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REVIEW

Plant-Derived Enzymes Producing Chiral Aroma Compounds and Potential Application

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ABSTRACT

Aroma (volatile) compounds play important ecological functions in plants, and also contribute to the quality of plant-derived foods. Moreover, chiral aroma compounds affect their functions in plants and lead to different flavor quality properties. Formations of chiral aroma compounds are due to the presence of enzymes producing these compounds in plants, which are generally involved in the final biosynthetic step of the aroma compounds. Here, we review recent progress in research on the plant-derived enzymes producing chiral aroma compounds, and their changes in response to environmental factors. The chiral aroma enzymes that have been reported produce (*R*)-linalool, (*S*)-linalool, (*R*)-limonene, and (*S*)-limonene, etc., and these enzymes are found in various plant species. We also discuss the origins of enantioselectivity in the plant-derived enzymes producing chiral aroma compounds and summarize the potential use of plants containing enzymes producing chiral aroma compounds for producing chiral flavors/fragrances.

KEYWORDS

Aroma; chiral; enantioselectivity; enzyme; plant volatile; stereochemistry

1 Chiral Aroma Compounds and Enzymes Producing Chiral Aroma Compounds in Plants

A number of aroma compounds with different enantioforms have been identified in plants. These can be divided into different categories, including volatile terpenes, volatile phenylpropanoids/benzenoids, and volatile fatty acid derivatives, based on their different metabolic pathways. The most common chiral aroma compounds described in the literature are volatile terpenes, such as dihydro-α-ionone, dihydro-γ-ionone, α-ionone, γ-ionone, linalool, linalool oxide, and α-terpineol [1–8].

Among the chiral aroma compounds, ionones and lactones generally have lower olfactory detection limits (ng/L level) [1,9]; and different enantioforms have different sensory and olfactory detection limits [2]. In addition, the fragrance delicately varies from isomer to isomer [2]. For example, (*S*)-(+)-γ-ionone has floral, green, and woody sensory properties, and has an olfactory detection limit of 0.07 ng/L, while (*R*)-(-)-γ-ionone possesses weak green, fruity, and pineapple-like properties, and has an olfactory

detection limit of 11 ng/L [1,2]. Moreover, (1*S*, 2*S*)-methyl jasmonate and its (1*S*, 2*R*)-isomer are odorless, while their (1*R*) isomers show typical floral, jasminic, slightly fruity properties, and have low detection limits [2,10]. In this review, Table 1 summarizes the sensory properties and olfactory detection limits of some chiral aroma compounds which are widely distributed in a diverse range of plants. Moreover, chiral aroma compounds occur in different plants with different enantioform ratios. In some plants, some chiral aroma compounds reach 100% enantioform ratio. Enantiomeric distributions of linalool in major plant essential oil sources have been reviewed previously [11,12]. Linalool is found in the essential oils of over 200 monocotyledonous and dicotyledonous plant species, accounting for more than 50% of plant families [12,13]. Over 90% of (*R*)-linalool is found in *Cinnamomum camphora* Nees & Eberm var. *linaloolifera*, and *Aniba rosaeodora* Ducke [14], while over 80% of (*S*)-linalool distributes in *Orthodon linalooliferum* Fujita and *Coriandrum sativum* L. [12]. Overall, (*R*)-linalool is more common in nature, compared with (*S*)-linalool [12]. In practical terms, the true assessment of the ratio of chiral aroma compounds may be affected by different chemical structures, vegetal matrix, processing methods and analytical techniques [12]. Therefore, it is important to study the enantiomeric distributions in plants themselves, not in the oils or flavor sources. In fact, the methods have been established to avoid the interference of extraction and analysis. Organic reagents, such as dichloromethane, ethyl acetate, were used in the extraction of chiral aroma compounds at room temperature (nearly 25°C). After the extraction, the samples were subjected to the gas chromatography–mass spectrometry analysis.

Table 1: Sensory properties and olfactory detection limit of some chiral aroma compounds

Pathway	Aroma compounds	Enantioform	Sensory properties	Olfactory detection limit (medium)	Reference
Volatile terpenes	Dihydro-α-ionone	(*R*)-(+)	Floral, violet-like, slightly fruity, woody	31 ng/L (air)	[1]
		(*S*)-(−)	Floral, orris-like, woody, honey	100 ng/L (air)	
	Dihydro-γ-ionone	(*R*)-(−)	Fatty-floral, orris-like nuances, earthy	6.2 ng/L (air)	[1]
		(*S*)-(+)	Fatty-floral, animalic undertone	39 ng/L (air)	
	α-Ionone	(*S*)-(−)	Floral, woody	0.04 ng/L	[1,3]
		(*R*)-(+)	Floral, fruity	0.8 ng/L	
	γ-Ionone	(*S*)-(+)	Floral, green, woody	0.07 ng/L (air)	[1]
		(*R*)-(−)	Weak green, fruity, pineapple-like	11 ng/L (air)	
	Carvone	(*R*)-(−)	Sweet spearmint, fresh herbal	6.7 ng/L	[15]
		(*S*)-(+)	Caraway, fresh herbal	1.0 ng/L	
	α-Damascone	(*R*)-(+)	Fruity, apple-like, woody, minty	100 µg/L	[16]
		(*S*)-(−)	Fruity, apple-like, woody, minty, camphor-like	1.5 µg/L	
	Rose oxide	(−)-(2*S*, 4*R*)-*cis*	Herbal, green, floral, earthy	50 µg/L	[16,17]
		(+)-(2*R*, 4*S*)-*cis*	Floral, green, clean, sharp, rose green	0.5 µg/L	
		(−)-(2*R*, 4*R*)-*trans*	Floral green, herbal, minty, fruity	160 µg/L	
		(+)-(2*S*, 4*S*)-*trans*	Herbal, green, floral, fruity, rose	80 µg/L	

(Continued)

Table 1 (continued)

Pathway	Aroma compounds	Enantioform	Sensory properties	Olfactory detection limit (medium)	Reference
	Dihydrorose oxide	(2*R*, 4*R*)-*cis*	Floral, green, clean, fruit, herbal, rose	17 µg/L	[16]
		(2*S*, 4*R*)-*trans*	Herbal, floral, fruity, minty, dusty, floral, green	150 µg/L	
		(2*S*, 4*S*)-*cis*	Herbal, green	450 µg/L	
		(2*R*, 4*S*)-*trans*	Herbal fresh, citrus, graperfruit	160 µg/L	
	Limonene	(*R*)-(+)	Fresh citrus, orange-like	200 µg/L	[15,18,19]
		(*S*)-(−)	Harsh, turpentine-like, lemon note	10 µg/L	
	Linalool	(*R*)-(−)	Woody, lavender, floral	0.8 µg/L	[4,15]
		(*S*)-(+)	Sweet, petigrain, floral	7.4 µg/L	
	Linalool oxide	(2*R*, 5*R*)-(+)-*trans*	Earthy, leafy	3000–4000 µg/L	[5–6,18]
		(2*R*, 5*S*)-(−)-*cis*	Stronger earthy, leafy	3000–4000 µg/L	
		(2*S*, 5*S*)-(−)-*trans*	Sweet, floral, creamy	3000–4000 µg/L	
		(2*S*, 5*R*)-(+)-*cis*	Sweet, floral, creamy	3000–4000 µg/L	
	α-Terpineol	(*S*)-(−)	Coniferous odor, tarry, fatty, cold pipe like	300,000 µg/L	[7–8,18]
		(*R*)-(+)	Heavy floral lilac-like odor	300,000 µg/L	
Volatile phenylpropanoids/ benzenoids	Benzenepropanal	(*R*)-(−)	Fresh, floral, reminiscent of lily of the valley, lindlenblossom, and cyclamen	-	[2,7]
		(*S*)-(+)	Fresh, floral, reminiscent of lily of the valley, lindlenblossom, and cyclamen	-	
	3-(3-Isopropylphenyl)butanal	(*R*)-(−)	Floral, fresh, green, muguet-like	0.88 ng/L (air)	[2]
		(*S*)-(+)	Floral, watery, green, with acidic touch	0.035 ng/L (air)	
	1,3,4,7,8-Hexahydro −4,6,6,7,8,8-hexamethyl-cyclopenta[g[-benzopyran	(4*S*,7*S*)	Pleasant clean musk	1.0 ng/L (air)	[2,20]
		(4*S*, 7*R*)	Pleasant clean musk	0.63 ng/L (air)	
		(4*R*, 7*S*)	A bit musk	130 ng/L (air)	
		(4*R*, 7*R*)	Fruity	440 ng/L (air)	

(Continued)

Table 1 (continued)

Pathway	Aroma compounds	Enantioform	Sensory properties	Olfactory detection limit (medium)	Reference
Volatile fatty acid derivatives	4-Methyldecan-5-olide	(4*R*, 5*R*)-*cis*	Reminiscent of δ-decalactone and cocos	30 ng/L	[9]
		(4*S*, 5*S*)-*cis*	Lactonic odour of *Aerangis confuse*, natural *Aerangis lactone*	0.13 ng/L	
		(4*R*, 5*S*)-*trans*	Slightly lactonic fragrance	100 ng/L	
		(4*S*, 5*R*)-*trans*	Reminiscent of δ-decalactone and cocos	50 ng/L	
	Methyl jasmonate	(1*S*, 2*S*)	Odourless	-	[2,10]
		(1*S*, 2*R*)	Odourless	-	
		(1*R*, 2*R*)	Typical floral, jasminic, slightly fruity	>70 ng/mL (ethanol)	
		(1*R*, 2*S*)	Typical floral, jasminic, slightly fruity	3 ng/mL (ethanol)	
	3-Mercapto-2-methylpentanol	(2*R*, 3*S*)	Broth-like, sweaty, and leek-like	40 ng/L	[2]
		(2*S*, 3*R*)	Broth-like, sweaty, and leek-like	30 ng/L	
		(2*R*, 3*R*)	Broth-like, sweaty, and leek-like	300 μg/L	
		(2*S*, 3*S*)	Broth-like, sweaty, and leek-like	1000 μg/L	
	1, 2-Propylene glycol	(*S*)	Wood, faint alcoholic	23.92 μg/L	[3]
		(*R*)	Sweet, fruity, faint alcoholic	4.66 μg/L	
	1-Octen-3-ol	(*R*)-(−)	Mushroom-like, fruity	10 μg/L	[15]
		(S)-(+)	Moldy, grassy	100 μg/L	

Note: Some information in this table is summarized based on reviews by Brenna et al. [2].

The enantiomeric distributions of linalool have been investigated in plants themselves, especially in flowers, e.g., in flower scents [21–23]. In this review, reports of chiral aroma compounds investigated only in plants themselves are summarized in Table 2. Consistent with the studies in oil sources, linalool is also the most widely studied in plants. Dötterl et al. investigated the flower scent of 15 plant species and found that 5 plant species only contain one isomer of linalool, i.e., (*S*)-linalool [21]. Furthermore, the enantiomeric composition of linalool in the flowers of kiwifruit (*Actinidia*) species has also been thoroughly investigated [23]. It was found that floral linalool from some species were not consistent inter-species enantiomeric ratios [23]. Chiral aroma compounds jasmine lactone and 1-phenylethanol have been reported in *Camellia sinensis* [24–26]. Ninety-two percent of (*S*)-jasmine lactone is distributed in *C. sinensis*, which is nearly the same as the amount of (*S*)-jasmine lactone found in an oil made from *Mangifera indica* [16]. An interesting phenomenon has been observed in *C. sinenesis*; the chiral ratio of the emitted 1-phenylethanol is different from that of the internal 1-phenylethanol [25,26].

Table 2: Distributions of some chiral aroma compounds in different plants

Aroma compounds	Plant species	Contribution of major enantiomer (%)	Reference
(*R*)-Linalool	*Jasminum grandiflorum*	≈85	[22]
	Phlox divaricata	95	[21]
	Actinidia arguta	59	[21]
	Arabidopsis thaliana	67	[27]
	Actinidia hemsleyana	100	[23]
	Actinidia macrosperma	100	[23]
	Actinidia glaucophylla	≥63	[23]
	Actinidia lanceolata	≥67	[23]
	Actinidia setosa	≥96	[23]
	Actinidia deliciosa	≥66	[23]
(*S*)-Linalool	*Penstemon digitalis*	100	[28]
	Linanthus dichotomus	100	[21]
	Prunus padus	100	[21]
	Silene otites	100	[21]
	Syringa vulgaris	100	[21]
	Cynanchum auriculatum	98	[21]
	Viburnum opulus	81	[21]
	Syringa vulgaris	>99	[29]
	Fragaria ananassa	>99	[30]
	Actinidia arguta	100	[23]
	Actinidia polygama	100	[23]
	Actinidia chrysantha	≥98	[23]
	Camellia sinensis	>76	[15]
(*R*)-Limonene	*Citrus*	90–100	[31]
(S)-Limonene	*Camellia sinensis*	>80	[15]
(S)-Terpineol	*Camellia sinensis*	>50	[15]
(*R*)-*cis*-Nerolidol	*Camellia sinensis*	>88	[15]
(*R*)-(−)-Carvone	*Camellia sinensis*	90	[15]
(*S*)-(+)-α-Ionone	*Camellia sinensis*	≥60	[15]
(*R*)-(−)-1-Octen-3-ol	*Camellia sinensis*	>58	[15]
(*S*)-β-Phellandrene	*Citrus*	92–99	[31]
(*R*)-Sabinene	*Citrus junos*	99	[31]
(*S*)-Sabinene	*Citrus limon*	82	[31]
	Citrus aurantifolia	80	[31]

(Continued)

Table 2 (continued)

Aroma compounds	Plant species	Contribution of major enantiomer (%)	Reference
(*S*)-Jasmine lactone	*Camellia sinensis*	92	[24]
(*R*)-1-Phenylethanol (internal)	*Camellia sinensis*	≥86	[25]
(*S*)-1-Phenylethanol (emitted)	*Camellia sinensis*	66	[26]
(*S*)-Diethyl malate	*Vitis vinifera*	100	[32]
(*R*)-2,3-Butanediol	*Vitis vinifera*	≥73	[32]

In contrast to identification of aroma compounds with different configurations in plants, very little information on the aroma synthases which produce these aroma compounds is available. The aroma enzymes that have been reported produce (*R*)-linalool, (*S*)-linalool, (*R*)-limonene, and (*S*)-limonene, and these enzymes are found in various plant species (Table 3) [22,30,33–35]. There is more than one enzyme responsible for the biosynthesis of each aroma compound isomer in a plant species, such as *Fragaria ananassa* and *Citrus unshiu* [30,33]. The co-occurrence of two enantiomers is a common feature in nature. For example, *Arabidopsis thaliana* is reported to produce both (*R*)-linalool and (*S*)-linalool. Gene coexpression analysis revealed the complex metabolism of linalool in *Arabidopsis* flowers, and revealed that there are two TPS enzymes that form the two linalool enantiomers [34].

Table 3: Distributions of enzymes that produce chiral aromatic compounds in different plants

Main product(s)	Designation[a]	Accession number	Plant species	Reference
(*R*)-Linalool	LIS	-	*Jasminum grandiflorum*	[22]
	TPS10	At2g24210	*Arabidopsis thaliana*	[34]
	LaLINS	ABB73045	*Lavandula angustivolia*	[35]
	LeMTS1	AAX69063	*Lycopersicon esculentum*	[36]
	-	AAL99381	*Mentha citrata*	[37]
	LIS	AAV63789	*Ocimum basilicum*	[38]
	RLIS	MT178265	*Camellia sinensis*	[39]
(*S*)-Linalool	At1g61680	AAO85533	*Arabidopsis thaliana*	[27]
	TPS14	At1g61680	*Arabidopsis thaliana*	[34]
	FaNES1	CAD57081	*Fragaria ananassa*	[30]
	FaNES2	CAD57106	*Fragaria ananassa*	[30]
	SLIS	AGX26045	*Camellia sinensis*	[39]
	AmNES/LIS-2	ABR24418	*Antirrhinum majus*	[40]
	Os02g02930	EU596453	*Oryza sativa*	[41]

(Continued)

Table 3 (continued)

Main product(s)	Designation[a]	Accession number	Plant species	Reference
(*R*)-Limonene	CitMTSE1	BAD27256	*Citrus unshiu*	[33]
	LaLIMS	ABB73044	*Lavandula angustivolia*	[35]
	ArLMS	AAL17636	*Agastache rugosa*	[42]
	Cl(+)LIMS1	AAM53944	*Citrus limon*	[43]
	Cl(+)LIMS2	AAM53946	*Citrus limon*	[43]
	CitMTSE2	BAD27257	*Citrus unshiu*	[44]
(*S*)-Limonene	Ag10	AAB70907	*Abies grandis*	[45]
	PaTPS-Lim	AAS47694	*Picea abies*	[46]
	PsTPS-Lim	ABA86248	*Picea sitchensis*	[47]
(*S*)-(*E*)-Nerolidol	ABR24417	ABR24417	*Antirrhinum majus*	[40]
	AAV36466	AAV36466	*Medicago truncatula*	[48]
(*R*)-1-PE	RPES	MH682198	*Camellia sinensis*	[49]
(*S*)-1-PE	SPES	MF977691	*Camellia sinensis*	[49]
		MF977692		
		MF977693		
		MF977694		
		MH682197		

Note: [a] The designation refers to the name in the original publication. '-' not provided in the original publication.

2 Influence of Environment Factors on the Plant-Derived Enzymes Producing Chiral Aroma Compounds

There are many reports concerning the effects of environmental factors, including biotic and abiotic factors, on plant volatiles and their formation-related enzymes. In most cases, the environmental factors activate phytophormone synthesis, which affects the genes encoding plant volatile synthases, and thus changes in plant volatile synthesis and emission [50,51]. As very few enzymes producing chiral aroma compounds have been identified and functionally characterized in plants, less is known about the influences of environmental factors on the plant-derived enzymes producing chiral aroma compounds. Pragadheesh et al. [22] investigated changes in linalool enantiomers at various developmental stages of *Jasminum grandiflorum* flowers. Linalool predominated as the (*R*) form in floral buds, whereas (*S*)-linalool was the major enantiomer found in the mature flowers. An (*R*)-linalool synthase gene was isolated and identified from *J. grandiflorum* flowers, and its expression correlated well with the high (*R*)-linalool emission at the bud stage. The change in the enantiomeric ratio from the (*R*)- to (*S*)-linalool moving from the bud to the mature stage may be due to the enantiospecific transformation and temporal decline of the (*R*)-linalool synthase gene in *J. grandiflorum*. We also investigated the effects of abiotic factors, such as mechanical damage and temperature, on stereochemical configurations of jasmine lactone in tea leaves (*C. sinensis*) [24]. (*S*)-Jasmine lactone was the major enantiomer, and it was found that different treatments affected the enantiomeric ratio of jasmine lactone in tea leaves. Under continuous mechanical damage, the ratio of (*R*) to (*S*) jasmine lactone was 23:77, but the ratio became 8:92 in tea leaves exposed to a combination of mechanical damage and low temperature (15°C). As the enzymes

which produce (*R*) or (*S*)-jasmine lactone are unknown in tea leaves, it remains to be determined if the genes encoding (*R*) or (*S*)-jasmine lactone synthases are affected by these abiotic factors.

There have been much fewer reports on the effects of biotic factors, such as insect attacks, on the stereochemical configurations of volatiles from vegetative or floral plant parts, although it is well known that insect visits/attacks change the quantity of volatiles emitted from these parts. An attack by the insect *Thrips hawaiiensis* (Morgan) was found to induce changes in the (*R*)-/(*S*)-1-phenylethanol ratio emitted from tea flowers [26]. In addition, the proportion of jasmonic acid (JA) was increased by the *T. hawaiiensis* attack. Interestingly, exposing flowers to *T. hawaiiensis* attack induced an (*R*)-/(*S*)-1-phenylethanol pattern that was similar to that emitted from flowers after exogenous JA treatment, suggesting that JA may be involved in the insect-induced changes in the (*R*)-/(*S*)-1-phenylethanol ratio [26].

3 Origins of Stereoselectivity in the Plant-Derived Enzymes Producing Chiral Aroma Compounds

Terpene synthases are a family of aroma synthases, which produce volatile terpene compounds with different stereoselectivities. Köllner et al. reported the stereoselectivity origins of two closely related maize terpene synthases encoding multiple stereoselective product enzymes [52]. The two terpene synthases in maize, TPS4 and TPS5, were found to produce volatile sesquiterpenes from the precursor farnesyl diphosphate, but with different proportions and stereoselectivity of products. TPS4 and TPS 5 share 98% identity at the amino acid level, and such high sequence similarity made it possible to determine which amino acid residues were responsible for the different stereoselectivity of products using site-directed mutagenesis. Four amino acids (positions 407, 409, 410, and 411) were different between TPS4 and TPS5, and these were located at the bottom of the active site cavity. Amino acid exchange experiments suggested that these amino acids located in the catalytic center determine the stereoselectivity of TPS4 and TPS5. In contrast to volatile sesquiterpene synthases, the origins of the volatile monoterpene synthase stereoselectivity are still unclear. Ginglinger et al. reported that the two TPS enzymes in *Arabidopsis* flowers, TPS10 and TPS14, can produce (-)-(*R*)-linalool and (+)-(*S*)-linalool, respectively [34]. However, phylogenetic analysis shows that the two TPSs are not closed class and belong to different clusters of TPS enzymes [53]. Therefore, their abilities to produce linalool may have evolved independently [34].

Ketoreductases are a family of enzymes which can reduce a wide range of ketones to alcohols with different stereoselectivities. These are the most commonly used enzymes for the manufacture of chiral alcohols in industrial pharmaceutical synthesis [54]. The stereoselectivity origins of plant-derived ketoreductases have not been reported, but there may be some hints from the reported findings in microorganisms. Recently, Noey et al. reported origins of stereoselectivity in evolved ketoreductases that reduce almost-symmetrical 3-oxacyclopentanone and 3-thiacyclopentanone in *Lactobacillus kefir* [55]. Certain point mutations in the active site, such as A94F and Y190F, lead to conformational variations in the active site that enlarge the small binding pocket, so that the larger S atom becomes easier to accommodate, and thus *S*-selectivity with 3-thiacyclopentanone is increased. In contrast, E145S shrinks the small binding pocket and amplifies the difference in size between an S atom and a CH_2 group. Shrinking the small binding pocket promotes *R*-selectivity, and also destabilizes the pro-*S* orientation.

4 Potential Use of the Plants Containing Enzymes Producing Chiral Aroma Compounds for Producing Chiral Flavors/Fragrances

In recent years, biocatalysis, especially plant-derived enzymatic catalysis, has attracted increased interest for the preparation of chiral alcohols. In contrast to a chemical synthesis approach, biocatalysis using plants has several advantages, including being environmentally-friendly, simple procedures, low cost, high efficiency, and excellent enantioselectivity [56]. In addition, plant extracts contain the oxido-reductase, cofactor (NAD(P)H) and its regeneration system, meaning that the enzyme-catalyzed process avoids the

addition of the expensive cofactor [57]. So far, carrot root (*Daucus carota*), apple (*Malus pumila*), cucumber (*Cucumis sativus*), onion (*Allium cepa*), potato (*Solanum tuberosum*), radish (*Raphanus sativus*), sweet potato (*Ipomoea batatas*), tea flowers (*C. sinensis*), clementine mandarin fruit (*Citrus reticulate*), strawberry tree (*Arbutus unedo* L.), and ginger roots (*Zingiber officinale*) have been reported for the production of chiral alcohols [25,56–61]. Among these plant resources, carrot root is the most frequently reported.

All the plant tissues should be used fresh to keep the enzymes active. The fresh plant tissues are simply extracted by water or buffer or directly used for the bioreductions. The plant-derived enzymes have a wide substrate-selectivity, and they not only catalyze the substrates present in the source plant itself to produce chiral alcohols but also are functional with substrates that may not occur in the source plant. Excellent yields and high enantioselectivities are the most important evaluation indices for biocatalysts. Low cost or abundant waste plant resources, such as strawberry trees and tea flowers, are being investigated as materials for industrial large-scale production [25,57]. Different plant resources have different substrate selectivities and enantioselectivities (Table 4), and each plant resource can form products with different enantioselectivity when using different substrates. The plant's geographical location, growing environment, and seasonal variation may result in the same plant resource catalyzing a substrate to give products with different enantioselectivities. Currently, plant tissues are mostly used to transform ketones to different chiral alcohols, while less is known about the potential for these plant tissues to be used for the production of other types of chiral aromas, not derived from ketones. As crude plant extracts are used for biocatalysis, there is a high likelihood of producing many by-products, which may cause issues for isolation and purification of the target products.

Table 4: Different plant resources have different substrate-selectivities and enantioselectivities

Plant resources	Substrate	Major enantio-products	Reference
Broccoli and Cauliflower (*Brassica oleracea*)	Phenylethanone	*S*	[56]
	Acetophenone	*S*	
Spinach beet (*Beta vulgatis*)	Phenylethanone	*S*	
	Acetophenone	*S*	
Spinach (*Spinacia oleraceae*)	Phenylethanone	*S*	
	Acetophenone	*S*	
Clementine mandarin (*Citrus reticulate*)	Acetophenone	*S*	[57]
	p-Chloroacetophenone	*S*	
	Indanone	*S*	
	Tetralone	*R*	
	Thiochromanone	*S*	
	Chromanone	*S*	
Strawberry (*Arbutus unedo* L.)	Acetophenone	*R*	
	p-Chloroacetophenone	*S*	
	Tetralone	*R*	
	Thiochromanone	*S*	
	Chromanone	*S*	
	2-Acetyl thiophene	*S*	

(Continued)

Table 4 (continued)

Plant resources	Substrate	Major enantio-products	Reference
Ginger (*Zingiber officinale*)	Acetophenone	*S*	
	p-Chloroacetophenone	S	
	m-Methylacetophenone	*S*	
	Indanone	*S*	
	Thiochromanone	*S*	
	Chromanone	*S*	
	2-Acetyl thiophene	*S*	
Tea (*Camellia sinensis*)	Acetophenone	*R*	[25]
	Jasmine lactone	*S*	[24]
	Linalool	*S*	[15,39]
	Limonene	*S*	[15]
	1-Octen-3-ol	*R*	
	Carvone	*R*	
	α-Ionone	*S*	
	Cis-Nerolidol	*R*	
Carrot (*Ducus carota*)	Acetophenone and its derivatives	*S*	[58]
	Cyclic ketones	*S*	
	Open-chain ketones	*S*	
	β-Ketoesters	*S*, *R*	
	Azidoketones	*S*, *R*	
	(+)-Camphorquinone	*3S-exo*	[59]
	(−)-Camphorquinone	*2S-exo*, *3R-exo*	
Apple (*Malus pumila*)	Acetophenone	*R*	[60]
	Chloroacetophenone	*R*	
	Ethyl 4-chloroacetoacetate	*S*	
	(+)-Camphorquinone	*3S-exo*, *3R-endo*	[59]
	(−)-Camphorquinone	*3R-exo*	
Cucumber (*Cucumis sativus*)	Acetophenone	*S*	[60]
	Chloroacetophenone	*S*	
	Ethyl 4-chloroacetoacetate	*S*	
	(+)-Camphorquinone	*3S-exo*, *3R-endo*	[59]
	(−)-Camphorquinone	*2S-exo*, *3R-exo*	

(Continued)

Table 4 (continued)

Plant resources	Substrate	Major enantio-products	Reference
Onion (*Allium cepa*)	Acetophenone	*S*	[60]
	Chloroacetophenone	*S*	
	Ethyl 4-chloroacetoacetate	*R*	
	(+)-Camphorquinone	*3S-exo*	[59]
	(−)-Camphorquinone	*3R-exo*	
Potato (*Solanum tuberosum*)	Acetophenone	*R*	[60]
	Chloroacetophenone	*R*	
	Ethyl 4-chloroacetoacetate	*S*	
	(+)-Camphorquinone	*2R-exo*, *3S-exo*, *3R-endo*	[59]
	(−)-Camphorquinone	*2S-exo*, *2R-endo*, *3R-exo*	
Radish (*Raphanus sativus*)	Acetophenone	*S*	[60]
	Chloroacetophenone	*S*	
	Ethyl 4-chloroacetoacetate	*S*	
	(+)-Camphorquinone	*3S-exo*	[59]
	(−)-Camphorquinone	*2S-exo*, *3R-exo*	
Sweet potato (*Ipomoea batatas*)	Acetophenone	*R*	[60]
	Chloroacetophenone	*R*	
	Ethyl 4-chloroacetoacetate	*S*	
	(+)-Camphorquinone	*2R-exo*	[59]
	(−)-Camphorquinone	*2S-exo*, *2R-endo*, *3R-*exo	
Burdock (*Arctium lappa*)	(+)-Camphorquinone	*3S-exo*	
	(−)-Camphorquinone	*3R-exo*	
Rape (*Brassica napus*)	Acetophenone derivative	*S*	[61]

5 Concluding Remarks and Perspectives

In this review, we have summarized the current knowledge of plant-derived enzymes producing chiral aroma compounds, their changes in response to environmental factors, origins of stereoselectivity in the plant-derived enzymes producing chiral aroma compounds, and the potential use of these enzymes for the stereoselective synthesis of important flavors/fragrances. The huge variety of enzymes producing chiral aroma compounds in different plants and their complex catalysis properties suggest that there is still much to learn. Several important points should be addressed in future studies:

(1) Authentic standards of aroma compounds with different stereoselectivities are not available to buy, but are usually synthesized by the researchers. Establishing a database detailing synthetic methods

and identification information of the known aroma compounds with different stereoselectivities will be very helpful for characterization of the aroma synthases.

(2) Current research has shown which plants contain which type of enzymes producing chiral aroma compounds. However, it is still unknown which exact enzyme is responsible for the production of chiral aroma compounds. Some plants may contain more than one particular enzymes with stereoselectivity. Identification of the exact enzymes and their subcellular locations will be helpful for us to understand their occurrences in plants.

(3) Not all plants contain enzymes producing chiral aroma compounds. Why do some enzymes producing chiral aroma compounds occur in many plants and some others are only present in certain plants? Why do some enzymes form products with different enantioselectivities with different substrates? In addition, what are the origins of stereoselectivity in the plant-derived enzymes producing chiral aroma compounds? Based on protein 3D structure experimental and computational theoretical studies, more direct evidence is needed in plants, and not simply by referring from microorganisms.

(4) For the future application of plant-derived enzymes for the stereoselective synthesis of important flavors/fragrances, several issues should be addressed. These include: establishing standard quality control for plant materials, reasonable design of plant resources as biocatalysts, and sequential design of multiple processes with sample pre-treatment, biocatalysis, extraction, isolation, and purification of the chiral target products.

(5) The directions of further studies will establish reliably the enantiomeric composition of aromatic compounds. In addition, an important point should be the study of the role of aroma synthases and their complex catalysis properties for the production of chiral aroma compounds.

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