plants

Review

Occurrence, Function, and Biosynthesis of the Natural Auxin Phenylacetic Acid (PAA) in Plants

Veronica C. Perez[1], Haohao Zhao[2], Makou Lin[1] and Jeongim Kim[1, 2,3]*

[1] Plant Molecular and Cellular Biology, University of Florida, Gainesville, FL, 32611
[2] Horticultural Sciences Department, University of Florida, Gainesville, FL, 32611
[3] Genetic Institute, University of Florida, Gainesville, FL, 32611
* Correspondence: jkim6@ufl.edu

Abstract: Auxins are a class of plant hormones playing crucial roles in plant growth and development and stress responses. Phenylacetic acid (PAA) is a phenylalanine-derived natural auxin found widely in plants. Although auxin activity of PAA in plants was identified several decades ago, PAA homeostasis and its function remain poorly understood, whereas indole-3-acetic acid (IAA), the most potent auxin, has been used for most auxin studies. Recent studies have revealed unique features of PAA distinctive from IAA and enzymes and intermediates of PAA biosynthesis pathway have been identified. Here, we summarize the occurrence and function of PAA in plants and highlight the recent progress made in PAA homeostasis, emphasizing PAA biosynthesis and a crosstalk between IAA and PAA metabolism.

Keywords: Auxins, Phenylacetic Acid, PAA, Growth hormone

Citation: To be added by editorial staff during production.

Academic Editor: Firstname Lastname

Received: date
Accepted: date
Published: date

1. Introduction

Auxins are best known as plant hormones crucial for plant growth and development and survival. Several endogenous auxins are found in plants [1–3]. Among them, indole-3-acetic acid (IAA) has been commonly used for studying auxin function and its biosynthesis. Phenylacetic acid (PAA) is a phenylalanine-derived auxin. Although the auxin activity of PAA was demonstrated nearly a century ago and has been detected widely in plants, PAA homeostasis and its function remain poorly understood. Here, we review the occurrence and function of PAA and recent findings on PAA homeostasis focusing on PAA biosynthesis.

2. Occurrence of PAA

Auxin activity of PAA was reported in the 1930s, but PAA was first isolated in plants in the 1960s. Acidic fractions of aqueous extract from etiolated seedlings of *Phaseolus* were shown to promote growth of oat coleoptile sections, and further analysis identified that these acidic fractions contained PAA [4]. Subsequently, PAA was detected in various plants. Interestingly, most organs and species accumulate PAA to significantly higher levels than IAA [5–7]. In Arabidopsis, PAA contents range from 200 to 3500 pmol/gFW depending on organs, which is higher than IAA in most organs except silique [7–11] (Table 1). Other dicots such as tomato, pea, sunflower, and tobacco accumulate around 600 to 1600 pmol/gFW of PAA in their shoots, which is also several folds greater than IAA contents [5,12]. However, PAA content in *Tropaeolum majus* (< 16 pmol/gFW) is lower than IAA (>70 pmol/gFW) [13]. Monocots and non-vascular plants accumulate 300 to 5000 pmol/gFW of PAA similar to other dicots [5,7,11,12,14,15] (Table 1). Taken together, PAA is widely distributed in the plant kingdom and overall, PAA accumulates more than IAA in most plants.

Table 1. Occurrence of PAA in plants, showing plant tissue, PAA and IAA contents (if available)

Species Name	Plant tissue (PAA content)	Plant tissue (IAA content)	Reference
Arabidopsis (*Arabidopsis thaliana*)	Seedling (413 pmol/gFW); Dry seed (3,250 pmol/gFW); Silique (800 pmol/gFW); Inflorescence (1,900 pmol/gFW); Cauline leaf (400 pmol/gFW); Rosette leaf (250 pmol/gFW); Stem (200 pmol/gFW); Root (1,100 pmol/gFW)	Seedling (49 pmol/gFW); Dry seed (1,950 pmol/gFW); Silique (2,000 pmol/gFW); Inflorescence (130 pmol/gFW); Cauline leaf (30 pmol/gFW); Rosette leaf (33 pmol/gFW); Stem (50 pmol/gFW); Root (130 pmol/gFW)	[7–11]
Bean (*Phaseolus vulgaris*)	Shoot	N/A	[4]
Tomato (*Lycopersicon esculentum*)	Shoot (1,616 pmol/gFW)	Shoot (211 pmol/gFW)	[5,12]
Pea (*Pisum sativum*)	Shoot (632 pmol/gFW); Root (347 pmol/gFW); Cotyledon (451 pmol/gFW); Epicotyl (427 pmol/gFW);	Shoot (126 pmol/gFW); Root (115 pmol/gFW); Cotyledon (13 pmol/gFW); Epicotyl (46 pmol/gFW)	[5,6,12]
Sunflower (*Helianthus annuus*)	Shoot (1,484 pmol/gFW)	Shoot (245 pmol/gFW)	[5,12]
Tobacco (*Nicotiana tabacum*)	Shoot (1,234 pmol/gFW)	Shoot (228 pmol/gFW)	[5,12]
Cotton (*Gossypium hirsutum*)	Cotyledon	N/A	[16]
Nasturtium (*Tropaeolum majus*)	Root (12 pmol/gFW); Hypocotyl (14 ng/gFW); Shoot (12 pmol/gFW); Leaf stalk (13 pmol/gFW); Older leaf (11 pmol/gFW)	Root (679 pmol/gFW); Hypocotyl (166 ng/gFW); Shoot (103 pmol/gFW); Leaf stalk (74 pmol/gFW); Older leaf (86 pmol/gFW)	[13]
Sorghum (*Sorghum bicolor*)	Leaf (300 pmol/gFW)	N/A	[15]
Maize (*Zea mays*)	Shoot (903 pmol/gFW)	Shoot (143 pmol/gFW);	[5,12]
Barley (*Hordeum vulgare*)	Shoot (514 pmol/gFW); Young shoot (4,353 pmol/gFW)	Shoot (63 pmol/gFW); Young shoot (30 pmol/gFW)	[5,7,12]
Oat (*Avena sativa*)	Young shoot (3,860 pmol/gFW)	Young shoot (31 pmol/gFW)	[7]
Ostrich fern (*Matteuccia struthiopteris*)	Crozier (2,790 pmol/gFW); Young rachis (1,470 pmol/gFW); Immature pinnae (4,860 pmol/gFW); Mature pinnae (2,380 pmol/gFW); Fertile pinnae (2,490 pmol/gFW)	Crozier (119 pmol/gFW); Young rachis (219 pmol/gFW); Immature pinnae (161 pmol/gFW); Mature pinnae (67 pmol/gFW); Fertile pinnae (70 pmol/gFW)	[14]
Moss (*Physcomitrella patens*)	1,049 pmol/gFW	14 pmol/gFW	[7]
Liverwort (*Marchantia polymorpha*)	469 pmol/gFW	74 pmol/gFW	[7]

[1]pmol/gFW is uniformly used as the unit of approximate amount of PAA

N/A ; not available in the same paper

3. Biological Function of PAA

Auxin activity of PAA was identified through three classical auxin activity tests: pea test, cylinder test, and oat bending test [17]. All three tests revealed PAA has less than 10% of IAA activity [17]. One of the most representative functions of PAA is the promotion of root growth and development [6,8,13,18,19]. PAA induced root formation in tomato, sunflower, marigold, artichoke, buckwheat, dahlia, and tobacco when applied to the stem [20]. PAA application promoted the formation of adventitious roots of cress hypocotyls, sugar-beet seedlings, and pea epicotyls [21]. Furthermore, leaf explants of *Ajuga bracteosa* on growth media supplemented with PAA increased frequency of root induction and biomass [19]. Arabidopsis seedlings treated with PAA increased the formation of lateral roots, although PAA showed 10- to 20-fold lower activity than IAA [7]. However, some studies showed stronger activity of PAA than IAA. In pea seedlings, PAA induced more lateral root primordia and emerged lateral roots and longer lengths of lateral roots compared to those of IAA [6,18].

PAA impacts aerial parts of plants as well [7,11,22,23]. Daily exogenous application of PAA on tomato plants for 2 weeks significantly increased tomato height [22]. PAA application led to epinastic leaves of artichokes [20], stimulated the elongation of wheat coleoptile and moss gametophore [7,23], and promoted elongation of the *Phaseolus* internode [24]. Arabidopsis plants with increased PAA production showed elongated hypocotyls and epinastic leaves, similar to what was observed in high-IAA Arabidopsis plants [11]. Supplementation of PAA induced callus formation in tobacco, sunflower, chickpea, and lentil, but the optimal concentration of PAA for tobacco callus induction was 3-4 times higher than IAA [25,26]. Similar to IAA, PAA application to leafless cotyledon retarded the petiole abscission in cotton and inhibits ethylene evolution [16].

PAA itself has anti-microbial and anti-fungal activities and exogenous application of PAA enhances tolerance to pathogen infection, whereas increased IAA in plants enhances susceptibility to pathogens [27–29]. For example, exogenous application of PAA on citrus inhibits the incidence of fungus molds caused by *Penicillium digitatum* and *P. italicum* [30]. Herbivore infestation in maize, poplar, and plumeria increases PAA production [31–33]. Application of PAA in oilseed rape enhances the prevention of *Sclerotinia sclerotiorum* and *in vitro* treatment with PAA demonstrated adverse effects through the disruption of cell wall and cytoplasm in mycelia [34]. However, any biological role of PAA in plant defense remains unknown.

The first step of auxin action starts from auxin sensing by auxin receptors (TIR1 and AFBs), which results in degradation of transcription repressors Aux/IAAs [35]. Shimizu-Mitao and Kakimoto showed PAA-dependent degradation of Aux/IAA [35]. Interaction of Aux/IAAs with auxin receptors TIR1 or AFB2 leads to degradation of Aux/IAA [35]. They showed that PAA induced Aux/IAA degradation with lower activity than IAA [35]. Sugawara *et al.* showed that PAA application rescued growth defects of IAA deficient plants yuc quadruple mutants (*yucQ*) [7]. In the same study, a yeast two-hybrid assay and a pull-down assay revealed that PAA promoted the interaction of auxin receptors and Aux/IAA in vitro, suggesting that sensing and signaling modes of PAA are similar to IAA [7].

It is noteworthy that PAA does not engage in polar auxin transport [7,16,36–38]. Labeled PAA transport assay using pea epicotyls revealed that the transport of PAA barely occurs in both the basipetal and acropetal direction [36]. PAA applied to the apical bud of intact pea plants did not move in the long-distance basipetal transport [38]. Auxin polar transport inhibitor naphthylphthalamic acid (NPA) inhibited IAA transport, but NPA did not affect PAA gradient patterns in cotton, pea, and maize [7,16,37]. Unlike IAA, PAA did not form concentration gradients in response to gravitropic stimulation via active and directional transport in maize [7]. However, PAA inhibited IAA polar transport in internode segments and long-distance movement of the pea apical bud [38].

4. PAA Homeostasis

As auxins regulate a vast array of processes, changes in content or distribution of auxins can have profound effects on plant growth and development and in extreme cases can lead to severe dwarfism or sterility [39–42]. Auxin homeostasis refers to the spatiotemporal distribution of auxin throughout plant tissues and organs which governs plant growth and development. Although several processes, including auxin transport, conjugation and degradation influence auxin homeostasis, *de novo* biosynthesis directly affects local concentration of auxins.

4.1 PAA Biosynthesis

The main route of IAA biosynthesis from tryptophan in plants is the YUCCA pathway [43–52] (Figure 1a). The first step of this pathway is the conversion of tryptophan to indole-3-pyruvate (IPA) by enzymes belonging to the Tryptophan Aminotransferase of Arabidopsis (TAA) family [53–56]. Then, flavin-containing monooxygenases belonging the YUCCA (YUC) family convert IPA to IAA [42,55,57–60]. This pathway is also believed to contribute towards PAA biosynthesis (Figure 1b), as several studies have shown that TAA and YUC enzymes can convert phenylalanine to phenylpyruvate (PPA) and PPA to PAA *in vitro*, respectively [7,54,59,61,62]. YUCCA overexpression increases endogenous PAA or PAA conjugate content [7]. However, *TAA* and *YUC* mutants sometimes show little or no change in PAA content despite significant alterations to IAA content. For example, the maize YUC1-deficient mutant *de18* has an over 90% reduction in free and total IAA contents while PAA content is not significantly affected, and the *tar2-1* pea mutant displays a near complete loss of free IAA but no change in PAA levels [61]. Similarly in Arabidopsis the *yuc1yuc2yuc6* triple and *yuc3yuc5yuc7yuc8yuc9* quintuple mutants have wild-type levels of PAA but 40-50% reductions in IAA content [7]. However the TAA1 deficient mutant *wei8-1* displays a 20% and 80% reduction in PAA and IAA, respectively [7]. These findings suggest that these enzymes may function in PAA biosynthesis in plants, but may not be major players in PAA biosynthesis in some species [35].

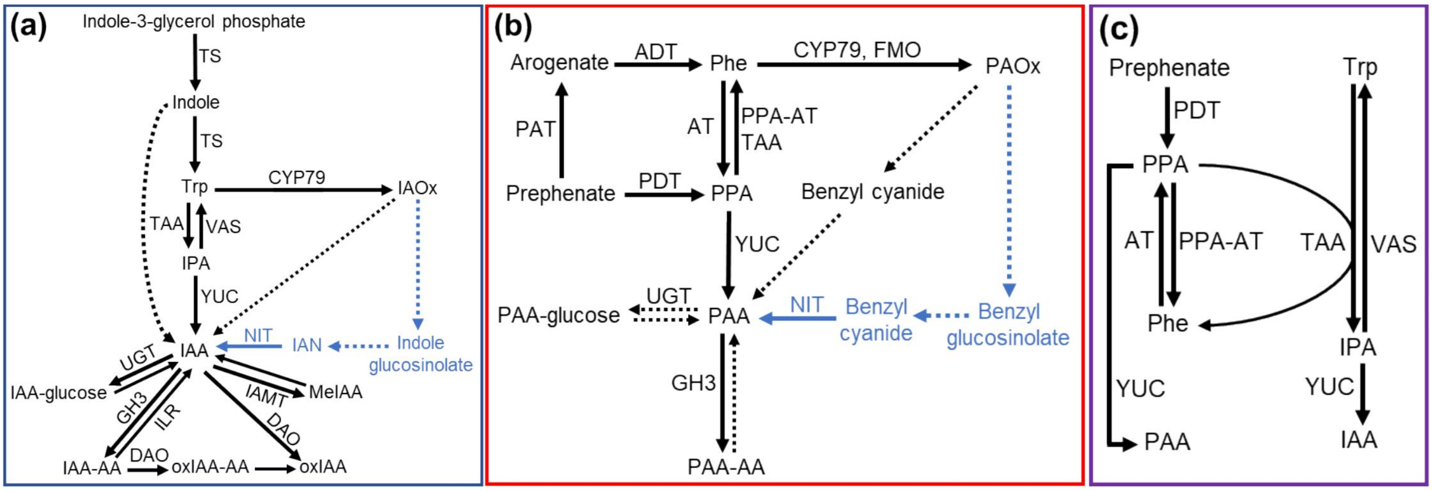

Figure 1. Schematic diagrams of IAA biosynthesis (a), PAA biosynthesis (b), and a link between IAA and PAA metabolism in plants (c). The pathways only include steps and enzymes that are demonstrated via genetic evidence. Solid arrows represent single reactions catalyzed by known enzymes, and dotted arrows represent predicted single or multiple steps. Blue arrows and metabolites represent pathways and metabolites present only in Brassicales species. IAA, indole-3-acetic acid; IAA-AA, amino acid-conjugated IAA; IAN, indole-3-acetonitrile; IAOx, indole-3-acetaldoxime; IPA, indole-3-pyruvate; MeIAA, methyl-conjugated IAA; oxIAA, 2-oxindole-3-acetic acid; oxIAA-AA, amino-acid conjugated oxIAA; PAA, phenylacetic acid; PAA-AA, amino-acid conjugated PAA; PAOx, phenylacetaldoxime; Phe, phenylalanine; PPA, phenylpyruvate; Trp, tryptophan; AT, amino transferase; CYP79, cytochrome P450 monooxygenase of the 79 family; DAO, dioxygenase for auxin oxidation; FMO, flavin-containing monooxygenase; GH3, Gretchen Hagen 3 auxin-amido synthetase; ILR, IAA-Leu Resistant IAA-Amino hydrolase; IAMT, IAA carboxymethyltransferase; NIT, nitrilase; PAT, prephenate aminotransferase; PDT, prephenate dehydratase; PPA-AT, phenylpyruvate aminotransferase; TAA, tryptophan aminotransferase of Arabidopsis; TS, tryptophan synthase; UGT, UDP-glucuronosyltransferase; YUC, YUCCA family of flavin-containing monooxygenase; VAS; methionine aminotransferase

In plants and prokaryotes, phenylalanine biosynthesis from prephenate occurs through two routes: transamination of prephenate to arogenate which is subsequently decarboxylated and dehydrated into phenylalanine, or decarboxylation and dehydration of prephenate to form phenylpyruvate (PPA) which is converted to phenylalanine through transamination [63–65] (Figure 1c). Generally, the PPA pathway is more commonly found in prokaryotes while the arogenate pathway is the major route of phenylalanine biosynthesis in plants; however, there is evidence for both pathways existing and making significant contributions in several plant and bacterial species [63–65]. Thus, modification of PPA metabolism may impact PAA biosynthesis not only directly by being converted to PAA but also indirectly by affecting phenylalanine pools in plants (Figure 1c).

Aoi *et al.* demonstrated that arogenate dehydratase (ADT), the enzyme that catalyzes the conversion of arogenate to phenylalanine, affects PAA biosynthesis, as overexpression or knockout of *ADT*s results in increased or decreased PAA content, respectively [10]. As arogenate serves as a precursor of phenylalanine, increased ADT activity results in increases in phenylalanine-derived metabolites such as PAA. They also detected changes in PPA levels upon modulation of ADT activity that followed the trends measured for PAA content (i.e. *ADT* overexpression resulted in increased levels of PAA and PPA) [10], supporting the role of PPA as a precursor of PAA.

Another PAA biosynthesis pathway is the aldoxime pathway using phenylalanine-derived aldoxime, phenylacetaldoxime (PAOx), as an intermediate [8,10,11,15,66]. Aldoximes such as indole-3-acetaldoxime (IAOx) and PAOx as well as aldoximes derived from other amino acids are well characterized as precursors of various specialized metabolites such as glucosinolates, cyanogenic glycosides, and camalexin as well as nitrogenous volatiles [31,33,67–72]. Several studies have shown that IAA can be made from IAOx in Brassicales and monocots [11,73–75] (Figure 1a). Similarly, it was shown that PAOx is a precursor of PAA in Arabidopsis and monocots [8,11,15] (Figure 1b). Arabidopsis plants overproducing PAOx increase PAA and display altered morphology such as epinasty leaves and elongated hypocotyls similar to shown in plants with increased IAA [8,11,42]. Maize and sorghum plants fed with labeled PAOx produce labeled PAA [11,15]. These findings indicate a wider distribution of the aldoxime-derived auxin biosynthesis pathway throughout the plant kingdom rather than limited to Brassicales.

The first step of the aldoxime pathway is the production of IAOx or PAOx by cytochrome P450 monooxygenases of the 79 family (CYP79s) [8,11,15,32,66]. In addition to CYP79 enzymes, flavin-containing monooxygenases (FMOs) in two fern species have been shown to catalyze conversion of phenylalanine to PAOx [76]. Aldoximes contribute to auxin pools through two routes (Figure 1a, 1b). In Brassicales plants, both IAOx and PAOx are precursors of family-specific glucosinolates. Glucosinolates and their degradation enzyme beta-thiol-glucosidases known as myrosinases are stored in separate cellular and subcellular compartments [77–80]. Upon herbivore or pathogen attack, however, these compartments are compromised, resulting in glucosinolate hydrolysis by myrosinases and the rapid release of toxic metabolites such as isothiocyanates, nitriles and epithionitriles [81–83]. Glucosinolate turnover has also been shown to occur *in vivo* without tissue damage or disruption [84–87]. Nitriles such as indole-3-acetonitrile (IAN) and benzyl cyanide are byproducts of glucosinolate degradation. These nitriles can then be acted upon by nitrilase enzymes to generate IAA and PAA [13,88–92]. On the other hand, aldoximes can be converted to auxins through the aldoxime-derived auxin pathway, which is glucosinolate-independent and is present in both Brassicales and non-Brassicales species as maize and sorghum [11,15]. A recent study demonstrated that benzyl cyanide serves as an intermediate of PAOx-derived PAA biosynthesis in maize and sorghum [15]. Application of benzyl cyanide increases PAA in maize and sorghum and both species convert labeled benzyl cyanide to labeled PAA [15], suggesting that nitriles may be key intermediates in both routes of the aldoxime pathway (Figure 1a, 1b). Unlike the YUCCA pathway, the aldoxime-derived auxin pathways do not appear to be the main route of auxin biosynthesis under normal growth conditions. For example, the Arabidopsis IAOx deficient mutant, *cyp79b2 cyp79b3* (*b2b3*) double mutant, grows normally under optimal temperatures [73], and the *CYP79A2* gene encoding the PAOx production enzyme is barely expressed in the vegetative tissue of Arabidopsis ecotype Col-0 [11]. However, at high temperature and under salt stress, the *b2b3* mutant displays a low auxin growth phenotype [73,93], suggesting that the aldoxime pathway contributes significantly towards stress-induced auxin production. Indeed, many CYP79 enzymes have their expression induced by stressors such as herbivory or by treatment with stress hormones such as jasmonic acid [31,32,68,72,94]. Given that aldoximes often serve as precursors of defense metabolites, the aldoxime pathway may play a role in modulating plant growth during the defense response.

Besides PPA, PAOx, and benzyl cyanide, several other metabolites have been implicated in PAA biosynthesis, although where they fit within the known biosynthetic pathways is unclear. Several labeled feeding experiments have demonstrated that phenylacetaldehyde (PAAld) is derived from phenylalanine metabolism and produced along with labeled PAA [5,95]. PAAld biosynthesis from PPA has been shown to occur in rose through the actions of phenylpyruvate decarboxylases [96]. Also, in rose as well as other species PAAld has been shown to be directly synthesized from phenylalanine by the action of aromatic aldehyde synthases or aromatic amino acid decarobylases [96–100]. Once PAAld is synthesized, it can potentially be acted upon by aldehyde oxidases to generate PAA which have been demonstrated to have activity for PAAld in maize [101]. Another metabolite, 4-phenylbutyric acid (4PBA), was recently shown to display an auxin-like effect during plant regeneration via conversion to PAA using a mechanism independent of IBR3-catalyzed oxidation [102]. Further study showing altered PAA contents upon removal of intermediate biosynthesis enzymes may reveal the role(s) that these metabolites play in PAA biosynthesis.

4.2 PAA Inactivation

Another major facet of auxin homeostasis is the conversion of active auxins to inactive forms. Inactivation of auxin not only supports the formation of auxin gradients and maintenance of auxin levels but is also necessary to prevent cytotoxic levels of auxins from accumulating in cells. IAA inactivation proceeds through two pathways: reversible IAA conjugation (to glucose, methyl, or amino acids) and irreversible IAA conjugation (to amino acids) and oxidation, with recent findings demonstrating that amino acid-conjugated IAA is oxidized and then subsequently hydrolyzed to form oxidized IAA [103,104]. As with biosynthesis, knowledge of PAA inactivation is limited compared to our understanding of IAA inactivation. Multiple studies have demonstrated that some Gretchen Hagen 3 IAA-amido synthetase (GH3) and UDP-glucuronosyltransferase (UGT) enzymes have activity towards PAA to generate PAA conjugates such as PAA-asp and PAA-glu and PAA-glucose, respectively [7,105–108] (Figure 1b).

4.3 Metabolic Interaction between IAA and PAA

More recent studies have shown a link between IAA and PAA metabolism. The homeostasis of IAA and PAA was shown to be maintained through modulation of auxin conjugation, with the accumulation of PAA resulting in the induction of *GH3* or *UGT* genes that preferentially act upon IAA and vice versa [8,9]. Lynch *et al.* showed that PPA can, in addition to its previously defined and proposed impacts of PAA biosynthesis, impact IAA biosynthesis by serving as amino acceptor in the TAA-catalyzed conversion of tryptophan to IPA [109]. This interaction not only promotes the production of IAA but may also impact PAA biosynthesis, as increasing flux through the PPA route of phenylalanine biosynthesis was shown to decrease steady state levels of phenylalanine [109] (Figure 1c). Perez *et al.* demonstrated that accumulation of PAA results in transcriptional downregulation of genes related to tryptophan and IAA biosynthesis in Arabidopsis [11], demonstrating a complex regulatory network for maintaining auxin homeostasis.

5. Conclusions

In the past decades, several biochemical and genetic studies have identified key metabolites, enzymes and pathways that contribute towards IAA metabolism. While many questions remain regarding PAA homeostasis, recent studies have greatly expanded our understanding on how PAA is synthesized and inactivated. The role of PPA as a metabolite linking together phenylalanine, IAA and PAA biosynthesis has been supported by genetic studies and suggests that PPA-derived PAA biosynthesis is more complex than the corresponding IAA biosynthetic pathway. Meanwhile, the occurrence of PAOx as a PAA precursor in Brassicales and monocots suggests that this hidden pathway may be distributed widely in the plant kingdom and contribute towards PAA homeostasis wherever PAOx is produced. Additionally, the identification of PAA-amino acid and PAA-glucose conjugates within Arabidopsis has provided mechanisms for PAA inactivation which may be shared among other species, and may employ similar pathways used in IAA inactivation. Future investigation is needed to reveal other potential PAA biosynthesis and inactivation pathways as well as the physiological roles of these pathways.

Author Contributions: V.P., H.Z., and M.L made tables and figures. V.P., H.Z., M.L. and J.K designed and wrote the review. All authors have read and agreed the final manuscript.

Funding: This research was funded by National Science Foundation CAREER Grant (IOS-2142898)

Data Availability Statement: Not applicable.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Simon, S.; Petrášek, J. Why Plants Need More than One Type of Auxin. *Plant Sci* **2011**, *180*, 454–460, doi:10.1016/j.plantsci.2010.12.007.
2. Damodaran, S.; Strader, L.C. Indole 3-Butyric Acid Metabolism and Transport in Arabidopsis Thaliana. *Front Plant Sci* **2019**, *10*, doi:10.3389/fpls.2019.00851.
3. Enders, T.A.; Strader, L.C. Auxin Activity: Past, Present, and Future. *Am J Bot* **2015**, *102*, 180–196, doi:10.3732/ajb.1400285.
4. Okamoto, T.; Koizumi, T.; Isogai, Y. Studies on Plant Growth Regulators. II. Isolation of Indole-3-Acetic Acid, Phenylacetic Acid, and Several Plant Growth Inhibitors from Etiolated Seedlings of Phaseolus. *Chem Pharm Bull* **1967**, *15*, 159–163.
5. Wightman, F.; Lighty, D.L. Identification of Phenylacetic Acid as a Natural Auxin in the Shoots of Higher Plants. *Physiol Plant* **1982**, *55*, 17–24, doi:10.1111/j.1399-3054.1982.tb00278.x.
6. Schneider, E.A.; Kazakoff, C.W.; Wightman, F. Gas Chromatography-Mass Spectrometry Evidence for Several Endogenous Auxins in Pea Seedling Organs. *Planta* **1985**, *165*, 232–241, doi:10.1007/BF00395046.
7. Sugawara, S.; Mashiguchi, K.; Tanaka, K.; Hishiyama, S.; Sakai, T.; Hanada, K.; Kinoshita-Tsujimura, K.; Yu, H.; Dai, X.; Takebayashi, Y.; et al. Distinct Characteristics of Indole-3-Acetic Acid and Phenylacetic Acid, Two Common Auxins in Plants. *Plant Cell Physiol* **2015**, *56*, 1641–1654, doi:10.1093/pcp/pcv088.
8. Aoi, Y.; Tanaka, K.; Cook, S.D.; Hayashi, K.-I.; Kasahara, H. GH3 Auxin-Amido Synthetases Alter the Ratio of Indole-3-Acetic Acid and Phenylacetic Acid in Arabidopsis. *Plant Cell Physiol* **2020**, *61*, 596–605, doi:10.1093/pcp/pcz223.
9. Aoi, Y.; Hira, H.; Hayakawa, Y.; Liu, H.; Fukui, K.; Dai, X.; Tanaka, K.; Hayashi, K.-I.; Zhao, Y.; Kasahara, H. UDP-Glucosyltransferase UGT84B1 Regulates the Levels of Indole-3-Acetic Acid and Phenylacetic Acid in Arabidopsis. *Biochem Biophys Res Commun* **2020**, *532*, 244–250, doi:10.1016/j.bbrc.2020.08.026.
10. Aoi, Y.; Oikawa, A.; Sasaki, R.; Huang, J.; Hayashi, K.; Kasahara, H. Arogenate Dehydratases Can Modulate the Levels of Phenylacetic Acid in Arabidopsis. *Biochem Biophys Res Commun* **2020**, *524*, 83–88, doi:10.1016/j.bbrc.2020.01.041.
11. Perez, V.C.; Dai, R.; Bai, B.; Tomiczek, B.; Askey, B.C.; Zhang, Y.; Rubin, G.M.; Ding, Y.; Grenning, A.; Block, A.K.; et al. Aldoximes Are Precursors of Auxins in Arabidopsis and Maize. *New Phytol* **2021**, *231*, 1449–1461, doi:10.1111/nph.17447.

12. Wightman, F.; Rauthan, B.S. Evidence for the Biosynthesis and Natural Occurrence of the Auxin, Phenylacetic Acid, in Shoots of Higher Plants. *Plant Growth Substances; Proceedings of the International Conference* **1974**.
13. Ludwig-Müller, J.; Cohen, J.D. Identification and Quantification of Three Active Auxins in Different Tissues of Tropaeolum Majus. *Physiol Plant* **2002**, *115*, 320–329.
14. Schneider, E.A.; Wightman, F. Auxins of Non-Flowering Plants. I. Occurrence of 3-Indoleacetic Acid and Phenylacetic Acid in Vegetative and Fertile Fronds of the Ostrich Fern (Matteucia Struthiopteris). *Physiol Plant* **1986**, *68*, 396–402, doi:10.1111/j.1399-3054.1986.tb03372.x.
15. Perez, V.C.; Dai, R.; Tomiczek, B.; Mendoza, J.; Wolf, E.S.A.; Grenning, A.; Vermerris, W.; Block, A.K.; Kim, J. Metabolic Link between Auxin Production and Specialized Metabolites in Sorghum Bicolor. *J Exp Bot* **2022**, erac421, doi:10.1093/jxb/erac421.
16. Suttle, J.C.; Mansager, E.R. The Physiological Significance of Phenylacetic Acid in Abscising Cotton Cotyledons. *Plant Physiol* **1986**, *81*, 434–438.
17. Haagen-Smit, S.A.J; Went, F.W. A Physiological Analysis of Growth Substances. *Proc K Ned Akad van Wet* **1935**, *38*, 852–857.
18. Wightman, F.; Schneider, E.A.; Thimann, K.V. Hormonal Factors Controlling the Initiation and Development of Lateral Roots. *Physiol Plant* **1980**, *49*, 304–314, doi:10.1111/j.1399-3054.1980.tb02669.x.
19. Saeed, S.; Ali, H.; Khan, T.; Kayani, W.; Khan, M.A. Impacts of Methyl Jasmonate and Phenyl Acetic Acid on Biomass Accumulation and Antioxidant Potential in Adventitious Roots of Ajuga Bracteosa Wall Ex Benth., a High Valued Endangered Medicinal Plant. *Physiol Mol Biol Plants* **2017**, *23*, 229–237, doi:10.1007/s12298-016-0406-7.
20. Zimmerman, P.W; Wilcoxon F. Several Chemical Growth Substances Which Cause Initiation of Roots and Other Responses in Plants. *Contrib Boyce Thompson Inst* **1935**, *7*, 209–229.
21. Wheeler, A. Auxin-like Growth Activity of Phenylacetonitrile. *Ann Bot* **1977**, *41*, 867–872.
22. Pearse, H.L. Effect of Phenylacetic Acid on the Growth of Tomato Plants. *Nature* **1936**, *138*, 363–364, doi:10.1038/138363b0.
23. Abe, H.; Uchiyama, M.; Sato, R. Isolation of Phenylacetic Acid and Its *p* -Hydroxy Derivative as Auxin-like Substances from *Undaria Pinnatifida*. *Agric Biol Chem* **1974**, *38*, 897–898, doi:10.1080/00021369.1974.10861257.
24. Small, D.K.; Morris, D.A. Promotion of Elongation and Acid Invertase Activity in Phaseolus Vulgaris L. Internode Segments by Phenylacetic Acid. *Plant Growth Regul* **1990**, *9*, 329–340.
25. Milborrow, B.V.; Purse, J.G.; Wightman, F. On the Auxin Activity of Phenylacetic Acid. *Ann Bot* **1975**, *39*, 1143–1146.
26. Leuba, V.; LeTourneau, D. Auxin Activity of Phenylacetic Acid in Tissue Culture. *J Plant Growth Regul* **1990**, *9*, 71–76, doi:10.1007/BF02041944.
27. Chen, Z.; Agnew, J.L.; Cohen, J.D.; He, P.; Shan, L.; Sheen, J.; Kunkel, B.N. Pseudomonas Syringae Type III Effector AvrRpt2 Alters Arabidopsis Thaliana Auxin Physiology. *PNAS* **2007**, *104*, 20131–20136, doi:10.1073/pnas.0704901104.
28. Mutka, A.M.; Fawley, S.; Tsao, T.; Kunkel, B.N. Auxin Promotes Susceptibility to Pseudomonas Syringae via a Mechanism Independent of Suppression of Salicylic Acid-Mediated Defenses. *Plant J* **2013**, *74*, 746–754, doi:10.1111/tpj.12157.
29. Kunkel, B.N.; Harper, C.P. The Roles of Auxin during Interactions between Bacterial Plant Pathogens and Their Hosts. *J Exp Bot* **2018**, *69*, 245–254, doi:10.1093/jxb/erx447.

30. Liu, P.; Cheng, Y.; Yang, M.; Liu, Y.; Chen, K.; Long, C.; Deng, X. Mechanisms of Action for 2-Phenylethanol Isolated from Kloeckera Apiculata in Control of Penicillium Molds of Citrus Fruits. *BMC Microbiol* **2014**, *14*, 242, doi:10.1186/s12866-014-0242-2.
31. Irmisch, S.; McCormick, A.C.; Boeckler, G.A.; Schmidt, A.; Reichelt, M.; Schneider, B.; Block, K.; Schnitzler, J.-P.; Gershenzon, J.; Unsicker, S.B.; et al. Two Herbivore-Induced Cytochrome P450 Enzymes CYP79D6 and CYP79D7 Catalyze the Formation of Volatile Aldoximes Involved in Poplar Defense. *Plant Cell* **2013**, *25*, 4737–4754, doi:10.1105/tpc.113.118265.
32. Irmisch, S.; Zeltner, P.; Handrick, V.; Gershenzon, J.; Köllner, T.G. The Maize Cytochrome P450 CYP79A61 Produces Phenylacetaldoxime and Indole-3-Acetaldoxime in Heterologous Systems and Might Contribute to Plant Defense and Auxin Formation. *BMC Plant Biol* **2015**, *15*, 128, doi:10.1186/s12870-015-0526-1.
33. Dhandapani, S.; Jin, J.; Sridhar, V.; Chua, N.-H.; Jang, I.-C. CYP79D73 Participates in Biosynthesis of Floral Scent Compound 2-Phenylethanol in *Plumeria Rubra*. *Plant Physiol* **2019**, *180*, 171–184, doi:10.1104/pp.19.00098.
34. Zhang, H.; Cheng, Q.; Wang, X.; Jia, W.; Xie, J.; Fan, G.; Han, C.; Zhao, X. Selenium Improved Phenylacetic Acid Content in Oilseed Rape and Thus Enhanced the Prevention of Sclerotinia Sclerotiorum by Dimethachlon. *J Fungi* **2022**, *8*, 1193, doi:10.3390/jof8111193.
35. Shimizu-Mitao, Y.; Kakimoto, T. Auxin Sensitivities of All Arabidopsis Aux/IAAs for Degradation in the Presence of Every TIR1/AFB. *Plant Cell Physiol* **2014**, *55*, 1450–1459, doi:10.1093/pcp/pcu077.
36. ProchÁzka, S.; Borkovec, V. Transport and Regulative Properties of Phenylacetic Acid. *Biol Plant* **1984**, *26*, 358–363, doi:10.1007/BF02898573.
37. Johnson, C.F.; Morris, D.A. Regulation of Auxin Transport in Pea (Pisum Sativum L.) by Phenylacetic Acid: Effects on the Components of Transmembrane Transport of Indol-3yl-Acetic Acid. *Planta* **1987**, *172*, 400–407, doi:10.1007/BF00398670.
38. Morris, D.A.; Johnson, C.F. Regulation of Auxin Transport in Pea (Pisum Sativum L.) by Phenylacetic Acid: Inhibition of Polar Auxin Transport in Intact Plants and Stem Segments. *Planta* **1987**, *172*, 408–416, doi:10.1007/BF00398671.
39. Boerjan, W.; Cervera, M.T.; Delarue, M.; Beeckman, T.; Dewitte, W.; Bellini, C.; Caboche, M.; Onckelen, H.V.; Montagu, M.V.; Inzé, D. Superroot, a Recessive Mutation in Arabidopsis, Confers Auxin Overproduction. *Plant Cell* **1995**, *7*, 1405–1419, doi:10.1105/tpc.7.9.1405.
40. Seo, M.; Akaba, S.; Oritani, T.; Delarue, M.; Bellini, C.; Caboche, M.; Koshiba, T. Higher Activity of an Aldehyde Oxidase in the Auxin-Overproducing Superroot1 Mutant of Arabidopsis Thaliana. *Plant Physiol* **1998**, *116*, 687–693, doi:10.1104/pp.116.2.687.
41. van der Graaff, E.; Boot, K.; Granbom, R.; Sandberg, G.; Hooykaas, P.J.J. Increased Endogenous Auxin Production in Arabidopsis Thaliana Causes Both Earlier Described and Novel Auxin-Related Phenotypes. *J Plant Growth Regul* **2003**, *22*, 240–252, doi:10.1007/s00344-003-0014-y.
42. Kim, J.I.; Sharkhuu, A.; Jin, J.B.; Li, P.; Jeong, J.C.; Baek, D.; Lee, S.Y.; Blakeslee, J.J.; Murphy, A.S.; Bohnert, H.J.; et al. Yucca6, a Dominant Mutation in Arabidopsis, Affects Auxin Accumulation and Auxin-Related Phenotypes. *Plant Physiol* **2007**, *145*, 722–735, doi:10.1104/pp.107.104935.
43. Woo, Y.-M.; Park, H.-J.; Su'udi, M.; Yang, J.-I.; Park, J.-J.; Back, K.; Park, Y.-M.; An, G. Constitutively Wilted 1, a Member of the Rice YUCCA Gene Family, Is Required for Maintaining Water Homeostasis and an Appropriate Root to Shoot Ratio. *Plant Mol Biol* **2007**, *65*, 125–136, doi:10.1007/s11103-007-9203-6.
44. Yamamoto, Y.; Kamiya, N.; Morinaka, Y.; Matsuoka, M.; Sazuka, T. Auxin Biosynthesis by the YUCCA Genes in Rice. *Plant Physiol* **2007**, *143*, 1362–1371, doi:10.1104/pp.106.091561.

45. Gallavotti, A.; Barazesh, S.; Malcomber, S.; Hall, D.; Jackson, D.; Schmidt, R.J.; McSteen, P. Sparse Inflorescence1 Encodes a Monocot-Specific YUCCA-like Gene Required for Vegetative and Reproductive Development in Maize. *PNAS* **2008**, *105*, 15196–15201, doi:10.1073/pnas.0805596105.
46. Abu-Zaitoon, Y.M.; Bennett, K.; Normanly, J.; Nonhebel, H.M. A Large Increase in IAA during Development of Rice Grains Correlates with the Expression of Tryptophan Aminotransferase OsTAR1 and a Grain-Specific YUCCA. *Physiol Plant* **2012**, *146*, 487–499, doi:10.1111/j.1399-3054.2012.01649.x.
47. Bernardi, J.; Lanubile, A.; Li, Q.-B.; Kumar, D.; Kladnik, A.; Cook, S.D.; Ross, J.J.; Marocco, A.; Chourey, P.S. Impaired Auxin Biosynthesis in the Defective Endosperm18 Mutant Is Due to Mutational Loss of Expression in the ZmYuc1 Gene Encoding Endosperm-Specific YUCCA1 Protein in Maize. *Plant Physiol* **2012**, *160*, 1318–1328, doi:10.1104/pp.112.204743.
48. Bernardi, J.; Li, Q.-B.; Gao, Y.; Zhao, Y.; Battaglia, R.; Marocco, A.; Chourey, P.S. The Auxin-Deficient Defective Kernel18 (Dek18) Mutation Alters the Expression of Seed-Specific Biosynthetic Genes in Maize. *J Plant Growth Regul* **2016**, *35*, 770–777, doi:10.1007/s00344-016-9581-6.
49. Kakei, Y.; Nakamura, A.; Yamamoto, M.; Ishida, Y.; Yamazaki, C.; Sato, A.; Narukawa-Nara, M.; Soeno, K.; Shimada, Y. Biochemical and Chemical Biology Study of Rice OsTAR1 Revealed That Tryptophan Aminotransferase Is Involved in Auxin Biosynthesis: Identification of a Potent OsTAR1 Inhibitor, Pyruvamine2031. *Plant Cell Physiol* **2017**, *58*, 598–606, doi:10.1093/pcp/pcx007.
50. Poulet, A.; Kriechbaumer, V. Bioinformatics Analysis of Phylogeny and Transcription of TAA/YUC Auxin Biosynthetic Genes. *Int J Mol Sci* **2017**, *18*, 1791, doi:10.3390/ijms18081791.
51. Shao, A.; Ma, W.; Zhao, X.; Hu, M.; He, X.; Teng, W.; Li, H.; Tong, Y. The Auxin Biosynthetic TRYPTOPHAN AMINOTRANSFERASE RELATED TaTAR2.1-3A Increases Grain Yield of Wheat. *Plant Physiol* **2017**, *174*, 2274–2288, doi:10.1104/pp.17.00094.
52. Cao, X.; Yang, H.; Shang, C.; Ma, S.; Liu, L.; Cheng, J. The Roles of Auxin Biosynthesis YUCCA Gene Family in Plants. *Int J Mol Sci* **2019**, *20*, 6343, doi:10.3390/ijms20246343.
53. Stepanova, A.N.; Robertson-Hoyt, J.; Yun, J.; Benavente, L.M.; Xie, D.-Y.; Doležal, K.; Schlereth, A.; Jürgens, G.; Alonso, J.M. TAA1-Mediated Auxin Biosynthesis Is Essential for Hormone Crosstalk and Plant Development. *Cell* **2008**, *133*, 177–191, doi:10.1016/j.cell.2008.01.047.
54. Tao, Y.; Ferrer, J.-L.; Ljung, K.; Pojer, F.; Hong, F.; Long, J.A.; Li, L.; Moreno, J.E.; Bowman, M.E.; Ivans, L.J.; et al. Rapid Synthesis of Auxin via a New Tryptophan-Dependent Pathway Is Required for Shade Avoidance in Plants. *Cell* **2008**, *133*, 164–176, doi:10.1016/j.cell.2008.01.049.
55. Won, C.; Shen, X.; Mashiguchi, K.; Zheng, Z.; Dai, X.; Cheng, Y.; Kasahara, H.; Kamiya, Y.; Chory, J.; Zhao, Y. Conversion of Tryptophan to Indole-3-Acetic Acid by TRYPTOPHAN AMINOTRANSFERASES OF ARABIDOPSIS and YUCCAs in Arabidopsis. *PNAS* **2011**, *108*, 18518–18523, doi:10.1073/pnas.1108436108.
56. Wang, Q.; Qin, G.; Cao, M.; Chen, R.; He, Y.; Yang, L.; Zeng, Z.; Yu, Y.; Gu, Y.; Xing, W.; et al. A Phosphorylation-Based Switch Controls TAA1-Mediated Auxin Biosynthesis in Plants. *Nat Commums* **2020**, *11*, 679, doi:10.1038/s41467-020-14395-w.
57. Zhao, Y.; Christensen, S.K.; Fankhauser, C.; Cashman, J.R.; Cohen, J.D.; Weigel, D.; Chory, J. A Role for Flavin Monooxygenase-Like Enzymes in Auxin Biosynthesis. *Science* **2001**, *291*, 306–309, doi:10.1126/science.291.5502.306.
58. Stepanova, A.N.; Yun, J.; Robles, L.M.; Novak, O.; He, W.; Guo, H.; Ljung, K.; Alonso, J.M. The Arabidopsis YUCCA1 Flavin Monooxygenase Functions in the Indole-3-Pyruvic Acid Branch of Auxin Biosynthesis. *Plant Cell* **2011**, *23*, 3961–3973, doi:10.1105/tpc.111.088047.

59. Dai, X.; Mashiguchi, K.; Chen, Q.; Kasahara, H.; Kamiya, Y.; Ojha, S.; DuBois, J.; Ballou, D.; Zhao, Y. The Biochemical Mechanism of Auxin Biosynthesis by an Arabidopsis YUCCA Flavin-Containing Monooxygenase. *J Biol Chem* **2013**, *288*, 1448–1457, doi:10.1074/jbc.M112.424077.
60. Wang, Y.; Yang, W.; Zuo, Y.; Zhu, L.; Hastwell, A.H.; Chen, L.; Tian, Y.; Su, C.; Ferguson, B.J.; Li, X. GmYUC2a Mediates Auxin Biosynthesis during Root Development and Nodulation in Soybean. *J Exp Bot* **2019**, *70*, 3165–3176, doi:10.1093/jxb/erz144.
61. Cook, S.D.; Nichols, D.S.; Smith, J.; Chourey, P.S.; McAdam, E.L.; Quittenden, L.; Ross, J.J. Auxin Biosynthesis: Are the Indole-3-Acetic Acid and Phenylacetic Acid Biosynthesis Pathways Mirror Images? *Plant Physiol* **2016**, *171*, 1230–1241.
62. Cook, S.D. An Historical Review of Phenylacetic Acid. *Plant Cell Physiol* **2019**, *60*, 243–254, doi:10.1093/pcp/pcz004.
63. Graindorge, M.; Giustini, C.; Kraut, A.; Moyet, L.; Curien, G.; Matringe, M. Three Different Classes of Aminotransferases Evolved Prephenate Aminotransferase Functionality in Arogenate-Competent Microorganisms. *J Biol Chem* **2014**, *289*, 3198–3208, doi:10.1074/jbc.M113.486480.
64. Pascual, M.B.; El-Azaz, J.; de la Torre, F.N.; Cañas, R.A.; Avila, C.; Cánovas, F.M. Biosynthesis and Metabolic Fate of Phenylalanine in Conifers. *Front Plant Sci* **2016**, *7*.
65. Qian, Y.; Lynch, J.H.; Guo, L.; Rhodes, D.; Morgan, J.A.; Dudareva, N. Completion of the Cytosolic Post-Chorismate Phenylalanine Biosynthetic Pathway in Plants. *Nat Commun* **2019**, *10*, 15, doi:10.1038/s41467-018-07969-2.
66. Wittstock, U.; Halkier, B.A. Cytochrome P450 CYP79A2 from Arabidopsis Thaliana L. Catalyzes the Conversion of L-Phenylalanine to Phenylacetaldoxime in the Biosynthesis of Benzylglucosinolate. *J Biol Chem* **2000**, *275*, 14659–14666, doi:10.1074/jbc.275.19.14659.
67. Glawischnig, E.; Hansen, B.G.; Olsen, C.E.; Halkier, B.A. Camalexin Is Synthesized from Indole-3-Acetaldoxime, a Key Branching Point between Primary and Secondary Metabolism in Arabidopsis. *PNAS* **2004**, *101*, 8245–8250, doi:10.1073/pnas.0305876101.
68. Luck, K.; Jirschitzka, J.; Irmisch, S.; Huber, M.; Gershenzon, J.; Köllner, T.G. CYP79D Enzymes Contribute to Jasmonic Acid-Induced Formation of Aldoximes and Other Nitrogenous Volatiles in Two Erythroxylum Species. *BMC Plant Biol* **2016**, *16*, 215, doi:10.1186/s12870-016-0910-5.
69. Kuwahara, Y.; Asano, Y. Generation of (2-Nitroethyl)Benzene and Related Benzenoids from L-Phenylalanine; Flower Scents of the Japanese Loquat Eriobotrya Japonica [Rosales: Rosaceae]. *Biosci Biotechnol Biochem* **2018**, *82*, 1855–1866, doi:10.1080/09168451.2018.1498319.
70. Sørensen, M.; Neilson, E.H.J.; Møller, B.L. Oximes: Unrecognized Chameleons in General and Specialized Plant Metabolism. *Mol Plant* **2018**, *11*, 95–117, doi:10.1016/j.molp.2017.12.014.
71. Lai, D.; Maimann, A.B.; Macea, E.; Ocampo, C.H.; Cardona, G.; Pičmanová, M.; Darbani, B.; Olsen, C.E.; Debouck, D.; Raatz, B.; et al. Biosynthesis of Cyanogenic Glucosides in Phaseolus Lunatus and the Evolution of Oxime-Based Defenses. *Plant Direct* **2020**, *4*, e00244, doi:10.1002/pld3.244.
72. Liao, Y.; Zeng, L.; Tan, H.; Cheng, S.; Dong, F.; Yang, Z. Biochemical Pathway of Benzyl Nitrile Derived from L-Phenylalanine in Tea (Camellia Sinensis) and Its Formation in Response to Postharvest Stresses. *J Agric Food Chem* **2020**, *68*, 1397–1404, doi:10.1021/acs.jafc.9b06436.
73. Zhao, Y.; Hull, A.K.; Gupta, N.R.; Goss, K.A.; Alonso, J.; Ecker, J.R.; Normanly, J.; Chory, J.; Celenza, J.L. Trp-Dependent Auxin Biosynthesis in Arabidopsis: Involvement of Cytochrome P450s CYP79B2 and CYP79B3. *Genes Dev* **2002**, *16*, 3100–3112, doi:10.1101/gad.1035402.

74. Sugawara, S.; Hishiyama, S.; Jikumaru, Y.; Hanada, A.; Nishimura, T.; Koshiba, T.; Zhao, Y.; Kamiya, Y.; Kasahara, H. Biochemical Analyses of Indole-3-Acetaldoxime-Dependent Auxin Biosynthesis in Arabidopsis. *PNAS* **2009**, *106*, 5430–5435, doi:10.1073/pnas.0811226106.
75. Zhang, D.; Song, Y.H.; Dai, R.; Lee, T.G.; Kim, J. Aldoxime Metabolism Is Linked to Phenylpropanoid Production in Camelina Sativa. *Front Plant Sci* **2020**, *11*, 10.3389/fpls.2020.00017, doi:10.3389/fpls.2020.00017.
76. Thodberg, S.; Sørensen, M.; Bellucci, M.; Crocoll, C.; Bendtsen, A.K.; Nelson, D.R.; Motawia, M.S.; Møller, B.L.; Neilson, E.H.J. A Flavin-Dependent Monooxygenase Catalyzes the Initial Step in Cyanogenic Glycoside Synthesis in Ferns. *Commun Biol* **2020**, *3*, 507, doi:10.1038/s42003-020-01224-5.
77. Koroleva, O.A.; Davies, A.; Deeken, R.; Thorpe, M.R.; Tomos, A.D.; Hedrich, R. Identification of a New Glucosinolate-Rich Cell Type in Arabidopsis Flower Stalk. *Plant Physiol* **2000**, *124*, 599–608, doi:10.1104/pp.124.2.599.
78. Koroleva, O.A.; Cramer, R. Single-Cell Proteomic Analysis of Glucosinolate-Rich S-Cells in Arabidopsis Thaliana. *Methods* **2011**, *54*, 413–423, doi:10.1016/j.ymeth.2011.06.005.
79. Shroff, R.; Schramm, K.; Jeschke, V.; Nemes, P.; Vertes, A.; Gershenzon, J.; Svatoš, A. Quantification of Plant Surface Metabolites by Matrix-Assisted Laser Desorption–Ionization Mass Spectrometry Imaging: Glucosinolates on Arabidopsis Thaliana Leaves. *Plant J* **2015**, *81*, 961–972, doi:10.1111/tpj.12760.
80. Burow, M.; Halkier, B.A. How Does a Plant Orchestrate Defense in Time and Space? Using Glucosinolates in Arabidopsis as Case Study. *Curr Opin Plant Biol* **2017**, *38*, 142–147, doi:10.1016/j.pbi.2017.04.009.
81. Cole, R.A. Isothiocyanates, Nitriles and Thiocyanates as Products of Autolysis of Glucosinolates in Cruciferae. *Phytochemistry* **1976**, *15*, 759–762, doi:10.1016/S0031-9422(00)94437-6.
82. Halkier, B.A.; Gershenzon, J. Biology and Biochemistry of Glucosinolates. *Annu Rev Plant Biol* **2006**, *57*, 303–333.
83. Wittstock, U.; Kurzbach, E.; Herfurth, A.-M.; Stauber, E.J. Chapter Six - Glucosinolate Breakdown. In *Advances in Botanical Research*; Kopriva, S., Ed.; Glucosinolates; Academic Press, 2016; Volume 80, pp. 125–169.
84. Wittstock, U.; Burow, M. Glucosinolate Breakdown in Arabidopsis: Mechanism, Regulation and Biological Significance. *Arabidopsis Book* **2010**, doi:10.1199/tab.0134.
85. Jeschke, V.; Weber, K.; Moore, S.S.; Burow, M. Coordination of Glucosinolate Biosynthesis and Turnover Under Different Nutrient Conditions. *Front Plant Sci* **2019**, *10*, doi:10.3389/fpls.2019.01560.
86. Sugiyama, R.; Hirai, M.Y. Atypical Myrosinase as a Mediator of Glucosinolate Functions in Plants. *Front Plant Sci* **2019**, *10*, doi: 10.3389/fpls.2019.01008.
87. Perez, V.C.; Dai, R.; Block, A.K.; Kim, J. Metabolite Analysis of Arabidopsis CYP79A2 Overexpression Lines Reveals Turnover of Benzyl Glucosinolate and an Additive Effect of Different Aldoximes on Phenylpropanoid Repression. *Plant Signal Behav* **2021**, *16*, 1966586, doi:10.1080/15592324.2021.1966586.
88. Lambrix, V.; Reichelt, M.; Mitchell-Olds, T.; Kliebenstein, D.J.; Gershenzon, J. The Arabidopsis Epithiospecifier Protein Promotes the Hydrolysis of Glucosinolates to Nitriles and Influences Trichoplusia Ni Herbivory. *Plant Cell* **2001**, *13*, 2793–2807, doi:10.1105/tpc.010261.
89. Vorwerk, S.; Biernacki, S.; Hillebrand, H.; Janzik, I.; Müller, A.; Weiler, E.W.; Piotrowski, M. Enzymatic Characterization of the Recombinant Arabidopsis Thaliana Nitrilase Subfamily Encoded by the NIT2/NIT1/NIT3-Gene Cluster. *Planta* **2001**, *212*, 508–516, doi:10.1007/s004250000420.
90. Janowitz, T.; Trompetter, I.; Piotrowski, M. Evolution of Nitrilases in Glucosinolate-Containing Plants. *Phytochemistry* **2009**, *70*, 1680–1686, doi:10.1016/j.phytochem.2009.07.028.
91. Urbancsok, J.; Bones, A.M.; Kissen, R. Benzyl Cyanide Leads to Auxin-Like Effects Through the Action of Nitrilases in Arabidopsis Thaliana. *Front Plant Sci* **2018**, *9*, doi:10.3389/fpls.2018.01240.

92. Vik, D.; Mitarai, N.; Wulff, N.; Halkier, B.A.; Burow, M. Dynamic Modeling of Indole Glucosinolate Hydrolysis and Its Impact on Auxin Signaling. *Front Plant Sci* **2018**, *9*, 550, doi:10.3389/fpls.2018.00550.
93. Julkowska, M.M.; Koevoets, I.T.; Mol, S.; Hoefsloot, H.; Feron, R.; Tester, M.A.; Keurentjes, J.J.B.; Korte, A.; Haring, M.A.; de Boer, G.-J.; et al. Genetic Components of Root Architecture Remodeling in Response to Salt Stress. *Plant Cell* **2017**, *29*, 3198–3213, doi:10.1105/tpc.16.00680.
94. Clavijo Mccormick, A.; Irmisch, S.; Reinecke, A.; Boeckler, G.A.; Veit, D.; Reichelt, M.; Hansson, B.S.; Gershenzon, J.; Köllner, T.G.; Unsicker, S.B. Herbivore-Induced Volatile Emission in Black Poplar: Regulation and Role in Attracting Herbivore Enemies. *Plant Cell Environ* **2014**, *37*, 1909–1923, doi:10.1111/pce.12287.
95. Quittenden, L.J.; Davies, N.W.; Smith, J.A.; Molesworth, P.P.; Tivendale, N.D.; Ross, J.J. Auxin Biosynthesis in Pea: Characterization of the Tryptamine Pathway. *Plant Physiol* **2009**, *151*, 1130–1138, doi:10.1104/pp.109.141507.
96. Hirata, H.; Ohnishi, T.; Tomida, K.; Ishida, H.; Kanda, M.; Sakai, M.; Yoshimura, J.; Suzuki, H.; Ishikawa, T.; Dohra, H.; et al. Seasonal Induction of Alternative Principal Pathway for Rose Flower Scent. *Sci Rep* **2016**, *6*, 20234, doi:10.1038/srep20234.
97. Kaminaga, Y.; Schnepp, J.; Peel, G.; Kish, C.M.; Ben-Nissan, G.; Weiss, D.; Orlova, I.; Lavie, O.; Rhodes, D.; Wood, K.; et al. Plant Phenylacetaldehyde Synthase Is a Bifunctional Homotetrameric Enzyme That Catalyzes Phenylalanine Decarboxylation and Oxidation. *J Biol Chem* **2006**, *281*, 23357–23366, doi:10.1074/jbc.M602708200.
98. Gutensohn, M.; Klempien, A.; Kaminaga, Y.; Nagegowda, D.A.; Negre-Zakharov, F.; Huh, J.-H.; Luo, H.; Weizbauer, R.; Mengiste, T.; Tholl, D.; et al. Role of Aromatic Aldehyde Synthase in Wounding/Herbivory Response and Flower Scent Production in Different Arabidopsis Ecotypes. *Plant J* **2011**, *66*, 591–602, doi:10.1111/j.1365-313X.2011.04515.x.
99. Hirata, H.; Ohnishi, T.; Ishida, H.; Tomida, K.; Sakai, M.; Hara, M.; Watanabe, N. Functional Characterization of Aromatic Amino Acid Aminotransferase Involved in 2-Phenylethanol Biosynthesis in Isolated Rose Petal Protoplasts. *J Plant Physiol* **2012**, *169*, 444–451, doi:10.1016/j.jplph.2011.12.005.
100. Koeduka, T.; Fujita, Y.; Furuta, T.; Suzuki, H.; Tsuge, T.; Matsui, K. Aromatic Amino Acid Decarboxylase Is Involved in Volatile Phenylacetaldehyde Production in Loquat (Eriobotrya Japonica) Flowers. *Plant Biotechnol (Tokyo)* **2017**, *34*, 193–198, doi:10.5511/plantbiotechnology.17.0926a.
101. Koshiba, T.; Saito, E.; Ono, N.; Yamamoto, N.; Sato, M. Purification and Properties of Flavin- and Molybdenum-Containing Aldehyde Oxidase from Coleoptiles of Maize. *Plant Physiol* **1996**, *110*, 781–789, doi:10.1104/pp.110.3.781.
102. Iwase, A.; Takebayashi, A.; Aoi, Y.; Favero, D.S.; Watanabe, S.; Seo, M.; Kasahara, H.; Sugimoto, K. 4-Phenylbutyric Acid Promotes Plant Regeneration as an Auxin by Being Converted to Phenylacetic Acid via an IBR3-Independent Pathway. *Plant Biotechnol (Tokyo)* **2022**, *39*, 51–58, doi:10.5511/plantbiotechnology.21.1224b.
103. Hayashi, K.; Arai, K.; Aoi, Y.; Tanaka, Y.; Hira, H.; Guo, R.; Hu, Y.; Ge, C.; Zhao, Y.; Kasahara, H.; et al. The Main Oxidative Inactivation Pathway of the Plant Hormone Auxin. *Nat Commun* **2021**, *12*, 6752, doi:10.1038/s41467-021-27020-1.
104. Müller, K.; Dobrev, P.I.; Pěnčík, A.; Hošek, P.; Vondráková, Z.; Filepová, R.; Malínská, K.; Brunoni, F.; Helusová, L.; Moravec, T.; et al. DIOXYGENASE FOR AUXIN OXIDATION 1 Catalyzes the Oxidation of IAA Amino Acid Conjugates. *Plant Physiol* **2021**, *187*, 103–115, doi:10.1093/plphys/kiab242.
105. Grubb, C.D.; Zipp, B.J.; Ludwig-Müller, J.; Masuno, M.N.; Molinski, T.F.; Abel, S. Arabidopsis Glucosyltransferase UGT74B1 Functions in Glucosinolate Biosynthesis and Auxin Homeostasis. *Plant J* **2004**, *40*, 893–908, doi:10.1111/j.1365-313X.2004.02261.x.

106. Staswick, P.E.; Serban, B.; Rowe, M.; Tiryaki, I.; Maldonado, M.T.; Maldonado, M.C.; Suza, W. Characterization of an Arabidopsis Enzyme Family That Conjugates Amino Acids to Indole-3-Acetic Acid. *Plant Cell* **2005**, *17*, 616–627, doi:10.1105/tpc.104.026690.
107. Westfall, C.S.; Sherp, A.M.; Zubieta, C.; Alvarez, S.; Schraft, E.; Marcellin, R.; Ramirez, L.; Jez, J.M. Arabidopsis Thaliana GH3.5 Acyl Acid Amido Synthetase Mediates Metabolic Crosstalk in Auxin and Salicylic Acid Homeostasis. *PNAS* **2016**, *113*, 13917–13922, doi:10.1073/pnas.1612635113.
108. Mashiguchi, K.; Hisano, H.; Takeda-Kamiya, N.; Takebayashi, Y.; Ariizumi, T.; Gao, Y.; Ezura, H.; Sato, K.; Zhao, Y.; Hayashi, K.; et al. Agrobacterium Tumefaciens Enhances Biosynthesis of Two Distinct Auxins in the Formation of Crown Galls. *Plant Cell Physiol* **2019**, *60*, 29–37, doi:10.1093/pcp/pcy182.
109. Lynch, J.H.; Qian, Y.; Guo, L.; Maoz, I.; Huang, X.-Q.; Garcia, A.S.; Louie, G.; Bowman, M.E.; Noel, J.P.; Morgan, J.A.; et al. Modulation of Auxin Formation by the Cytosolic Phenylalanine Biosynthetic Pathway. *Nat Chem Biol* **2020**, *16*, 850–856, doi:10.1038/s41589-020-0519-8.