Etherolenic acid	–	++++	–	+++	– +	–	++	–	–	–	+	–	+
(±)-cis-12,13-Epoxy-9(Z)-octadecenoic acid	–	–	–	++	–	+++	–	–	+	++	–	–	+++
(±)-cis-9,10-Epoxy-12(Z)-octadecenoic acid	–	++	–	–	–	+++	–	++	+	–	–	–	++
(±)-threo-12,13-Dihydroxy-9(Z)-octadecenoic acid	–	–	–	++	–	+++	–	+++	–	+	–	–	–
(±)-threo-9,10-Dihydroxy-12(Z)-octadecenoic acid	–	– +	+	++	–	–	–	–	–	+	–	–	–
10(S),11(S)-Epoxy-9(S)hydroxy12(Z),15(Z)-octadecadienoate	–	–	–	x	–	–	–	x	–	x	x	–	–
11(S),12(S)-Epoxy-13(S)hydroxy9(Z),15(Z)-octadecadienoate	–	++	–	x	+	–	–	x	–	x	x	+	–
13(S)-**Hydroperoxy9**(Z),11(E),15(Z)-octadecatrienoic acid (13-HPOT)	–	–	–	++	++++	++++	+ ++	–	–	–	–	+++	+
13(S)-Hydroperoxy-9(Z),11(E)-octadecadienoic acid (13-HPOD)	–	+	–	–	–	++++	–	–	–	–	–	–	++++
13(S)(Z),11(E),15(Z)octadecatrienoic acid (13-HOT)	–	–	–	+	++++	++++	–	+++	–	–	–	–	++++
13(S)-Hydroxy-9(Z),11(E)-octadecadienoic acid (13-HOD)	–	+	–	–	+	++++	+	–	–	–	–	+	++++

[a] Oxylipins were tested at concentrations up to 100 µM, and measurements were made after a 24-hour incubation period. [b] Test bacteria: *Pectobacterium carotovorum* (Pc), *Pseudomonas syringae* (Ps) and *Xanthomonas campestris* (Xc). Tested fungi: *Alternaria brassicae* (Ab), *Botrytis cinerea* (Bc), *Cladosporium herbarum* (Ch), *Fusarium oxysporum* (Fo), *Leptosphaeria maculans* (Lm), *Rhizopus* sp. (Rsp), *Sclerotinia sclerotiorum* (Ss) and *Verticillium longisporum* (VI). Test oomycetes: *Phytophthora infestans* (Pi) and *Phytophthora parasitica* (Pp). ++++, very high efficiency; +++, highly effective; ++, moderately effective; +, effective; –, ineffective; x, not tested. Source: own based on [116], and modified by D. Skiba.

8. Conclusions and Future Perspectives

Some of the latest developments in oxylipin biology have been presented, which could inform researchers in the field, and could help attract additional researchers to this growing area of plant oxylipin research. In summary, the conclusions are as follows:

1. The development of research on the resistance to primary or applied herbicides should provide information on resistance management for growers and farmers. Maintaining the usefulness of existing herbicides and guidelines for the effective management of herbicide-resistant crops will continue to require innovation in research and development, in order to meet these challenges. However, the adoption of farmers' best management practices may require financial incentives from the private or public sector.
2. New approaches in science are necessary to identify patterns of crop disease occurrence using new intelligent techniques, to identify crop resistance genes, and for molecular characterizations of plant resistance genes and other mechanisms that influence crop–pathogen interactions; novel and/or efficient use of crop resistance genes, as well as innovative breeding strategies, can and will serve to improve disease resistance of crops.
3. Jasmonates participate in all types of active immunity; a significant increase in the concentration of these compounds in tissues has been observed, both as a result of wounding, and from contact of the plant with the pathogen.
4. JA and MeJA and ET are very important components of the signaling pathway; they regulate the ISR response in plants, while SA and MeSA are essential for inducing SAR. However, the individual pathways that lead to the activation of immune mechanisms are not independent, and influence each other through many different interactions.
5. The effect of the signaling mechanism that is involved in jasmonates may involve the abandonment or partial limitation of the use of transgenic plants, with introduced herbicide and pathogen resistance genes, and the abandonment of synthetic pesticides.
6. Recent discoveries add importance for a deeper understanding of how the innate immunity and defenses of plants work. In the current context of looking for alternatives to intensive farming, it is a difficult research area. Increasing our knowledge about how plants respond to stresses, at the molecular, physiological and metabolic levels, will be crucial for the development of new biopesticides.
7. The physiological role of different classes of oxylipins in plant defense mechanisms has been elucidated, but there are still gaps to be filled, such as the following:
    (a) perception of signals related to wounds or pathogen initiators and mechanisms at the cellular level, and the means by which they induce a rapid response of damaged tissues;
    (b) contribution of transduction signals (air, chemical, physical signals) to the systemic defense response of healthy tissues;
    (c) discovery of the molecular mechanisms that are involved in the inactivation of the stress signal;
    (d) explanation of the role of unstable stress signals;
    (e) the emission of OPs by damaged plants, and their influence on plant condition and agronomic performance.
8. Plant crops associated with herbicide-tolerant weeds should be protected through biochemical, genetic and crop control strategies.
9. Implementation of the principles of biological protection into practice requires full commitment and focus on professional cultivation. This requires extensive knowledge of the farmer and agronomist, as well as an increased workload. The main problem lies in attitude; when using biological products, the recommendations for their use must be strictly followed. These are not easy solutions, and often require a change in technology. In the case of "biology", the basis is prevention and consistency in action.

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List of Abbreviations

LA	linoleic acid
LLE	liquid-liquid extraction
LOX	lipoksygenazy
LOX	lipoxygenase
MAMP	molecular patterns associated with micro-organisms,
MeJA	jasmonic acid methyl ester
MeSA	methyl salicylate
OPDA	12-oxo-phytodienic acid
P450	cytochrome peroxygenase
PAMP	patterns molecular pathogen-related,
PGG_2	prostaglandyn of G_2
PGPR	plant growth-promoting bacteria
Ph. infestans	*Phytopthora infestans*
OP	plants oxylipin
PPAR	peroxisome proliferators
PPT	protein precipitation,
PR	pathogenesis-related proteins
PRR	molecular pattern recognition receptors
PTI	resistance induced by molecular patterns,
PUFA	polyunsaturated fatty acids
R	resistance gene/protein
SA	salicylic acid
SAR	systemic acquired resistance
SOA-sites of action	
SPE	extraction until solid phase is obtained
STA	stearic acid [18: 4 n-3]
TD	threonine diamines
A. thaliana	*Arabidopsis thaliana*
ACC	jasmonoyl (JA-ACC)
ALA	α-linolenic acid
ALS	resistance to acetolactate synthetase inhibitors
ARA	arachidonic acid
CLA	linoleic acid (C18:2 n-6).
COX	cyclooxygenase
CYP 450	cytochrome P450
DGLA	dihomo-γ-linolenowy [DGLA]
DHA	docosahexaenoic acid [22:6 n-3]
E	effector
EPA	eicosapentaenoic acid
EPA	eicosapentaenoic acid [20:5 n-3]
ET	ethylene
ETI	effector-induced resistance
ETS	effector-triggered sensitivity
G. fujikuroi	*Gibberella fujikuroi*
GA	gibberellic acid
GLA	γ-linolenic acid
GLV	green leaf volatiles
GPCR	protein coupled with the protein G receptors
H. parasitica	*Hyaloperonospora parasitica*
HPL	a key enzyme in GLV biosynthesis
HR	herbicide resistance
ISR	induced systemic immunity
ISR	induced systemic resistance
JA	jasmonic acid
JA-Ile	jasmonoil isoleucine

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