agronomy

MDPI

Review

Camelina sativa (L.) Crantz as a Promising Cover Crop Species with Allelopathic Potential

Martina Ghidoli, Michele Pesenti, Federico Colombo, Fabio Francesco Nocito, Roberto Pilu and Fabrizio Araniti *

Department of Agricultural and Environmental Sciences—Production, Landscape, Agroenergy, University of Milan, Via G. Celoria 2, 20133 Milan, Italy; martina.ghidoli@unimi.it (M.G.); michele.pesenti@unimi.it (M.P.); federico.colombo@unimi.it (F.C.); fabio.nocito@unimi.it (F.F.N.); salvatore.pilu@unimi.it (R.P.)
* Correspondence: fabrizio.araniti@unimi.it

Abstract: The ability of plants to release chemicals that affect the growth of other plants offers potential benefits for weed management and sustainable agriculture. This review explores the use of *Camelina sativa* as a promising cover crop with weed control potential. *Camelina sativa*, known for its high oil content and adaptability to diverse climatic conditions, exhibits allelopathic potential by releasing chemical compounds that inhibit weed growth. The crop's vigorous growth and canopy architecture contribute to effective weed suppression, reducing the prevalence and spread of associated pathogens. Furthermore, the chemical compounds released by camelina through the solubilization of compounds from leaves by rain, root exudation, or deriving from microbial-mediated decay of camelina's tissues interfere with the growth of neighbouring plants, indicating allelopathic interactions. The isolation and identification of benzylamine and glucosinolates as allelochemicals in camelina highlight their role in plant–plant interactions. However, the studies carried out on this species are outdated, and it cannot be excluded that other chemicals deriving from the breakdown of the glucosinolates or belonging to other classes of specialized metabolites can be involved in its allelopathic potential. *Camelina sativa* also demonstrates disease suppression capabilities, with glucosinolates exhibiting fungicidal, nematocidal, and bactericidal activities. Additionally, camelina cover crops have been found to reduce root diseases and enhance growth and yields in corn and soybeans. This review sheds light on the allelopathic and agronomic benefits of *Camelina sativa*, emphasizing its potential as a sustainable and integrated pest management strategy in agriculture.

Keywords: *Camelina sativa*; allelopathy; cover crop; glucosinolates; weed control

Citation: Ghidoli, M.; Pesenti, M.; Colombo, F.; Nocito, F.F.; Pilu, R.; Araniti, F. *Camelina sativa* (L.) Crantz as a Promising Cover Crop Species with Allelopathic Potential. *Agronomy* **2023**, *13*, 2187. https://doi.org/10.3390/agronomy13082187

Academic Editors: Carolina G. Puig and Nuria Pedrol

Received: 13 June 2023
Revised: 12 August 2023
Accepted: 16 August 2023
Published: 21 August 2023

1. Introduction

Allelopathy is the ability of plants to release chemicals that affect the growth and development of other plants. These chemicals can be released into the soil or air and may affect neighbouring plants' germination, growth, or reproduction [1]. The allelopathic potential of crops has been recognized for many years. There is growing interest in using allelopathic crops for weed management since they can reduce the need for synthetic commercial herbicides, which can have negative environmental and health impacts, promote sustainable agriculture by reducing weed pressure and improving soil health, and be cost-effective for farmers, as they may not need to purchase and apply herbicides [1]. Depending on their activity, allelopathic crops can be classified into direct and indirect. Direct allelopathic crops release allelopathic compounds that directly affect the growth and development of weeds. Indirect allelopathic crops release allelopathic compounds that stimulate the growth and development of beneficial microorganisms, suppressing the growth of weeds [2]. The use of allelopathic crops is a promising strategy for managing herbicide-resistant weeds, even without a detailed understanding of the underlying mechanisms. While understanding the allelopathic effects and optimizing their application is important, mechanistic aspects

are also crucial to the success of such initiatives. A greater understanding of plant–plant communication, recognition, and the potential non-target effects of allelochemicals, would elevate allelopathic plants from blunt tools for weed control to intelligent components of an integrated weed management program [3]. However, using allelopathic crops for weed management also has some challenges. First, the effectiveness of allelopathic crops may be influenced by environmental factors, such as soil moisture and temperature, which can affect the release and activity of allelopathic compounds [4–7]. Moreover, the development of allelopathic cash crops has also to satisfy the demand for high yields. Agriculture has traditionally prioritized breeding for yield improvement over other traits, so any form of weed suppression must consider its net effect on productivity, given that reduced yield in a weed-free environment can be compensated by the yield benefit provided by effective weed suppression. For example, Kong et al. [8] bred allelopathic rice cultivars that were high-yielding and weed-suppressive, but further research is needed to characterize the trade-offs related to yield and plant defence [9]. Genetic engineering techniques offer a sophisticated but largely underappreciated approach to developing allelopathic crops for weed management [1]. Recent efforts to identify genetic regions involved in sorgoleone biosynthesis in sorghum [10] pave the way for future up-regulation of these genes for a more significant allelopathic effect. There is also evidence that cytochrome P-450 monooxygenases play a role in allelochemical synthesis in various plant species, including sorghum [11] and benzoxazinoid allelochemical biosynthesis in cereals [12], indicating some consistency between species in their genetic tools for allelochemical synthesis. Specific genes involved in allelochemical biosynthesis can also be edited for examination or upregulation of specific compounds in the pathway [1]. Another approach to using allelopathic species for weed suppression is to apply them as cover or intercrops in rotation with a less weed-suppressive cash crop [13]. Recently, besides cereals, huge attention has been paid to brassicaceous species as cover crops with allelopathic activity [14–17]. The Brassicaceae family, or the mustard family, is a diverse group of plants that includes 375 genera and over 3200 species [17]. This family is known for its economic importance, as many members are cultivated as food crops or for their medicinal properties [18–20]. In addition, the Brassicaceae family is known for its allelopathic potential, particularly related to the presence of glucosinolates [17]. Glucosinolates are a class of sulfur-containing compounds found in high concentrations in many members of the Brassicaceae family. When the plant tissues are damaged by herbivores or mechanical stress, glucosinolates are hydrolyzed by the enzyme myrosinase, producing a variety of breakdown products, including isothiocyanates, nitriles, and thiocyanates [21]. The breakdown products of glucosinolates have been shown to have allelopathic effects on neighbouring plants [22,23]. For example, isothiocyanates have been shown to inhibit the germination and growth of various plant species, including lettuce and velvetleaf [24–26]. In addition, isothiocyanates have been shown to inhibit the growth of specific soilborne pathogens [27–29]. The Brassicaceae family includes several species that are known for their allelopathic potential, including *Brassica napus* (oilseed rape), *Brassica juncea* (Indian mustard), and *Sinapis alba* (white mustard). These species have been shown to release allelopathic compounds that inhibit the growth and development of weeds, and they are being investigated as potential allelopathic crops for weed management [30–33]. Research has shown that allelopathic crops, including those in the Brassicaceae family, can effectively reduce weed growth and suppress weed seed production. For example, one study found that using allelopathic cover crops, including *Brassica napus*, reduced weed biomass by 50–90% compared with a fallow control. Another study found that the use of *Brassica juncea* as a cover crop reduced the density and biomass of certain weed species by over 80%.

2. *Camelina sativa*: A Promising Cover Crop

Camelina sativa is an oilseed crop that has gained interest as a biofuel and food source due to its high oil content and potential health benefits, and is an annual plant belonging

to the Brassicaceae family. The plant grows up to 60–120 cm in height and has a slender, branching stem covered with narrow, lanceolate leaves (Figure 1).

Figure 1. *Camelina sativa* at flowering stage.

The leaves are alternate, and the plant produces yellow flowers with four petals. Following pollination, the flowers develop into fruits, known as siliques, which contain small, round seeds. *Camelina sativa* is adapted to grow in temperate regions but can also tolerate a wide range of climatic conditions. It is known for its ability to grow in marginal lands with low fertility and limited water availability, making it suitable for cultivation in arid and semi-arid regions. The recommended seeding rate is approximately 10–15 kg per hectare, and the plant requires full sun exposure for optimal growth and development. *Camelina sativa* prefers well-drained soil with a pH ranging from 5.5 to 8.0, and its cultivation offers several environmental benefits. Its deep root system improves soil structure, reduces erosion, and enhances water infiltration. The crop requires fewer pesticides and fertilizers than conventional oilseed crops, reducing potential negative environmental impacts. It is a cool-season crop that can withstand frost and has a relatively short growing season of around 85–105 days [34–36]. One of the primary uses of *Camelina sativa* is for oil production. The plant's seeds are rich in oil, typically containing 30–45% oil content. Camelina oil is characterized by its high levels of omega-3 fatty acids, particularly alpha-linolenic acid (ALA). It is considered a valuable alternative to fish oil and can be used for human consumption, animal feed, and biodiesel production [37,38]. Beyond its economic and environmental benefits, camelina cultivation has been found to have implications for pathogen management, highlighting its potential as a sustainable and integrated pest management

strategy. In fact, numerous studies have demonstrated the ability of *Camelina sativa* to suppress various plant pathogens, thereby reducing the incidence and severity of diseases. The mechanisms underlying disease suppression include direct antimicrobial properties of plant-specialized metabolites and the activation of systemic acquired resistance (SAR) and induced systemic resistance (ISR) in neighbouring plants. For example, camelina plants produce glucosinolates, which are known to exhibit fungicidal and bactericidal activities against a range of pathogens [39,40]. For example, both jatropha and camelina seed meals possess biofumigant properties and can have varying effects on soil microbial communities, which tend to persist over time. Furthermore, the microbial functional patterns were unaffected. This knowledge will be valuable in appropriately utilising jatropha and camelina SMs for pathogen control while minimizing detrimental effects on non-target microorganisms [41]. *C. sativa* showed good fungicidal activity against *M. phaseolina,* which caused charcoal rot diseases in soybean [42].

One of the most important biotic stresses in soybean production is soybean cyst nematode (Heterodera glycines Ichinohe, SCN), a serious pest that affects 90% of the soybean-producing areas in the U.S. [43]. A study conducted by Acharya et al. [43] found that winter camelina and brown mustard are non-hosts for SCN populations and reduced egg numbers [43].

In another study, a three-year field experiment was conducted to investigate the effects of winter cereal rye (*Secale cereale* L.) and winter camelina (*Camelina sativa* [L.] Crantz) cover crops, used either continuously or in rotation on the growth, root disease, and yield of corn (*Zea mays* L.) and soybeans (*Glycine max.* [L.] Merr.). Results showed that corn following a camelina cover crop experienced reduced root disease, a lower *Pythium* fungi population in seedling roots, and exhibited greater growth and yields than corn following a rye cover crop. Furthermore, a winter camelina cover crop grown before corn had less detrimental effects on corn seedling growth, root disease, and final yield compared with a winter rye cover crop preceding corn. This study provides valuable insights into the effects of winter cover crops on root disease and growth in corn and soybeans, suggesting the potential benefits of using camelina as a cover crop before corn cultivation [44]. The integration of cover crops, specifically green manures, alongside cash crops has been widely practised for many decades.

Extensive research consistently confirms the positive effects of green manure cover crops on soil quality, especially in low-carbon or degraded soils. These advantages encompass enriching soil organic carbon content, enhancing soil structure, preventing erosion, and mitigating crop diseases [45]. Furthermore, green manures play a pivotal role in nurturing the soil's microbial community, improving nutrient availability, and fostering beneficial interactions between crop plants and microorganisms. The presence of green manures creates competition for niches, effectively curbing the proliferation of harmful microbial pathogens and ultimately resulting in increased yields of cash crops [46]. A particular type of green manure, referred to as biofumigants, harnesses the power of certain plants that release toxic compounds into the soil to control crop pests, pathogens, and weeds. Notably, Brassica species are known for producing glucosinolates; these compounds break down in the soil, they give rise to isothiocyanates, highly toxic to various organisms, including common crop pests and pathogens [47]. The reduced weed density and biomass observed in crops grown after incorporating brassica cover crops indicate that they can play a role in weed management within agricultural systems.

Green manure and biofumigant crops are widespread in cropping rotations, aimed at maintaining or improving agricultural soil yields by preventing degradation and protecting vital ecosystem services. In recent decades, there have been significant advancements in our understanding of soil microbiomes in agriculture. The use of advanced techniques like metagenomics has enabled researchers to delve deeply into soil microbiomes, providing unprecedented insights [48]. As a result, we now recognize the crucial role of the soil microbiome in delivering essential ecosystem services that are vital for agriculture [49]. This growing awareness has spurred investigations into management practices that aim

to restore, protect, and enhance soil ecosystem health, with organic amendments such as green manure being among the promising approaches. For example, brassica biofumigants release glucosinolates during their growth, which subsequently convert into toxic isothiocyanates in the soil, influencing the structure of soil microbial communities both during the biofumigant's growth and shortly after its incorporation [47,50]. Glucosinolates can be degraded even without the presence of the hydrolytic enzyme myrosinase, potentially contributing to their bioactive effects. For example, Hanshen and coauthors examined the stability of glucosinolate hydrolysis products derived from Brassicaceae plants and pure glucosinolates in three different soils (a model simulating biofumigation).

Additionally, the research focused on the degradation of pure 2-propenyl glucosinolate and the effect on the soil bacterial community composition. The results obtained showed a significant impact on the bacterial community composition. Interestingly, significant alterations in the soil community due to biofumigant exudates were observed, despite the ferrosol's high clay and organic matter content. These results suggest that brassica biofumigation might be effective on ferrosols and similar soil types with high clay and organic matter content [50]. In another study conducted by Walker et al. [46] in 2022, the authors investigated the long-term effects of continuous ryegrass green manuring and brassica biofumigation on fertile, clay-rich soil (Red Ferrosol) in an intensive vegetable cropping rotation spanning 10 to 13 years. The results showed that both ryegrass green manuring and brassica biofumigation resulted in alterations to the soil microbial communities, promoting the growth of copiotrophic bacteria and fungi involved in organic matter degradation.

In addition, both treatments significantly increased the relative abundance of arbuscular mycorrhizal fungi compared with the fallow plots. Overall, this study provides valuable insights into brassica biofumigation that positively impacts soil characteristics, microbial communities, and crop yields, making important contributions to sustainable agricultural practices [46]. Furthermore, isothiocyanates have been shown to possess strong inhibitory effects on seed germination leading to stunted seedling growth [51]. Field studies further support the role of brassica residues, including canola, rapeseed, and mustards in weed management [14]. Compared with fallow or other non-brassica cover crops, preceding brassica cover crops have shown effectiveness in reducing weed biomass and weed density in various crops because most weed seeds have considerably smaller masses than the seeds of the crops they infest [52].

Camelina also exhibits a capacity for weed suppression (Figure 2); in fact, *Camelina sativa*'s vigorous growth and canopy architecture can effectively suppress weed populations, subsequently reducing the prevalence and spread of associated pathogens. However, the careful selection of cover crop species and the timing of interseeding play a crucial role in obtaining advantages while maintaining optimal sugar beet yield. In North Dakota, when camelina was interseeded during the V1–V3 growth stages of corn and the V1–V2 growth stages of soybean (*Glycine max* (L.) Merr.), there was a reduction of 14% in corn yield and 10% in soybean yield [53].

Furthermore, by releasing chemical compounds that inhibit weed growth, camelina's allelopathic potential can further contribute to weed control and indirectly influence pathogen dynamics. For example, originating in North America, *Ambrosia artemisiifolia* L. is an invasive alien species widely recognized as one of Europe's most harmful plant species. In a study conducted by Scepanovic et al. [54] where the objective was to assess the impact of different concentrations of aqueous extracts from Brassicaceae cover crops (including *Sinapis alba*, *Raphanus sativus*, *Camelina sativa*, *Fagopyrum esculentum*, and *Guizotia abyssinica*) on the germination and early growth of *Ambrosia artemisiifolia* L., allelopathic effects were found to be dependent on the species and concentration of the aqueous extracts. *Camelina sativa* exhibited the highest potential for inhibiting germination, shoot, and radicle length, and fresh seedling weight. Analysis using liquid chromatography-tandem mass spectrometry identified 15 phenolic compounds in the Brassicaceae, with *Camelina sativa* having the highest content of vanillin, chlorogenic acid, vanillic acid, caffeic acid, and

syringic acid. These findings suggest that *Camelina sativa* is the most allelopathic among the species used in this study and that the seeds of *Camelina sativa* are particularly rich in allelochemicals [54].

Figure 2. Camelina capacity for weed suppression.

3. *Camelina sativa*: A Potential Allelopathic Crop

The allelopathic potential of *Camelina sativa* has been widely investigated in the past. But the analytical and chemical approaches used were mainly based on targeted analysis, which strongly reduced the amount and the complexity of chemicals being characterized. Moreover, there are no available studies focused on the bio-guided fractionation of the phytocomplex of this species aimed at identifying the classes of compounds involved in the allelopathic phenomenon and/or on the phytotoxicity of the plant extracts. Therefore, despite the evidence of camelina's allelopathy, this field of research is superficially explored, and new coupled to classical approaches should be used to shed light on this phenomenon.

The first study reporting the allelopathic potential of *Camelina sativa* was published by Grummer and Beyer [55], which observed that the presence of camelina in fields cropped with linseed significantly reduced crop yield. They highlighted that this phenomenon was observable when significant rainfall was in conjunction with specific phenological stages of camelina and linseed plants, suggesting that the allelochemical release through the solubilization of compounds from leaves by rain was responsible for the phytotoxic effects observed [55,56]. After almost twenty years, a clearer understanding of this phenomenon was achieved thanks to studies on the effects of camelina's leaf lixiviates on seedlings' growth and their interaction with soil bacteria [57]. In particular, such studies demonstrated that under controlled conditions, the lixiviates collected from camelina's intact leaves were interfering with the growth of germinating *Linum usitatissimum* seedlings.

Moreover, they demonstrated that gram-negative bacteria mediated these growth alterations in the camelina phyllosphere [56,57]. Successively, Lovett and Jackson [58] reported that the effects observed on linseed seedlings were also observable on several species of higher plants, and the main bacteria mediating the effects were *Enterobacter cloacae* or *Pseudomonas fluorescens*. Moreover, they highlighted that the bacterial activity rapidly produced the allelochemical involved in plant interference, which probably was an organic compound produced by degrading a more complex metabolite commonly found in plants belonging to the Brassicaceae family. The isolation and identification of this specialized metabolite involved in this plant–plant interaction were achieved only after a year when benzylamine was identified as an allelochemical influencing the association of *C. sativa* with linseed [59,60]. It was demonstrated that camelina leaves contain organic acids that support rapid bacterial growth, breaking complex organic compounds into simpler molecules. One of these compounds, benzylamine, exhibits allelopathic properties, as reported by Lovett and Duffield [59,60]. Successively, it was reported that the release of the precursor, benzyl isothiocyanate, may require damage to the leaves, and the highest concentration of allelopathic activity may occur during the senescent stage of the life cycle when bacterial populations are at their peak. Lovett reported that in Petri dishes, low benzylamine concentrations stimulated germinating linseed seedlings similar to camelina leaf washings, but higher concentrations had an inhibitory effect, as is typical of allelochemicals [61]. Studies on this molecule highlighted its inhibitory effects mainly due to its ability to disrupt cellular membranes and reduce food reserve mobilization [56,62]. More recent studies demonstrated that *C. sativa* only seemed to suppress weeds during the initial growth phase (seedling establishment), as it had a significant impact on annuals such as *Sonchus oleraceus*, *Matricaria recutita*, and *Fallopia convolvulus* but had no effect on the major perennials *Elytrigia repens* and *Cirsium arvense*. In row-cropped peas, *C. sativa* played the dual role of a smother crop and weed antagonist without exhibiting phytotoxicity to the crop [63]. More recently, Walsh et al. [64] tested the impact of various camelina plant components, including leaf washings, aqueous extracts, soil-incorporated fresh plant residues, and root exudates, on the seedling growth of different species. Results indicated that *C. sativa* leaf washings increased radish seedling weight, while the germination of wild oat, flax, and radishes was reduced by its aqueous extracts. Wild oat and radish seedlings also displayed a decrease in root weight and an increase in shoot weight in response to aqueous extracts. Incorporating fresh camelina plant residues into growth media increased radish weight, while camelina exudates reduced flax weight. The chemical characterization of the biologically active camelina's aqueous extract highlighted that the main potential allelochemicals were volatile sulfur-containing compounds, such as methanethiol, dimethyl sulfide, dimethyl disulfide, and dimethyl trisulfide, which were predominantly present. These results have given a significant turning point to the study of camelina. They have highlighted that, besides benzylamines, the species can produce a plethora of specialized metabolites belonging to the sulfur metabolism with allelopathic activity, such as glucosinolates (GSLs) and their corresponding degradation products [65]. Different organs can differentially produce GSLs depending on the phenological stage of the plant. In particular, it has been demonstrated that the adult plants of *C. sativa* are characterized by an organ-specific production of GSLs. The main organs characterized by their accumulation are the roots and the siliques, whereas the leaves contain a significantly low amount since their content is reduced along with plant development [66]. Three days after germination could be found 60% of the GSLs accumulated in the seeds, and their content dropped to 25% seven days after germination [67]. In addition, it has been estimated that in seed meal, depending on the accession, the GSL content can vary from 19.6 to 40.3 mmol kg^{-1} dry weight [68]. Therefore, it has been suggested that adult plants release GSLs into the environment mainly through root exudation or their decay [69], making the study of the root exudate dynamics and its chemical characterization a crucial step in exploiting the potential use of camelina as a cover crop, since the modulation through genetic improvement of their composition and release can strongly improve its effectiveness in weed control. Moreover,

Quéro et al. [70], studying the glucosinolate profile during seed development, observed that the buildup of glucosinolates primarily takes place within a timeframe of 15 to 25 days following the onset of flowering. The concentration of glucoarabin, glucocamelinin, and gluconesliapaniculatin between these two time points is amplified by factors of 4.0, 3.4, and 2.8, respectively. These three compounds exhibit similar accumulation patterns, maintaining consistent levels between 25 and 35 days after flowering. When examining the glucosinolate profiles of mature seeds, glucocamelinin exhibits a higher level of intensity in terms of area compared with glucoarabinin and gluconesliapaniculatin. The studies aimed at characterizing GSLs in *Camelina sativa* extracts predominantly relied on techniques primarily focused on targeted studies using pure standards. This approach facilitated the identification of three key GSLs (glucoarabin, glucocamelinin, and gluconesliapaniculatin) and a few others (Table 1). However, with the advent of mass spectrometric techniques coupled with gas chromatography or ultra-high-performance liquid chromatography, the exploration of unknown chemicals or biochemical intermediates can expand significantly. These advanced analytical methods offer a unique opportunity to delve deeper into the allelopathic activity of *Camelina sativa* and uncover new aspects regarding its chemical interactions with other species. Moreover, these cutting-edge techniques can shed light on previously undiscovered allelochemicals that may be present in the plant, broadening our understanding of its ecological role and potential applications. By embracing these modern analytical tools, researchers can unveil a wealth of information, opening new doors for further investigations in the field of allelopathy.

Table 1. Main glucosinolates identified and quantified in different *C. sativa* tissues.

Classes	Iupac Name	Tissue	Bibliography
Aliphatic glucosinolates	3-(methylthio)propyl glucosinolate	Whole plant	[66]
	9-(methylthio)nonyl glucosinolate	Whole plant	[66]
	3-(methylsulfinyl)propyl glucosinolate	Whole plant	[66]
	4-(methylsulfinyl)butyl glucosinolate	Whole plant	[66]
	8-(methylsulfinyl)octyl glucosinolate	Whole plant	[66]
	9-(methylsulfinyl)nonyl glucosinolate *	Whole plant, seeds, root exudates	[66,67,70]
	10-(methylsulfinyl)decyl glucosinolate *	Whole plant, seeds, root exudates	[66,67,70]
	11-(methylsulfinyl)undecyl-glucosinolate *	seed, root exudates	[66,67,70]
Indole glucosinolates	3-indolylmethyl glucosinolate	Whole plant	[66,67,70]
	4-hydroxy-3-indolylmethyl glucosinolate	Whole plant	[66]
	4-methoxy-3-indolylmethyl glucosinolate	Whole plant	[66]
	ds-glucobrassicin	Seedlings	[71]
	ds-4-methoxy-glucobrassicin	Seedlings	[71]
	ds-neoglucobrassicin	Seedlings	[71]

* The compounds 9-(methylsulfinyl) nonyl glucosinolate, 10-(methylsulfinyl) decyl glucosinolate and 11-(methylsulfinyl)undecyl-glucosinolate are commonly known as glucoarabin, glucocamelinin, and gluconesliapaniculatin, respectively.

4. Sulfur Availability and Glucosinolates Production

Sulfur is an essential macronutrient for plant growth and development [72]. Photosynthetic organisms use sulfur to synthesize various sulfur-containing metabolites, including cysteine, methionine, glutathione, vitamins, cofactors, and chloroplastic sulfolipids and a wide variety of specialized compounds, such as GSLs in the Brassicaceae family [73,74]. Recent studies demonstrated that GSLs, generally considered end-products of the metabolism, can serve as a reservoir for sustaining a retrograde flow of sulfur atoms for cysteine production under sulfur deficiency [75]. GSLs are sulfur-rich secondary metabolites with plant-protective and medicinal properties, such as antimicrobial and anticarcinogenic activities [76–78]. Plants suppress GSL biosynthesis under sulfur deficiency, which affects field performance and medicinal quality due to insufficient sulfate supply. A recent study [79] identified the genes *Sulfur Deficiency Induced 1* and *2* (*SDI1* and *SDI2*) as major repressors of GSL biosynthesis in Arabidopsis under sulfur deficiency conditions. The expression of *SDI1*

and *SDI2* negatively correlated with GSL biosynthesis at the transcript and metabolite levels. Principal components analysis revealed that *SDI1* regulates aliphatic GSL biosynthesis as part of the sulfur deficiency response. SDI1 protein localizes to the nucleus, interacting with MYB28, a key transcription factor promoting aliphatic GSL biosynthesis in yeast and plant cells [79]. Through the formation of an SDI1-MYB28 complex, SDI1 inhibited the transcription of aliphatic GSL biosynthetic genes, leading to the down-regulation of GSL biosynthesis and prioritization of sulfate utilization for the synthesis of primary metabolites under sulfur-limiting conditions. Since plant sulfur nutritional status controls both GSL biosynthesis and degradation in a bidirectional way, the final accumulation of GSLs in plant tissues can be finely modulated through sulfur fertilization, breeding programs, or genetic modifications to improve plant sulfur use efficiency.

5. Biosynthesis of Glucosinolates

Glucosinolates can be categorized into three main classes based on their biosynthesis: aliphatic, derived from methionine; aromatic, derived from phenylalanine; and indolic, derived from tyrosine or tryptophan [80]. The biosynthesis of glucosinolates involves inserting methylene groups into the side chains of aliphatic and aromatic amino acids. The elongated amino acid moiety undergoes reconfiguration through metabolic processes, resulting in the characteristic core structure of glucosinolates, which undergoes further structural modifications [80]. Aliphatic glucosinolates originate from methionine, converted to a 2-oxo acid through amination catalysed by the enzyme BCAT4. This initial biosynthetic step occurs in the cytosol, while subsequent enzymatic activities in the elongation process occur in the chloroplasts. Within the chloroplasts, the aliphatic chain of the 2-oxo acid is elongated by three enzymes: methylthioalkylmalate synthase (MAMS), isopropylmalate isomerase (IPMI), and isopropylmalate dehydrogenase (IPM-DH). The elongated 2-oxo acid can be transaminated to homomethionine or proceed for further chain elongation (Figure 3a). The overall process generates a range of chain-elongated derivatives of methionine [81–87]. The core formation of glucosinolates involves the participation of homomethionine, which undergoes a series of enzymatic reactions in the cytosol. These reactions are common to all three classes of glucosinolates (aliphatic, aromatic, and indolic) (Figure 3a). Enzymes from the CYP79 gene family, specifically cytochrome P450s, convert the elongated amino acids derived from methionine, tyrosine, tryptophan, and phenylalanine into aldoximes. Different members of the CYP79 family catalyse the conversion depending on the amino acid derivative. Aldoximes are then converted to oxidized forms (aci-nitro compounds and/or nitrile oxides) by cytochrome P450s from the CYP83 gene family. The sulfur donor for conjugation with the activated aldoxime was initially thought to be cysteine, but recent studies indicate that glutathione (GSH) serves as the sulfur donor instead [88,89]. The products resulting from cytochrome P450 activity are conjugated to glutathione by glutathione-S-transferases, forming S-alkyl-thiohydroximates. These are substrates for the enzyme carbon-sulfur lyase SUR1, initiating thiohydroximate biosynthesis [90]. The desulfoglucosinolates produced by UGT74 enzymes are sulfated to form glucosinolates, the second step in glucosinolate biosynthesis [91–98]. Sulfotransferases (SOTs) from the sulfotransferases family catalyse this reaction using 3′-phosphoadenylyl sulfate (PAPS) as the sulfate donor [99–103]. PAPS biosynthesis depends on sulfur nutrition and involves ATP sulfurylase (ATPS) and adenosine 5′-phosphosulfate (APK) kinase [91–98]. Glucosinolate activity is primarily influenced by their side chain structure [104]. Aliphatic glucosinolates can undergo various modifications, such as alkenylations, oxidations, benzoylations, and hydroxylations. Indolic glucosinolates are mainly subjected to methoxylations and hydroxylations [105,106]. These modifications occur in an organ and development-specific pattern [107,108]. Genetic studies have identified three loci involved in the side-chain modification of aliphatic glucosinolates [109]. The Gsl-oxid locus controls the oxidation process, catalysed by the flavin-monooxygenase (FMO) enzyme FMOGS-OX1, converting methylthio- to methylsulfinylalkylglucosinolates [110]. The Gsl-alk and Gsl-oh loci regulate the removal of the methylsulfinyl residue, the introduction of a double bond, and

the hydroxylation of butenylglucosinolate, respectively. Another locus, Gsl-ohp, converts methylsulfinylpropyl- to hydroxypropylglucosinolate in *Arabidopsis thaliana* [87]. Additionally, three genes (AOP1, AOP2, and AOP3) encoding 2-oxoglutarate-dependent dioxygenases are involved in glucosinolate modification. AOP2 converts 3-methylsulfinylpropyl- and 4-methylsulfinylbutylglucosinolate to alkenylglucosinolates, while AOP3 converts 3-methylsulfinylpropyl- to 3-hydroxypropylglucosinolate [111,112].

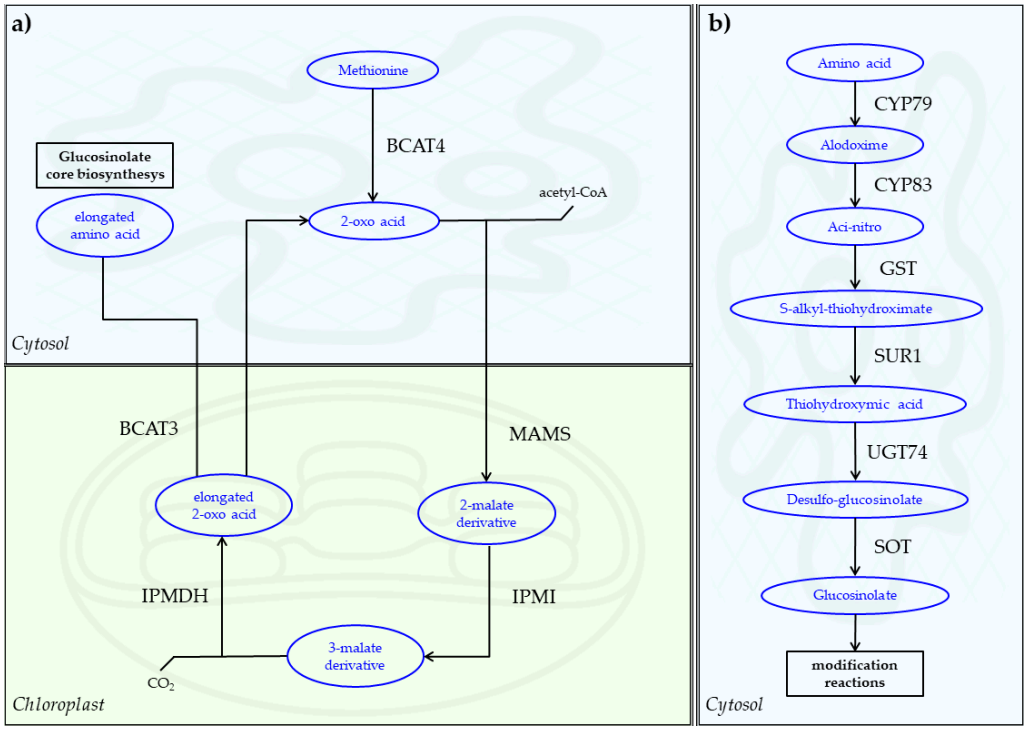

Figure 3. (**a**) Schematic representation of the biochemical processes involved in the aliphatic Glucosinolate Chain Elongation machinery; (**b**) Glucosinolate Core Biosynthesis. Amino acids, including elongated aliphatic methionine-derived molecules, can be converted to aldoximes by CYP79 cytochrome P450 family members to start building up the core glucosinolate scaffold. BCAT4—branched-chain aminotransferase 4; MAMS—methylthioalkylmalate synthase; IPMI—isopropylmalate isomerase; IPM-DH—isopropylmalate dehydrogenase; BCAT3—branched-chain aminotransferases-3; CYP79; GST; SUR1; UGT74; SOT. The pathway was built using the open-source software Pathvisio vs. 3.3.0.

6. Glucosinolate Transport

Transport processes are essential for redistributing specialized metabolites like glucosinolates, which protect vital tissues for species survival. In Arabidopsis, a significant portion of glucosinolates is transferred to maturing seeds [107]. Glucosinolate biosynthesis occurs in both the cytosol and chloroplasts, and their transport involves both short- and long-distance movement facilitated by transport proteins. The bile acid:sodium symporter family protein 5 (BAT5) plays a key role in short-distance transport. BAT5 imports 2-oxo acids into the chloroplast for side chain elongation and exports the resulting products into the cytosol for glucosinolate conversion [83]. BAT5 is activated by aliphatic glucosinolate regulators HAG1/MYB28, HAG2/MYB76, and HAG3/MYB29 [83]. In Arabidopsis, BAT5-defective mutants show reduced aliphatic glucosinolate levels [83,85]. Glucosinolates produced by maternal tissues are long-distance transported and accumulated in seeds [113–115]. In Arabidopsis, the transporters GTR1 and GTR2, belonging to the peptide transporter (PTR/NRT1) superfamily, mediate the movement of aliphatic and indolic glucosinolates between source and sink tissues [116,117]. GTR2 plays a prominent role [117–120].

Additionally, GTR1 and GTR2 are involved in the distribution of long-chain aliphatic glucosinolates between roots and shoots [121,122]. Genetic manipulation of plants to inhibit

the activity of GTR1 and GTR2 offers potential benefits in terms of reducing glucosinolate accumulation in seeds without affecting biosynthesis, thereby maintaining inherent defence capabilities [118,123]. Knock-out mutants of GTR1 and GTR2 in Brassica juncea showed changes in plant phenotype. GTR1 mutants had slightly reduced seed glucosinolate levels and significantly lower levels in source tissues. GTR2 mutants exhibited a significant decrease in seed glucosinolates but increased accumulation in leaves and pods. Moreover, GTR2 mutants demonstrated higher resistance to Spodoptera litura, suggesting the potential for enhancing crop production through manipulation of GTR2 to improve defence mechanisms or reduce anti-nutritional glucosinolate concentrations in seeds [39,118].

7. Glucosinolates Breakdown Product

Glucosinolate activation occurs when plants are wounded, for example, through chewing, which leads to contact between glucosinolates and myrosinases. This interaction triggers the hydrolysis of glucosinolates, resulting in an unstable aglucone that spontaneously rearranges into the corresponding isothiocyanate [124]. Isothiocyanates are highly reactive and toxic to various plant competitors and enemies, including microbes, fungi, insects, nematodes, and other plants species [125–129].

Despite the defensive capabilities of isothiocyanates, many Brassicaceae species have evolved alternative activation pathways through the involvement of specifier proteins. These specifier proteins, characterized by kelch domains, influence the structural outcome of myrosinase-catalysed glucosinolate hydrolysis [130–133]. In the presence of these proteins, the production of isothiocyanates is reduced in favour of other breakdown products, such as simple nitriles, epithionitriles, and organic thiocyanates. This introduces additional structural diversification, besides the biosynthesis process, and may provide further defence mechanisms through direct or indirect effects on plant enemies [134,135].

8. Conclusions

In conclusion, based on the field observations of *Camelina sativa*'s weed-reducing capacity, more studies are needed to evaluate its allelopathic potential and its effects on sensitive species. The existing studies on the phytochemical characterization of glucosinolates are outdated and rely on dated approaches. Therefore, conducting new metabolomics analyses using mass spectrometry-based techniques is recommended. These analyses would enable the identification of the most abundant metabolites, the glucosinolates produced by *Camelina sativa*, including metabolic intermediates of GSL and break down products (simple nitriles, epithionitriles, organic thiocyanates sulfides, and thiols), and new classes of potentially phytotoxic compounds involved in the allelopathic phenomenon, which are superficially explored in this species. Therefore, the use of new holistic techniques can expand the knowledge of the bioactive molecules involved in allelopathic interactions.

Furthermore, it is important to note that glucosinolate production in *Camelina sativa* is strongly influenced by sulfur-based fertilization and regulated by the SDI1 and SDI2 genes. Furthermore, root exudates appear to be the main route by which this species exerts its allelopathic potential. Therefore, it is crucial to deepen the studies on the chemical composition of these compounds, their dynamics during the crop cycle, and their fate once released into the environment (i.e., transformation and/or microbial degradation phenomena).

Consequently, it is advisable to develop fertilization, breeding, and/or genetic improvement strategies using transgenic approaches to enhance the production and release of these specialized metabolites. Adopting such agroecological approaches can significantly improve the sustainable management capacity for weed control.

Author Contributions: Conceptualization, M.G., M.P., F.C., F.F.N., R.P. and F.A.; writing—original draft preparation, M.G., M.P., F.C., F.F.N., R.P. and F.A.; writing—review and editing, M.G., M.P., F.C., F.F.N., R.P. and F.A., Funding acquisition R.P. and F.A. All authors have read and agreed to the published version of the manuscript.

Funding: Agritech National Research Centre and received funding from the European Union NextGenerationEU (PIANO NAZIONALE DI RIPRESA E RESILIENZA (PNRR)–MISSIONE 4 COMPONENTE 2, INVESTIMENTO 1.4–D.D. 1032 17/06/2022, CN00000022). This manuscript reflects only the authors' views and opinions; neither the European Union nor the European Commission can be considered responsible for them.

Data Availability Statement: Not applicable.

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

References

1. Aci, M.M.; Sidari, R.; Araniti, F.; Lupini, A. Emerging Trends in Allelopathy: A Genetic Perspective for Sustainable Agriculture. *Agronomy* **2022**, *12*, 2043. [CrossRef]
2. Choudhary, C.S.; Behera, B.; Raza, M.B.; Mrunalini, K.; Bhoi, T.K.; Lal, M.K.; Nongmaithem, D.; Pradhan, S.; Song, B.; Das, T.K. Mechanisms of Allelopathic Interactions for Sustainable Weed Management. *Rhizosphere* **2023**, *25*, 100667. [CrossRef]
3. Hickman, D.T.; Comont, D.; Rasmussen, A.; Birkett, M.A. Novel and Holistic Approaches Are Required to Realize Allelopathic Potential for Weed Management. *Ecol. Evol.* **2023**, *13*, e10018. [CrossRef] [PubMed]
4. Gealy, D.R.; Dilday, R.H.; Rutger, J.N. Interaction of Flush Irrigation Timing and Suppression of Barnyardgrass with Potentially Allelopathic Rice Lines. *Res. Ser.-Ark. Agric. Exp. Stn.* **1998**, *460*, 49–55.
5. He, H.-Q.; Shen, L.-H.; Xiong, J.; Jia, X.-L.; Lin, W.-X.; Wu, H. Conditional Genetic Effect of Allelopathy in Rice (*Oryza sativa* L.) under Different Environmental Conditions. *Plant Growth Regul.* **2004**, *44*, 211–218. [CrossRef]
6. Scavo, A.; Abbate, C.; Mauromicale, G. Plant Allelochemicals: Agronomic, Nutritional and Ecological Relevance in the Soil System. *Plant Soil* **2019**, *442*, 23–48. [CrossRef]
7. Scavo, A.; Mauromicale, G. Crop Allelopathy for Sustainable Weed Management in Agroecosystems: Knowing the Present with a View to the Future. *Agronomy* **2021**, *11*, 2104. [CrossRef]
8. Kong, C.-H.; Chen, X.-H.; Hu, F.; Zhang, S.-Z. Breeding of Commercially Acceptable Allelopathic Rice Cultivars in China. *Pest Manag. Sci.* **2011**, *67*, 1100–1106. [CrossRef]
9. Worthington, M.; Reberg-Horton, C. Breeding Cereal Crops for Enhanced Weed Suppression: Optimizing Allelopathy and Competitive Ability. *J. Chem. Ecol.* **2013**, *39*, 213–231. [CrossRef]
10. Shehzad, T.; Okuno, K. Genetic Analysis of QTLs Controlling Allelopathic Characteristics in Sorghum. *PLoS ONE* **2020**, *15*, e0235896. [CrossRef]
11. Pan, Z.; Baerson, S.R.; Wang, M.; Bajsa-Hirschel, J.; Rimando, A.M.; Wang, X.; Nanayakkara, N.P.D.; Noonan, B.P.; Fromm, M.E.; Dayan, F.E.; et al. A Cytochrome P450 CYP71 Enzyme Expressed in Sorghum Bicolor Root Hair Cells Participates in the Biosynthesis of the Benzoquinone Allelochemical Sorgoleone. *New Phytol.* **2018**, *218*, 616–629. [CrossRef] [PubMed]
12. Hussain, M.I.; Araniti, F.; Schulz, M.; Baerson, S.; Vieites-Álvarez, Y.; Rempelos, L.; Bilsborrow, P.; Chinchilla, N.; Macías, F.A.; Weston, L.A.; et al. Benzoxazinoids in Wheat Allelopathy—From Discovery to Application for Sustainable Weed Management. *Environ. Exp. Bot.* **2022**, *202*, 104997. [CrossRef]
13. Jabran, K.; Mahajan, G.; Sardana, V.; Chauhan, B.S. Allelopathy for Weed Control in Agricultural Systems. *Crop Prot.* **2015**, *72*, 57–65. [CrossRef]
14. Haramoto, E.R.; Gallandt, E.R. Brassica Cover Cropping: I. Effects on Weed and Crop Establishment. *Weed Sci.* **2005**, *53*, 695–701. [CrossRef]
15. Haramoto, E.R.; Gallandt, E.R. Brassica Cover Cropping for Weed Management: A Review. *Renew. Agric. Food Syst.* **2004**, *19*, 187–198. [CrossRef]
16. Kruger, D.H.M.; Fourie, J.C.; Malan, A.P. Cover Crops with Biofumigation Properties for the Suppression of Plant-Parasitic Nematodes: A Review. *S. Afr. J. Enol. Vitic.* **2013**, *34*, 287–295. [CrossRef]
17. Rehman, S.; Shahzad, B.; Bajwa, A.A.; Hussain, S.; Rehman, A.; Cheema, S.A.; Abbas, T.; Ali, A.; Shah, L.; Adkins, S.; et al. Utilizing the Allelopathic Potential of Brassica Species for Sustainable Crop Production: A Review. *J. Plant Growth Regul.* **2019**, *38*, 343–356. [CrossRef]
18. Francisco, M.; Tortosa, M.; Martínez-Ballesta, M.d.C.; Velasco, P.; García-Viguera, C.; Moreno, D.A. Nutritional and Phytochemical Value of Brassica Crops from the Agri-Food Perspective. *Ann. Appl. Biol.* **2017**, *170*, 273–285. [CrossRef]
19. Rakow, G. Species Origin and Economic Importance of Brassica. In *Brassica*; Pua, E.-C., Douglas, C.J., Eds.; Biotechnology in Agriculture and Forestry; Springer: Berlin/Heidelberg, Germany, 2004; pp. 3–11. ISBN 978-3-662-06164-0.
20. Soodabeh Saeidnia Importance of *Brassica napus* as a Medicinal Food Plant. *J. Med. Plants Res.* **2012**, *6*, 2700–2703. [CrossRef]
21. Halkier, B.A.; Gershenzon, J. Biology and Biochemistry of Glucosinolates. *Annu. Rev. Plant Biol.* **2006**, *57*, 303–333. [CrossRef]
22. Bialy, Z.; Oleszek, W.; Lewis, J.; Fenwick, G.R. Allelopathic Potential of Glucosinolates (Mustard Oil Glycosides) and Their Degradation Products against Wheat. *Plant Soil* **1990**, *129*, 277–281. [CrossRef]
23. Rivera-Vega, L.J.; Krosse, S.; de Graaf, R.M.; Garvi, J.; Garvi-Bode, R.D.; van Dam, N.M. Allelopathic Effects of Glucosinolate Breakdown Products in Hanza [*Boscia senegalensis* (Pers.) Lam.] Processing Waste Water. *Front. Plant Sci.* **2015**, *6*, 532. [CrossRef] [PubMed]

24. Intanon, S.; Reed, R.L.; Stevens, J.F.; Hulting, A.G.; Mallory-Smith, C.A. Identification and Phytotoxicity of a New Glucosinolate Breakdown Product from Meadowfoam (*Limnanthes alba*) Seed Meal. *J. Agric. Food Chem.* **2014**, *62*, 7423–7429. [CrossRef] [PubMed]
25. Wolf, R.B.; Spencer, G.F.; Kwolek, W.F. Inhibition of Velvetleaf (*Abutilon theophrasti*) Germination and Growth by Benzyl Isothiocyanate, a Natural Toxicant. *Weed Sci.* **1984**, *32*, 612–615. [CrossRef]
26. Yamane, A.; Fujikura, J.; Ogawa, H.; Mizutani, J. Isothiocyanates as Alleopathic Compounds from *Rorippa indica* Hiern. (Cruciferae) Roots. *J. Chem. Ecol.* **1992**, *18*, 1941–1954. [CrossRef]
27. Baysal-Gurel, F.; Liyanapathiranage, P.; Addesso, K.M. Effect of Brassica Crop-Based Biofumigation on Soilborne Disease Suppression in Woody Ornamentals. *Can. J. Plant Pathol.* **2020**, *42*, 94–106. [CrossRef]
28. Harvey, S.G.; Hannahan, H.N.; Sams, C.E. Indian Mustard and Allyl Isothiocyanate Inhibit *Sclerotium rolfsii*. *J. Am. Soc. Hortic. Sci.* **2002**, *127*, 27–31. [CrossRef]
29. Wang, T.; Li, Y.; Bi, Y.; Zhang, M.; Zhang, T.; Zheng, X.; Dong, Y.; Huang, Y. Benzyl Isothiocyanate Fumigation Inhibits Growth, Membrane Integrity and Mycotoxin Production in *Alternaria alternata*. *RSC Adv.* **2020**, *10*, 1829–1837. [CrossRef]
30. Barani, E.; Shafaat, G. Allelopathic Effect of *Brassica napus* Residues and Etalfluraline Herbicide on Germination and Some Cotton Characteristics of Bakhtegan Cultivar. *J. Plant Prod. Sci.* **2022**, *12*, 47–61. [CrossRef]
31. Rehman, S.U. Allelopathic Potential of *Sinapis alba* L. Residues in Weeds Management System. *J. Arable Crops Mark.* **2021**, *3*, 39–43. [CrossRef]
32. Toosi, F.; Baki, B.B. Allelopathic Potential of *Brassica juncea* (L.) Czern. Var. Ensabi. In Proceedings of the 23rd Asian-Pacific Weed Science Society Conference, Cairns, QLD, Australia, 26–29 September 2011; Volume 1, pp. 555–558.
33. Zhou, X.; Xing, C.; Jiang, B.; Li, C.; Liu, X. Allelopathic effects of water extracts of *Brassica juncea* var. *tumida* leaf on seed germination of three species of crops. *J. Henan Agric. Sci.* **2015**, *44*, 117–121.
34. Sainger, M.; Jaiwal, A.; Sainger, P.A.; Chaudhary, D.; Jaiwal, R.; Jaiwal, P.K. Advances in Genetic Improvement of *Camelina sativa* for Biofuel and Industrial Bio-Products. *Renew. Sustain. Energy Rev.* **2017**, *68*, 623–637. [CrossRef]
35. Francis, A.; Warwick, S.I. The Biology of Canadian Weeds. 142. *Camelina alyssum* (Mill.) Thell.; *C. microcarpa* Andrz. Ex DC.; *C. sativa* (L.) Crantz. *Can. J. Plant Sci.* **2009**, *89*, 791–810. [CrossRef]
36. Gehringer, A.; Friedt, W.; Lühs, W.; Snowdon, R.J. Genetic Mapping of Agronomic Traits in False Flax (*Camelina sativa* Subsp. *sativa*). *Genome* **2006**, *49*, 1555–1563. [CrossRef]
37. Liu, X.; Brost, J.; Hutcheon, C.; Guilfoil, R.; Wilson, A.K.; Leung, S.; Shewmaker, C.K.; Rooke, S.; Nguyen, T.; Kiser, J.; et al. Transformation of the Oilseed Crop *Camelina sativa* by Agrobacterium-Mediated Floral Dip and Simple Large-Scale Screening of Transformants. *Vitro Cell. Dev. Biol.-Plant* **2012**, *48*, 462–468. [CrossRef]
38. Liu, J.; Rice, A.; McGlew, K.; Shaw, V.; Park, H.; Clemente, T.; Pollard, M.; Ohlrogge, J.; Durrett, T.P. Metabolic Engineering of Oilseed Crops to Produce High Levels of Novel Acetyl Glyceride Oils with Reduced Viscosity, Freezing Point and Calorific Value. *Plant Biotechnol. J.* **2015**, *13*, 858–865. [CrossRef]
39. Nour-Eldin, H.H.; Madsen, S.R.; Engelen, S.; Jørgensen, M.E.; Olsen, C.E.; Andersen, J.S.; Seynnaeve, D.; Verhoye, T.; Fulawka, R.; Denolf, P.; et al. Reduction of Antinutritional Glucosinolates in Brassica Oilseeds by Mutation of Genes Encoding Transporters. *Nat. Biotechnol.* **2017**, *35*, 377–382. [CrossRef]
40. Amyot, L.; McDowell, T.; Martin, S.L.; Renaud, J.; Gruber, M.Y.; Hannoufa, A. Assessment of Antinutritional Compounds and Chemotaxonomic Relationships between *Camelina sativa* and Its Wild Relatives. *J. Agric. Food Chem.* **2019**, *67*, 796–806. [CrossRef]
41. Hu, P.; Wu, L.; Hollister, E.B.; Wang, A.S.; Somenahally, A.C.; Hons, F.M.; Gentry, T.J. Fungal Community Structural and Microbial Functional Pattern Changes after Soil Amendments by Oilseed Meals of *Jatropha curcas* and *Camelina sativa*: A Microcosm Study. *Front. Microbiol.* **2019**, *10*, 537. [CrossRef]
42. Arora, C.; Kaushik, R. Fungicidal Activity of Plants Extracts from Uttaranchal Hills against Soybean Fungal Pathogens. *Allelopath. J.* **2003**, *11*, 217–228.
43. Acharya, K.; Yan, G.; Berti, M. Can Winter Camelina, Crambe, and Brown Mustard Reduce Soybean Cyst Nematode Populations? *Ind. Crops Prod.* **2019**, *140*, 111637. [CrossRef]
44. Acharya, J.; Moorman, T.B.; Kaspar, T.C.; Lenssen, A.W.; Robertson, A.E. Cover Crop Rotation Effects on Growth and Development, Seedling Disease, and Yield of Corn and Soybean. *Plant Dis.* **2020**, *104*, 677–687. [CrossRef]
45. Powell, S.; Mcphee, J.; Dean, G.; Hinton, S.; Sparrow, L.; Wilson, C.; Tegg, R. Managing Soil Health and Crop Productivity in Potato: A Challenging Test System. *Soil Res.* **2020**, *58*, 697–712. [CrossRef]
46. Walker, B.A.R.; Powell, S.M.; Tegg, R.S.; Doyle, R.B.; Hunt, I.G.; Wilson, C.R. Soil Microbial Community Dynamics during Ryegrass Green Manuring and Brassica Biofumigation. *Appl. Soil Ecol.* **2022**, *179*, 104600. [CrossRef]
47. Morra, M.J.; Kirkegaard, J.A. Isothiocyanate Release from Soil-Incorporated Brassica Tissues. *Soil Biol. Biochem.* **2002**, *34*, 1683–1690. [CrossRef]
48. Fierer, N. Embracing the Unknown: Disentangling the Complexities of the Soil Microbiome. *Nat. Rev. Microbiol.* **2017**, *15*, 579–590. [CrossRef]
49. Trivedi, P.; Delgado-Baquerizo, M.; Anderson, I.C.; Singh, B.K. Response of Soil Properties and Microbial Communities to Agriculture: Implications for Primary Productivity and Soil Health Indicators. *Front. Plant Sci.* **2016**, *7*, 990. [CrossRef]
50. Hanschen, F.S.; Yim, B.; Winkelmann, T.; Smalla, K.; Schreiner, M. Degradation of Biofumigant Isothiocyanates and Allyl Glucosinolate in Soil and Their Effects on the Microbial Community Composition. *PLoS ONE* **2015**, *10*, e0132931. [CrossRef]

51. Petersen, J.; Belz, R.; Walker, F.; Hurle, K. Weed Suppression by Release of Isothiocyanates from Turnip-Rape Mulch. *Agron. J.* **2001**, *93*, 37–43. [CrossRef]
52. Mohler, C.L. Ecological Bases for the Cultural Control of Annual Weeds. *J. Prod. Agric.* **1996**, *9*, 468–474. [CrossRef]
53. Berti, M.; Samarappuli, D.; Johnson, B.L.; Gesch, R.W. Integrating Winter Camelina into Maize and Soybean Cropping Systems. *Ind. Crops Prod.* **2017**, *107*, 595–601. [CrossRef]
54. Šćepanović, M.; Sarić-Krsmanović, M.; Šoštarčić, V.; Brijačak, E.; Lakić, J.; Špirović Trifunović, B.; Gajić Umiljendić, J.; Radivojević, L. Inhibitory Effects of Brassicaceae Cover Crop on *Ambrosia artemisiifolia* Germination and Early Growth. *Plants* **2021**, *10*, 794. [CrossRef] [PubMed]
55. Grummer, G.; Beyer, H. The influence exerted by species of Camelina on flax by means of toxic substances. *Biol. Weeds Symp. Brit. Ecol. Soc.* **1960**, 153–157.
56. Lovett, J. Defensive Stratagems of Plants, with Special Reference to Allelopathy. *Pap. Proc. R. Soc. Tasman.* **1985**, *119*, 31–37. [CrossRef]
57. Lovett, J.V.; Sagar, G.R. Influence of Bacteria in the Phyllosphere of *Camelina sativa* (L.) Crantz on Germination of *Linum usitatissimum* L. *New Phytol.* **1978**, *81*, 617–625. [CrossRef]
58. Lovett, J.V.; Jackson, H.F. Allelopathic Activity of *Camelina sativa* (L.) Crantz in Relation to Its Phyllosphere Bacteria. *New Phytol.* **1980**, *86*, 273–277. [CrossRef]
59. Lovett, J.V. The Science of Allelopathy. In *Allelopathy: The Australian Experience*; Putnam, A.R., Tang, C.S., Eds.; John Wiley & Sons Inc.: New York, NY, USA, 1986; pp. 75–99.
60. Lovett, J.V.; Duffield, A.M. Allelochemicals of *Camelina sativa*. *J. Appl. Ecol.* **1981**, *18*, 283–290. [CrossRef]
61. Lovett, J.V. Allelopathy and Self-Defence in Plants. *Aust. Weeds* **1982**, *2*, 33–36.
62. Lovett, J.V. The Effects of Allelochemicals on Crop Growth and Development. In *Chemical Manipulation of Crop Growth and Development*; McLaren, J.S., Ed.; Butterworths: London, UK, 1982; pp. 93–110.
63. Saucke, H.; Ackermann, K. Weed Suppression in Mixed Cropped Grain Peas and False Flax (*Camelina sativa*). *Weed Res.* **2006**, *46*, 453–461. [CrossRef]
64. Walsh, K.; Sanderson, D.; Hall, L.; Mugo, S.; Hills, M. Allelopathic Effects of Camelina (*Camelina sativa*) and Canola (*Brassica napus*) on Wild Oat, Flax and Radish. *Allelopathy J.* **2014**, *33*, 83.
65. Jabran, K. Brassicaceae Allelopathy for Weed Control. In *Manipulation of Allelopathic Crops for Weed Control*; Jabran, K., Ed.; Springer Briefs in Plant Science; Springer International Publishing: Cham, Switzerland, 2017; pp. 21–27. ISBN 978-3-319-53186-1.
66. Czerniawski, P.; Piasecka, A.; Bednarek, P. Evolutionary Changes in the Glucosinolate Biosynthetic Capacity in Species Representing Capsella, Camelina and Neslia Genera. *Phytochemistry* **2021**, *181*, 112571. [CrossRef]
67. Berhow, M.A.; Vaughn, S.F.; Moser, B.R.; Belenli, D.; Polat, U. Evaluating the Phytochemical Potential of Camelina: An Emerging New Crop of Old World Origin. In *Phytochemicals—Biosynthesis, Function and Application: Volume 44*; Jetter, R., Ed.; Recent Advances in Phytochemistry; Springer International Publishing: Cham, Switzerland, 2014; pp. 129–148. ISBN 978-3-319-04045-5.
68. Russo, R.; Reggiani, R. Glucosinolates and Sinapine in Camelina Meal. *Food Nutr. Sci.* **2017**, *8*, 1063–1073. [CrossRef]
69. Hofmann, D.; Thiele, B.; Siebers, M.; Rahmati, M.; Schütz, V.; Jeong, S.; Cui, J.; Bigler, L.; Held, F.; Wu, B.; et al. Implications of Below-Ground Allelopathic Interactions of *Camelina sativa* and Microorganisms for Phosphate Availability and Habitat Maintenance. *Plants* **2023**, *12*, 2815. [CrossRef]
70. Quéro, A.; Molinié, R.; Mathiron, D.; Thiombiano, B.; Fontaine, J.-X.; Brancourt, D.; Van Wuytswinkel, O.; Petit, E.; Demailly, H.; Mongelard, G.; et al. Metabolite Profiling of Developing *Camelina sativa* Seeds. *Metabolomics* **2016**, *12*, 186. [CrossRef]
71. Bäuerle, R.; Wagner, H.; Schraudolf, H. Distribution of 4-Methoxy-3-Indolylmethyl-Glucosinolate (4-Methoxy-Glucobrassicin) in Brassicaceae. *Experientia* **1986**, *42*, 86. [CrossRef]
72. Droux, M. Sulfur Assimilation and the Role of Sulfur in Plant Metabolism: A Survey. *Photosynth. Res.* **2004**, *79*, 331–348. [CrossRef] [PubMed]
73. Saito, K. Sulfur Assimilatory Metabolism. The Long and Smelling Road. *Plant Physiol.* **2004**, *136*, 2443–2450. [CrossRef] [PubMed]
74. Takahashi, H.; Kopriva, S.; Giordano, M.; Saito, K.; Hell, R. Sulfur Assimilation in Photosynthetic Organisms: Molecular Functions and Regulations of Transporters and Assimilatory Enzymes. *Annu. Rev. Plant Biol.* **2011**, *62*, 157–184. [CrossRef]
75. Sugiyama, R.; Li, R.; Kuwahara, A.; Nakabayashi, R.; Sotta, N.; Mori, T.; Ito, T.; Ohkama-Ohtsu, N.; Fujiwara, T.; Saito, K.; et al. Retrograde Sulfur Flow from Glucosinolates to Cysteine in *Arabidopsis thaliana*. *Proc. Natl. Acad. Sci. USA* **2021**, *118*, e2017890118. [CrossRef]
76. Abdel-Massih, R.M.; Debs, E.; Othman, L.; Attieh, J.; Cabrerizo, F.M. Glucosinolates, a Natural Chemical Arsenal: More to Tell than the Myrosinase Story. *Front. Microbiol.* **2023**, *14*, 1130208. [CrossRef]
77. Eugui, D.; Escobar, C.; Velasco, P.; Poveda, J. Glucosinolates as an Effective Tool in Plant-Parasitic Nematodes Control: Exploiting Natural Plant Defenses. *Appl. Soil Ecol.* **2022**, *176*, 104497. [CrossRef]
78. Miękus, N.; Marszałek, K.; Podlacha, M.; Iqbal, A.; Puchalski, C.; Świergiel, A.H. Health Benefits of Plant-Derived Sulfur Compounds, Glucosinolates, and Organosulfur Compounds. *Molecules* **2020**, *25*, 3804. [CrossRef] [PubMed]
79. Aarabi, F.; Kusajima, M.; Tohge, T.; Konishi, T.; Gigolashvili, T.; Takamune, M.; Sasazaki, Y.; Watanabe, M.; Nakashita, H.; Fernie, A.R.; et al. Sulfur Deficiency–Induced Repressor Proteins Optimize Glucosinolate Biosynthesis in Plants. *Sci. Adv.* **2016**, *2*, e1601087. [CrossRef] [PubMed]

80. 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. [CrossRef]
81. Diebold, R.; Schuster, J.; Däschner, K.; Binder, S. The Branched-Chain Amino Acid Transaminase Gene Family in Arabidopsis Encodes Plastid and Mitochondrial Proteins. *Plant Physiol.* **2002**, *129*, 540–550. [CrossRef]
82. Falk, K.L.; Vogel, C.; Textor, S.; Bartram, S.; Hick, A.; Pickett, J.A.; Gershenzon, J. Glucosinolate Biosynthesis: Demonstration and Characterization of the Condensing Enzyme of the Chain Elongation Cycle in *Eruca sativa*. *Phytochemistry* **2004**, *65*, 1073–1084. [CrossRef]
83. Gigolashvili, T.; Yatusevich, R.; Rollwitz, I.; Humphry, M.; Gershenzon, J.; Flügge, U.-I. The Plastidic Bile Acid Transporter 5 Is Required for the Biosynthesis of Methionine-Derived Glucosinolates in *Arabidopsis thaliana*. *Plant Cell* **2009**, *21*, 1813–1829. [CrossRef]
84. Knill, T.; Reichelt, M.; Paetz, C.; Gershenzon, J.; Binder, S. *Arabidopsis thaliana* Encodes a Bacterial-Type Heterodimeric Isopropylmalate Isomerase Involved in Both Leu Biosynthesis and the Met Chain Elongation Pathway of Glucosinolate Formation. *Plant Mol. Biol.* **2009**, *71*, 227–239. [CrossRef]
85. Sawada, Y.; Toyooka, K.; Kuwahara, A.; Sakata, A.; Nagano, M.; Saito, K.; Hirai, M.Y. Arabidopsis Bile Acid:Sodium Symporter Family Protein 5 Is Involved in Methionine-Derived Glucosinolate Biosynthesis. *Plant Cell Physiol.* **2009**, *50*, 1579–1586. [CrossRef]
86. Schuster, J.; Knill, T.; Reichelt, M.; Gershenzon, J.; Binder, S. Branched-Chain Aminotransferase4 Is Part of the Chain Elongation Pathway in the Biosynthesis of Methionine-Derived Glucosinolates in Arabidopsis. *Plant Cell* **2006**, *18*, 2664–2679. [CrossRef]
87. Textor, S.; Bartram, S.; Kroymann, J.; Falk, K.L.; Hick, A.; Pickett, J.A.; Gershenzon, J. Biosynthesis of Methionine-Derived Glucosinolates in *Arabidopsis thaliana*: Recombinant Expression and Characterization of Methylthioalkylmalate Synthase, the Condensing Enzyme of the Chain-Elongation Cycle. *Planta* **2004**, *218*, 1026–1035. [CrossRef] [PubMed]
88. Bednarek, P.; Piślewska-Bednarek, M.; Svatoš, A.; Schneider, B.; Doubský, J.; Mansurova, M.; Humphry, M.; Consonni, C.; Panstruga, R.; Sanchez-Vallet, A.; et al. A Glucosinolate Metabolism Pathway in Living Plant Cells Mediates Broad-Spectrum Antifungal Defense. *Science* **2009**, *323*, 101–106. [CrossRef] [PubMed]
89. Schlaeppi, K.; Bodenhausen, N.; Buchala, A.; Mauch, F.; Reymond, P. The Glutathione-Deficient Mutant Pad2-1 Accumulates Lower Amounts of Glucosinolates and Is More Susceptible to the Insect Herbivore *Spodoptera littoralis*. *Plant J.* **2008**, *55*, 774–786. [CrossRef] [PubMed]
90. Mikkelsen, M.D.; Naur, P.; Halkier, B.A. Arabidopsis Mutants in the C–S Lyase of Glucosinolate Biosynthesis Establish a Critical Role for Indole-3-Acetaldoxime in Auxin Homeostasis. *Plant J.* **2004**, *37*, 770–777. [CrossRef] [PubMed]
91. Ravilious, G.E.; Jez, J.M. Structural Biology of Plant Sulfur Metabolism: From Assimilation to Biosynthesis. *Nat. Prod. Rep.* **2012**, *29*, 1138–1152. [CrossRef] [PubMed]
92. Jez, J.M.; Ravilious, G.E.; Herrmann, J. Structural Biology and Regulation of the Plant Sulfation Pathway. *Chem. Biol. Interact.* **2016**, *259*, 31–38. [CrossRef]
93. Mugford, S.G.; Lee, B.-R.; Koprivova, A.; Matthewman, C.; Kopriva, S. Control of Sulfur Partitioning between Primary and Secondary Metabolism. *Plant J.* **2011**, *65*, 96–105. [CrossRef]
94. Mugford, S.G.; Matthewman, C.A.; Hill, L.; Kopriva, S. Adenosine-5′-Phosphosulfate Kinase Is Essential for Arabidopsis Viability. *FEBS Lett.* **2010**, *584*, 119–123. [CrossRef]
95. Mugford, S.G.; Yoshimoto, N.; Reichelt, M.; Wirtz, M.; Hill, L.; Mugford, S.T.; Nakazato, Y.; Noji, M.; Takahashi, H.; Kramell, R.; et al. Disruption of Adenosine-5′-Phosphosulfate Kinase in Arabidopsis Reduces Levels of Sulfated Secondary Metabolites. *Plant Cell* **2009**, *21*, 910–927. [CrossRef]
96. Ravilious, G.E.; Nguyen, A.; Francois, J.A.; Jez, J.M. Structural Basis and Evolution of Redox Regulation in Plant Adenosine-5′-Phosphosulfate Kinase. *Proc. Natl. Acad. Sci. USA* **2012**, *109*, 309–314. [CrossRef]
97. Ravilious, G.E.; Jez, J.M. Nucleotide Binding Site Communication in *Arabidopsis thaliana* Adenosine 5′-Phosphosulfate Kinase. *J. Biol. Chem.* **2012**, *287*, 30385–30394. [CrossRef]
98. Yatusevich, R.; Mugford, S.G.; Matthewman, C.; Gigolashvili, T.; Frerigmann, H.; Delaney, S.; Koprivova, A.; Flügge, U.-I.; Kopriva, S. Genes of Primary Sulfate Assimilation Are Part of the Glucosinolate Biosynthetic Network in *Arabidopsis thaliana*. *Plant J.* **2010**, *62*, 1–11. [CrossRef]
99. Hirschmann, F.; Papenbrock, J. The Fusion of Genomes Leads to More Options: A Comparative Investigation on the Desulfo-Glucosinolate Sulfotransferases of Brassica Napus and Homologous Proteins of *Arabidopsis thaliana*. *Plant Physiol. Biochem.* **2015**, *91*, 10–19. [CrossRef]
100. Klein, M.; Reichelt, M.; Gershenzon, J.; Papenbrock, J. The Three Desulfoglucosinolate Sulfotransferase Proteins in Arabidopsis Have Different Substrate Specificities and Are Differentially Expressed. *FEBS J.* **2006**, *273*, 122–136. [CrossRef]
101. Klein, M.; Papenbrock, J. Kinetics and Substrate Specificities of Desulfo-Glucosinolate Sulfotransferases in *Arabidopsis thaliana*. *Physiol. Plant.* **2009**, *135*, 140–149. [CrossRef]
102. Klein, M.; Papenbrock, J. The Multi-Protein Family of Arabidopsis Sulphotransferases and Their Relatives in Other Plant Species. *J. Exp. Bot.* **2004**, *55*, 1809–1820. [CrossRef]
103. Piotrowski, M.; Schemenewitz, A.; Lopukhina, A.; Müller, A.; Janowitz, T.; Weiler, E.W.; Oecking, C. Desulfoglucosinolate Sulfotransferases from *Arabidopsis thaliana* Catalyze the Final Step in the Biosynthesis of the Glucosinolate Core Structure. *J. Biol. Chem.* **2004**, *279*, 50717–50725. [CrossRef]

104. Hopkins, R.J.; van Dam, N.M.; van Loon, J.J.A. Role of Glucosinolates in Insect-Plant Relationships and Multitrophic Interactions. *Annu. Rev. Entomol.* **2009**, *54*, 57–83. [CrossRef]
105. Ouassou, M.; Mukhaimar, M.; El Amrani, A.; Kroymann, J.; Chauveau, O. Biosynthesis of indole glucosinolates and ecological role of secondary modification pathways. *Comptes Rendus Biol.* **2019**, *342*, 58–80. [CrossRef]
106. Sønderby, I.E.; Geu-Flores, F.; Halkier, B.A. Biosynthesis of Glucosinolates—Gene Discovery and Beyond. *Trends Plant Sci.* **2010**, *15*, 283–290. [CrossRef]
107. Brown, P.D.; Tokuhisa, J.G.; Reichelt, M.; Gershenzon, J. Variation of Glucosinolate Accumulation among Different Organs and Developmental Stages of *Arabidopsis thaliana*. *Phytochemistry* **2003**, *62*, 471–481. [CrossRef]
108. Petersen, B.; Chen, S.; Hansen, C.; Olsen, C.; Halkier, B. Composition and Content of Glucosinolates in Developing *Arabidopsis thaliana*. *Planta* **2002**, *214*, 562–571. [CrossRef]
109. Giamoustaris, A.; Mithen, R. Genetics of Aliphatic Glucosinolates. IV. Side-Chain Modification in *Brassica oleracea*. *Theor. Appl. Genet.* **1996**, *93*, 1006–1010. [CrossRef]
110. Hansen, B.G.; Kliebenstein, D.J.; Halkier, B.A. Identification of a Flavin-Monooxygenase as the S-Oxygenating Enzyme in Aliphatic Glucosinolate Biosynthesis in Arabidopsis. *Plant J.* **2007**, *50*, 902–910. [CrossRef] [PubMed]
111. Kliebenstein, D.J.; Kroymann, J.; Brown, P.; Figuth, A.; Pedersen, D.; Gershenzon, J.; Mitchell-Olds, T. Genetic Control of Natural Variation in Arabidopsis Glucosinolate Accumulation. *Plant Physiol.* **2001**, *126*, 811–825. [CrossRef]
112. Uda, Y.; Kurata, T.; Arakawa, N. Effects of PH and Ferrous Ion on the Degradation of Glucosinolates by Myrosinase. *Agric. Biol. Chem.* **1986**, *50*, 2735–2740. [CrossRef]
113. Chen, S.; Petersen, B.L.; Olsen, C.E.; Schulz, A.; Halkier, B.A. Long-Distance Phloem Transport of Glucosinolates in Arabidopsis. *Plant Physiol.* **2001**, *127*, 194–201. [CrossRef]
114. Ellerbrock, B.L.J.; Kim, J.H.; Jander, G. Contribution of Glucosinolate Transport to Arabidopsis Defense Responses. *Plant Signal. Behav.* **2007**, *2*, 282–283. [CrossRef]
115. Du, L.; Ann Halkier, B. Biosynthesis of Glucosinolates in the Developing Silique Walls and Seeds of *Sinapis alba*. *Phytochemistry* **1998**, *48*, 1145–1150. [CrossRef]
116. Léran, S.; Varala, K.; Boyer, J.-C.; Chiurazzi, M.; Crawford, N.; Daniel-Vedele, F.; David, L.; Dickstein, R.; Fernandez, E.; Forde, B.; et al. A Unified Nomenclature of Nitrate Transporter 1/Peptide Transporter Family Members in Plants. *Trends Plant Sci.* **2014**, *19*, 5–9. [CrossRef]
117. Nour-Eldin, H.H.; Andersen, T.G.; Burow, M.; Madsen, S.R.; Jørgensen, M.E.; Olsen, C.E.; Dreyer, I.; Hedrich, R.; Geiger, D.; Halkier, B.A. NRT/PTR Transporters Are Essential for Translocation of Glucosinolate Defence Compounds to Seeds. *Nature* **2012**, *488*, 531–534. [CrossRef]
118. Nambiar, D.M.; Kumari, J.; Augustine, R.; Kumar, P.; Bajpai, P.K.; Bisht, N.C. GTR1 and GTR2 Transporters Differentially Regulate Tissue-Specific Glucosinolate Contents and Defence Responses in the Oilseed Crop *Brassica juncea*. *Plant Cell Environ.* **2021**, *44*, 2729–2743. [CrossRef]
119. Nour-Eldin, H.H.; Halkier, B.A. The Emerging Field of Transport Engineering of Plant Specialized Metabolites. *Curr. Opin. Biotechnol.* **2013**, *24*, 263–270. [CrossRef]
120. Xu, D.; Hunziker, P.; Koroleva, O.; Blennow, A.; Crocoll, C.; Schulz, A.; Nour-Eldin, H.H.; Halkier, B.A. GTR-Mediated Radial Import Directs Accumulation of Defensive Glucosinolates to Sulfur-Rich Cells in the Phloem Cap of Arabidopsis Inflorescence Stem. *Mol. Plant* **2019**, *12*, 1474–1484. [CrossRef]
121. Andersen, T.G.; Nour-Eldin, H.H.; Fuller, V.L.; Olsen, C.E.; Burow, M.; Halkier, B.A. Integration of Biosynthesis and Long-Distance Transport Establish Organ-Specific Glucosinolate Profiles in Vegetative Arabidopsis. *Plant Cell* **2013**, *25*, 3133–3145. [CrossRef]
122. Jørgensen, M.E.; Nour-Eldin, H.H.; Halkier, B.A. Transport of Defense Compounds from Source to Sink: Lessons Learned from Glucosinolates. *Trends Plant Sci.* **2015**, *20*, 508–514. [CrossRef]
123. 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: Cambridge, MA, USA, 2016; Volume 80, pp. 125–169.
124. Poveda, J.; Eugui, D.; Velasco, P. Natural Control of Plant Pathogens through Glucosinolates: An Effective Strategy against Fungi and Oomycetes. *Phytochem. Rev.* **2020**, *19*, 104497. [CrossRef]
125. Shofran, B.G.; Purrington, S.T.; Breidt, F.; Fleming, H.P. Antimicrobial Properties of Sinigrin and Its Hydrolysis Products. *J. Food Sci.* **1998**, *63*, 621–624. [CrossRef]
126. Agrawal, A.A.; Kurashige, N.S. A Role for Isothiocyanates in Plant Resistance against the Specialist Herbivore Pieris Rapae. *J. Chem. Ecol.* **2003**, *29*, 1403–1415. [CrossRef]
127. Aissani, N.; Tedeschi, P.; Maietti, A.; Brandolini, V.; Garau, V.L.; Caboni, P. Nematicidal Activity of Allylisothiocyanate from Horseradish (*Armoracia rusticana*) Roots against *Meloidogyne incognita*. *J. Agric. Food Chem.* **2013**, *61*, 4723–4727. [CrossRef]
128. Jeschke, V.; Gershenzon, J.; Vassão, D.G. A Mode of Action of Glucosinolate-Derived Isothiocyanates: Detoxification Depletes Glutathione and Cysteine Levels with Ramifications on Protein Metabolism in *Spodoptera littoralis*. *Insect Biochem. Mol. Biol.* **2016**, *71*, 37–48. [CrossRef] [PubMed]
129. Tookey, H.L. Crambe Thioglucoside Glucohydrolase (EC 3.2.3.1): Separation of a Protein Required for Epithiobutane Formation. *Can. J. Biochem.* **1973**, *51*, 1654–1660. [CrossRef] [PubMed]

130. 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. [CrossRef] [PubMed]
131. Wittstock, U.; Burow, M. Tipping the Scales--Specifier Proteins in Glucosinolate Hydrolysis. *IUBMB Life* **2007**, *59*, 744–751. [CrossRef]
132. Kuchernig, J.C.; Burow, M.; Wittstock, U. Evolution of Specifier Proteins in Glucosinolate-Containing Plants. *BMC Evol. Biol.* **2012**, *12*, 127. [CrossRef]
133. Jander, G.; Cui, J.; Nhan, B.; Pierce, N.E.; Ausubel, F.M. The TASTY Locus on Chromosome 1 of Arabidopsis Affects Feeding of the Insect Herbivore Trichoplusia Ni. *Plant Physiol.* **2001**, *126*, 890–898. [CrossRef]
134. Mumm, R.; Burow, M.; Bukovinszkine'kiss, G.; Kazantzidou, E.; Wittstock, U.; Dicke, M.; Gershenzon, J. Formation of Simple Nitriles upon Glucosinolate Hydrolysis Affects Direct and Indirect Defense against the Specialist Herbivore, Pieris Rapae. *J. Chem. Ecol.* **2008**, *34*, 1311–1321. [CrossRef]
135. de Vos, M.; Kriksunov, K.L.; Jander, G. Indole-3-Acetonitrile Production from Indole Glucosinolates Deters Oviposition by *Pieris rapae*. *Plant Physiol.* **2008**, *146*, 916–926. [CrossRef]