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Edited by Sreeraj Gopi, Nimisha Pulikkal Sukumaran, Joby Jacob, and Sabu Thomas

Natural Flavours, Fragrances, and Perfumes

Chemistry, Production, and Sensory Approach

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Editors

Dr. Sreeraj Gopi
Chemical Faculty
Gdansk University of Technology
Gdansk
Poland
Overseas Expert Professor - Shanghai University
China

Mrs Nimisha Pulikkal Sukumaran
Aurea Biolabs (P) Ltd
R&D Center
Kolenchery
Cochin
682311 Kerala
India

Dr. Joby Jacob
Aurea Biolabs (P) Ltd
R&D Center
Kolenchery
Cochin
682311 Kerala
India

Prof. Sabu Thomas
Mahatma Gandhi University
Center for Nanoscience and Nanotechnology
Priyadarshini Hills
686-560 Kottayam, Kerala
India

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Preface

It has been a while since a book was put together to address the natural flavors in industrial formulations, including concise treatments of the relation between sophisticated methods and better comprehension of consumer perception and behavior using a multidisciplinary metabolic engineering methodology by connecting with fields. It appears, however, that a gap has arisen between the new advances in basic information and the direct application to product situations, with a critical requirement for scientific data. Besides, flavor innovation is a developing powerful field, which keeps on expanding its applications from its foundations in food and beverage to incorporate categories as different as personal care products and household products. But, consumer perceptions of naturalness and perceived healthiness influence their product choices and increase the preference for products labeled as natural. Consequently, keeping in mind the negative health perceptions brought about by many factors, including artificial flavors, ingredient unfamiliarity, advancements in processing, and so on, researchers all over the world have recently focused on flavors from natural resources with much success.

The idea of compiling the book *Natural Flavors, Fragrances, and Perfumes: Chemistry, Production, and Sensory Approach* took seed in mid-2018. The urge to foster such a book originated from the perspective of growing in this area, giving special emphasis on fundamental and applied research findings, and more persuasively in a food manufacturing business, to enhance product quality, and extend the shelf life of the products and improve process efficiency. This book is a systematic, complete, sequential compilation of information about the engineering of flavors and flavor products in the area of its application to provide insights to help guide development and in commercial strategy. Indeed, the goal of this book is to bring together some of the core knowledge in the field to provide a practical and wide-ranging guide for molecular biologists, new product researchers, and scientists involved in the commercial development of natural flavors and flavor-related compounds, and their use in applications as varied as pharmaceuticals, nutraceuticals, or fragrances.

This book is divided into 5 parts, including 13 chapters encompassing from natural product diversity and synthesis of flavor compounds to all different kinds of applications in the food and fragrance industries. It begins with a part devoted to the natural product diversity and its biomolecular aspects. Chapters 2 and 3 present advances in the strategies of metabolic pathway engineering and the biogenesis of plant-derived aroma compounds. The next part of the book (Chapters 4–6) focuses on flavor technology and the different kinds of flavor-delivering systems, signatures, and biochemistry of beverages. Chapters 7 and 8 are oriented to specific examples and applications of seasonings, herbs, spices, and resinoids to get a better understanding of their chemistry and uses. The last chapters are focused on regulatory aspects, sensory science and its challenges, advances in *in silico* approaches, and sensory perceptions.

A book like this is impossible without the support and effort of the contributors who have taken the time to submit their manuscripts during the pandemic period. Our editors wish to thank the authors who have generously contributed material to this book. They are experts in their fields and have provided valuable information and insights into the naturally derived flavors. The contributors include Valsaraj T.V.; Akhila Nair; Józef T. Haponiuk; Sumith K.; Anjali Anil; Neha Naijo Areekal; Sneha George; Irene Mary Peter; Roshin Thankachan, Maurício Bonatto Machado de Castilhos; Ana Paula Garrido de Queiroga; Lia Lúcia Sabino; Jorge Roberto dos Santos Júnior; Jorge Alejandro Santiago-Urbina; Hipócrates Nolasco-Cancino; Francisco Ruíz-Terán; Vanildo Luiz Del Bianchi; Daniel Jan Strub; Maria Strub; Nicolas Baldovini; Vaishak Ramachandran; Anirudh Jayakumar; Constantina Tzia; Virginia Giannou; Tryfon Kekes; Charikleia Chranioti; Maria Katsouli; Nirosha Pulikkal; and Dhanesh Haridas.

25 August 2022

Sreeraj Gopi
Nimisha P. Sukumaran
Joby Jacob
Sabu Thomas
Kochi, India

Part I

Biodiversity

1

Natural Product Diversity and its Biomolecular Aspects in Flavors and Fragrances

Themanamveedu Valsaraj, Akhila Nair, and Joby Jacob

Aurea Biolabs (P) Ltd., R&D Centre, Kolenchery, Cochin, Kerala, 682311, India

1.1 Introduction

In pharmaceutical, food, cosmetic, and nutraceutical industries, flavors and fragrances play a vital role. The natural selection method or processes facilitate unique as well as wide chemical diversity with optimal interactions with other biological macromolecules. Moreover, since a millennium, it is observed that the introduction of continental and conventional selective breeding efforts has resulted in land race, elite cultivars that could not only adapt to globally diverse habitats but also ensure vivid quality and productivity in flavors and fragrances worldwide. However, unraveling the genomic basis of these vivid adaptations remains indecipherable. For example, the world's oldest and most popular caffeine-containing beverage, the tea, comes along with immense medicinal, economic, and cultural virtues. Constant research will definitely pave way for a diverse metabolic, functional, and genomic refinement for the evaluation of their biosynthetic pathways [1]. Although it is well recognized that the differential accumulation of the three major characteristic constituents in tea tree leaves largely determines the quality of tea, little genomic information is currently available. Sequencing of the tea tree genome would facilitate to uncover the molecular mechanisms underlying secondary metabolic biosynthesis with the promise to improve breeding efficiency and thus develop better tea cultivars with even higher quality. The development of tea clones with more desirable quality traits and enhanced stress resistance becomes a necessity. Strategizing such crop improvement procedures based on miRNAs requires a detailed understanding of the miRNA–mRNA modules associated with stress tolerance and quality in tea plants [2].

Natural Flavours, Fragrances, and Perfumes: Chemistry, Production, and Sensory Approach,
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Biosynthesis of aroma compounds involves metabolic pathways in which the main precursors are fatty acids and amino acids, and the main products are aldehydes, alcohols, and esters. Some enzymes are crucial in the production of volatile compounds, such as lipoxygenase, alcohol dehydrogenase, and alcohol acyltransferase. Composition and concentration of volatiles in apples may be altered by pre- and postharvest factors that cause a decline in apple flavor [3]. Among the volatile aroma compounds produced by ripe apples, esters account for the majority. For example, among the volatile aroma compounds of Golden Delicious and Starking Delicious, esters account for 80% [4]. This chapter discusses the genetic resources and plant breeding, agricultural diversity, conservation of agrobiodiversity, and the economically useful natural products used as flavors and fragrances.

1.2 Genetic Resources and Plant Breeding

From time immemorial, the breeding and domestication of plant varieties and/or species for flavor, aroma, and other characteristics have been a constant and ongoing process. Novel heterogeneity in concentration and combination of secondary metabolites has been a constant source to develop new varieties of flavors and fragrances. These variations in the composition of secondary metabolites are affected by human preferences and domestication in flavors and aromas [5]. Moreover, the need for a higher nutrition crop or fruit variety in terms of sustainable agriculture has put into limelight the genomic breeding approaches inclusive of marker-assisted selection, backcrossing, haplotype breeding, and genomic prediction methods in synergy with artificial intelligence and machine learning to increase the speed of these breeding approaches. Figure 1.1 depicts an example of the use of an integrated framework of genomic resources [7].

1.3 Agricultural Diversification

Globally, in an agricultural system, aromatic plants are those with aromatic compounds. These aromatic plants synthesize secondary metabolites to produce essential oils, which provide relief from biotic and environmental stress. In addition, these essential oils are used in diverse applications like flavors, perfumes, and fragrance, which will provide economic returns to farmers and manufacturing industries. The increasing interest of research scholars worldwide encourages agricultural activities like proper land utilization as well as focuses on economic returns for aromatic crops. The ecological applications of these aromatic plants in agricultural systems lie in soil erosion control, carbon sequestration, phytoremediation, utilization of low-quality water, pest and disease management, and augmentation of soil properties [8]. The sensory evaluation or validation of spices depends on dominant attributes like color, aroma, and pungency, which is heavily influenced by the varieties, primary processing cultivation, and the processed products.

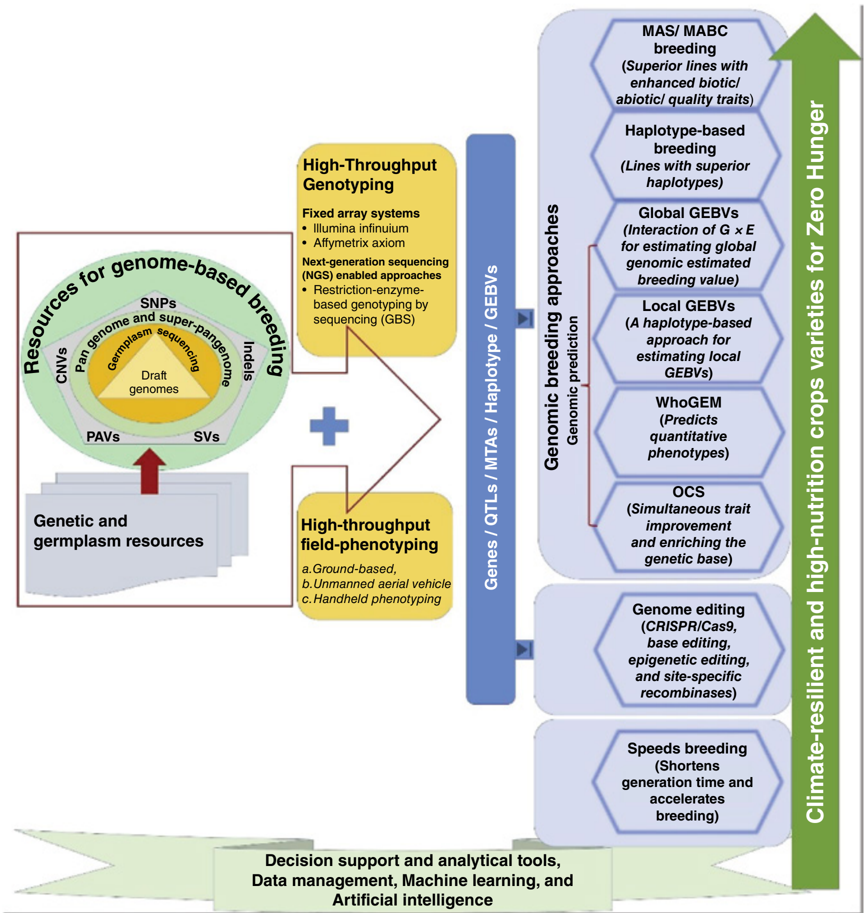

Figure 1.1 A unified framework of using genomic resources for genomic breeding to tailor climate resilient and high nutrition crops. Source: Adapted from Ashry et al. [6].

1.4 Conservation of Agrobiodiversity

The natural product diversity witness difficulties at economic level due to denial of traditional collective seed ownership, make people helpless to grow, harvest, and channel sufficient surplus food. There are many internationally acclaimed reciprocated responses that work in favor of the intellectual property law of farmers. Furthermore, the United States of America have designed vivid grassroot agricultural and biodiverse conservation projects to regulate the open pollinated seeds within fraternities of similar interest. This project involves exploration of the functions of pollinated seeds and focuses on various other strategies for agricultural biodiversity conservation. There are research projects that collectively disseminate and document open-pollinated seed around Appalachian Mountains and Ozark highlands of southeastern United States. The research methods involve an anthropology team who can conduct ethnographic interviews and make participant observation that cover the growing and sharing of seed varieties with local farmers, seed savers, gardeners, and activists with a definite aim of constructing more integrated, sustainable, and sovereign local food systems.

1.4.1 Strategies for Conservation of Medicinal Plants

The conservation strategies of near-to-extinct species of medicinal and food or aroma importance can be determined through social and scientific actions. The strategies for conservation of medicinal plants to be used for vivid purposes can be classified into (i) the importance of genebanks, (ii) molecular-based phylogenetics, and (iii) chemosystematics [9].

1.4.1.1 Importance of Genebanks

To compensate the emergent loss of genetic diversity in medicinal crops, the establishment and maintenance of large *ex situ* plant genetic resources (PGRs) was started where systemic breeding was developed by using genetically uniform cultivars to substitute traditional land races around the world. The seeds stocked in genebanks were considered as vital due to the fact it gave an insight of the historical background of the agriculture [10]. To illustrate, *Elettaria cardamomum*, which is an economically important crop, faces limitation in its genomic analysis because of the limitation of inefficient nucleic acid extraction due to its high polysaccharide and polyphenolic content. Therefore, genebanks provide an extraction protocol for nucleic acids that help to develop genetic markers for cardamom, perform gene expression, clone cardamom genes, analyze small RNAs, and clone cardamom-infecting viral genes [11].

1.4.2 Molecule-Based Phylogenetics

Cryptic diversity is often not recognized due to the incapability of recognizing the distinguishable morphological traits and because of inability to quantify the chemical communication systems. For certain plants or animals, species-level taxonomy is obstructed because of its distortion upon preservation and morphological plasticity. The morphological characteristics to differentiate likely related species using these methods become difficult, but recent advances in morphological characteristic-based studies imply several differences in the phenotypes. The revisions in taxonomic as well as molecular-based phylogenetic studies have proved to be promising to garner information related to large species groups with different genera [12].

1.4.3 Metabolomic-Based Phylogeny or Chemosystematics

The initial part of the last century witnessed the evolution of metabolomics-based phylogeny or chemosystematics that eventually gained its popularity in the 1970s [13]. However, these studies centered on the intrafamily classification at the species level as well as the measurement of particular components of single biochemical families, especially alkaloids, in accordance with the technologies of that period. For example, the chemical systematics of the family Rutaceae and the order Rutales received immense research attention. The authenticity of chemosystematic classification was proved by comparison with the phylogeny determined by molecular polymorphism analyses.

1.5 Economically Important Natural Products Used in Flavors and Fragrances

The economically most important plants serving the purpose of flavors and fragrances are cardamom, cinnamon, cocoa, fenugreek, marigold, nutmeg, vanilla, paprika, rosemary, davana oil, olibanum carterii/serrata, lavender, vetiver, and so on (Tables 1.1 and 1.2)

1.5.1 Flavors

1.5.1.1 Cardamom

Cardamom (*Elettaria cardamomum*) has been associated with numerous pharmacological properties [14]. This aromatic plant is one of the most expensive species in the world. India provides the most favorable warm humid climate with loamy-rich organic soil, well-distributed rainfall, and unique cultivation and processing methods that result in unique aroma, flavor, size, and green color. It has been used in culinary, confectionary, sweets, and medicines since time immemorial [33].

The diverse metabolites impose restriction to provide a standard method for RNA isolation for the available plants. The polysaccharide and polyphenol content of cardamom tissues obstruct the RNA extraction procedure. However, the combination of commercial kits as well as conventional cetyl trimethylammonium bromide (CTAB) method yields RNA with higher yield, good purity, and good integrity. The total RNA isolated from this approach was found compatible for small RNA analysis and transcriptome through next-generation sequencing platforms [34].

1.5.1.2 Cinnamon

Globally, cinnamon is a valuable source as an antioxidant compound [35]. Cinnamic aldehyde is widely used as a flavoring agent in foods and dentifrices [36] due to their antibacterial effects of cinnamon essential oil, cinnamon extracts, and pure compounds against different oral pathogens [37]. It is known for its aroma and essence in culinary, perfumes, and medicinal products. The active constituents of cinnamon, which are found in its essential oils, are cinnamaldehyde and trans-cinnamaldehyde that constitute its immense biological activities and fragrances. Cinnamon bark contains catechins and procyanidins. The components of procyanidins include both procyanidin A-type and B-type linkages. These procyanidins extracted from cinnamon and berries also possess antioxidant activities [36].

Table 1.1 Economically important plants and their ingredients.

Plant source	Active ingredients	Economic importance
Cardamom [14]	1,8-cineole, α-pinene, α-terpineol, linalool, linalyl acetate and nerolidol, and the ester constituent α-terpinyl acetate	Antioxidant, antimicrobial, antibacterial, anti-inflammatory
Cinnamon [15]	Cinnamaldehyde, trans-cinnamic acid, *o*-methoxycinnamaldehyde, eugenol, and monoterpenoids	Antioxidant, anti-inflammatory, antidiabetic, antimicrobial, anticancer, lipid-lowering, and cardiovascular-disease-lowering compound
Cocoa [16]	Theobromine, serotonin, anandamide, phenylethylamine	Antioxidation, anticancer, anti-microbial, anti-inflammation, anti-diabetes, cardioprotective, physical improvement, antiphotoaging, antidepression, and blood glucose regulation
Fenugreek [17]	Carbohydrates, proteins, lipids, alkaloids, flavonoids, fibers, saponins, steroidal saponins	Hypocholesterolemia, lactation aid, antibacterial, gastric stimulant, for anorexia, antidiabetic agent, galactagogue, hepatoprotective effect, and anticancer
Marigold [18]	Carotenoids, flavonoids, saponins, sterols, phenolic acids	Anti-inflammatory, anti-edematous activity, antioxidant, antibacterial and antifungal activity, immunostimulant activity, genotoxic and antigen-toxic activity, spasmogenic and spasmolytic activity, hepatoprotective activity
Nutmeg [19]	Terpenes (α-pinene, *p*-cymene, sabinene, camphene, myrcene, and γ-terpinene), terpene derivatives (terpinol, geraniol, and linalool), and phenylpropanes	Antioxidant activity, immuno-modulatory and radioprotective activities, anti-carcinogenic and hepatoprotective activity, anti-inflammatory activity, antimicrobial activity
Paprika [20]	Carotenoids	Antioxidant activity, antifungal activity Anti-inflammatory properties
Rosemary [21]	Triterpenes, phenolic diterpenes rosmarinic acid, carnosic acid, rosmanol, carnosol, ursolic acid, betulinic acid	Anti-depressant, antispasmodic antimicrobial, anti-inflammatory, anti-tumorigenic
Black pepper [22]	Piperine, alkaloids, amides, essential volatile oils	Anti-inflammatory, antioxidant improves blood sugar control, antithyroid activity
Oregano [23]	Carvacrol, β-fenchyl alcohol, thymol, and γ-terpinene	Antioxidant, antimicrobial
Annatto [24]	Carotenoids, Terpenoids, and terpenes	Anti-inflammatory, antibacterial, anti-endemic, and antifungal activity
Turmeric [25]	Curcumin	Anti-inflammatory, antioxidant, antimicrobial

Table 1.2 Important aromatic plants and their bioactives.

Fragrance source	Active ingredients	Properties
Davana oil [26]	Davanone, bicyclogermacrene, linalool, caryophyllene oxide, phytol	Antioxidant, antibacterial
Olibanum Carterii/ Serrata [27]	Boswellic acid	Anti-inflammatory, antifungal activity, antibacterial activity, antioxidant activity, anti-arthritic activity
Lavender [28]	Linalool, linalyl acetate, 1,8-cineole, β-ocimene terpinen-4-ol, and camphor	Antifungal activity, antibacterial activity, ascaricidal activity
Vetiver [29]	cedr-8-en-13-ol, β-guaiene Cycloisolongifolene	Antifungal activity, antibacterial activity, antioxidant activity
Red Sandalwood [30]	Carbohydrates, flavonoids, terpenoids, phenolic compounds, alkaloids, saponins, tannins, glycosides	Antibacterial activity, hepatoprotective, hypolipidemic activity, angiogenesis, and wound-healing activity
Lemongrass [31]	Myrcene, limonene, citral, geraniol, citronellol, geranyl acetate, neral, nerol	Anticancer and chemopreventive activity, anti-inflammatory, antifungal activity, antibacterial activity, antioxidant, allelopathic, insect repellent, anthelmintic activities
Elemi [32]	Elemol, limonene, elemicin, coumarins, furans, phenols	Hepatoprotective activities, antifungal activity, antibacterial activity, antioxidant, analgesic Antidiabetic
Myrrh [6]	Myrrhol, Myrrhin	Antihealing, antiseptic, antimicrobial

1.5.1.3 Cocoa

Cocoa seeds are a valuable food as well as a wellness product. These fruits are the main source of chocolate that is relished all over the world. The major producer of cocoa is Brazil [38]. The protein fractions of cocoa have an influence on the sensory and bioactive potential of cocoa products. The possible modifications during ripening, maturation, and post-harvest processing (drying, roasting, fermentation, and alkalization); composition of the phenolic compounds; and modifications in manufacturing processes are well documented [39, 40].

The phenolic compounds of cocoa contain antiradical and antioxidant properties with different biological properties like protection against cardiovascular diseases. Clovamide, a minor component of cocoa, is effective against oxidative stress induced in the rat cardiomyoblast cell line as compared to rosmarinic acid, other bio-isosteric forms, and epicatechin. All these three components were analyzed with DNA fragmentation, annexin V positivity, and caspase release as well as activation and were found to be effective to inhibit the production of reactive oxygen species and apoptosis [40].

1.5.1.4 Fenugreek

Trigonella foenum-graecum (fenugreek), belonging to the family Fabaceae, is a legume cultivated as a semiarid crop in India, Canada, Northern Africa, and Mediterranean region. This spice is known worldwide to enrich the sensory quality of foods and has high nutraceutical value. The presence of alkaloids, steroid saponin, and fiber in *Trigonella* seeds shows antidiabetic activity. Other bioactive compounds like trigonelline, orientin, isoorientin, isovitexin, and vitexin were quantified by high-performance liquid chromatography (HPLC). Other compounds identified by ultrahigh-performance liquid chromatography-hybrid electrospray triple quadrupole linear ion trap mass spectrometry were trigonelline, pinitol, isoorientin, sarsapogenin, and isovitexin [41]. The bioassay-guided isolation revealed 1 new pterocarpan and 12 known pterocarpans. These pterocarpans are important in terms of nutritional value as functional foods, foods, or antioxidants [18]. Moreover, fenugreek gum, a natural galactomannan, originates from the endosperm of *Trigonella foenum-graecum* seeds. This gum is composed of (1 → 4)-β-D-mannose (Man) backbone attached to a single α-D-galactose (Gal) group at the O-6 position with a Gal/Man ratio of 1 : 1 or in few cases of 1 : 2. It has been over a decade that fenugreek gums are used in food and pharmaceutical industry as a stabilizing and thickening agent [13, 42].

1.5.1.5 Marigold

Tagetes (marigold) is mainly found in America and is also cultivated in Europe, Asia, and Africa. Many species of this plant, including *T. erecta*, *T. patula*, *T. minuta*, and *T. tenuifolia*, are researched as medicinal plants. The major bioactive components of marigold are carotenoids, which are lipophilic pigments and well recognized as health-promoting agents. Although the native profile of carotenoids is not much studied because of the difficult analysis of carotenoid esters, it is observed that the hydroxyl carotenoids are found in both esterified and free form in numerous plant matrices. These carotenoids are used as supplements or marigold with no saponification process. The marigold petals contain lutein esters as major compounds. 18 caratenoids, 20 monoesters, 30 diesters (zeaxanthin, auroxanthin, violaxanthin, zeinoxanthin, and β-cryptoxanthin) were identified [43]. Various parts of the plants of *Tagetes* species are used to treat dental, stomach, and digestive disorders as well as anxiety and depression. These plants are also used for their fungicidal, bactericidal, insecticidal, anti-inflammatory, antioxidant, and enzyme inhibitory properties. They likewise find applications as a food additive and for their antimicrobial activities [43].

1.5.1.6 Nutmeg

Nutmeg is a plant found in tropical regions and its seeds are known for the unique flavor, nutritive value, and medicinal properties [44]. Occurrences of misuse have been accounted for nutmeg, including a family zest produced by crushing the seeds of *Myristica fragrans*, inferable from its stimulating properties [45]. A review of tangible metabolite dispersion in nutmeg has given a most far-reaching guide of its tactile metabolites. The key flavoring agent myristicin (40% in organic products) and 53 volatiles were differentiated in various classes, namely fragrant ethers, monoterpenes, and sesquiterpenes. In any case, monoterpene hydrocarbons are considered significant unstable structures in seeds [44].

1.5.1.7 Vanilla

Beginning from the locale of Mexico, *Vanilla planifolia* is a blooming climbing orchid that is internationally appreciated for the "vanilla" flavor created from its cases. The plant is distributed everywhere, particularly in tropical countries, for example, Madagascar, Uganda, Papua New Guinea, Indonesia, India, and islands like Comoros, Mayotte, Tahiti, and La Réunion. In addition to producing vanillin, the significant compound of vanilla concentrate, vanilla cases are the main wellspring of the more mind-boggling vanilla flavor. The photosynthesis process of *V. planifolia* also known as "Crassulacean Acid Metabolism (CAM) plant" involves the intake of carbon dioxide during the evening and its eventual stockpiling in cell vacuoles as malate. The very next day, during daytime, malate is secreted from the vacuoles, and carbon dioxide is produced by malate decarboxylation that enters the Calvin cycle and is utilized as a substrate for Rubisco to produce sugars and different carbohydrates for the plant. Albeit many investigations have been conducted on the natural chemistry of vanilla beans and the vanillin biosynthetic pathway, very little work has been performed on vanilla leaf metabolites [46]. Sun et al. detailed the presence of *p*-ethoxymethylphenol, *p*-butoxymethylphenol, vanillin, *p*-hydroxy-2-methoxycinnamaldehyde, and 3,4-dihydroxyphenylacetic compounds in the ethanol concentrate of vanilla leaves as well as stems. Tokoro et al. (1990) detailed the presence of bis[4-(*b*-D-glucopyranosyloxy)-benzyl]-2-isopropyltartrate (glucoside A) and bis[4-(*b*-D-glucopyranosyloxy)-benzyl]-2-(2-butyl)-tartrate (glucoside B) in vanilla leaves and stems. [47].

During the restoring process of Hainan vanilla beans, the key vanilla flavors, vanillin antecedents, and principal catalysts are removed. During handling, vanillin content increased, while glucovanillin content decreased, and vanillic content is found in beans; however, this content is decreased in drying beans. Both p-hydroxybenzaldehyde and p-hydroxybenzoic compounds show the highest content in restored beans. The ferulic compound is fundamentally produced in dry beans and is decreased in restored beans. The content of the *p*-coumaric compound is increased during the restoration process. During the relieving stage Vanillyl liquor in drying beans (0.22%) is subjected to hydrolysis of glucoside, that then changes. Besides, the enzymatic action of β-glucosidase is not observed in whitened and perspiring beans. But after drying, peroxidase activity reduces by 94% during relieving in restored beans. Polyphenol oxidase activity is low in early stages, while cellulose activity in handled beans is higher than in green beans, apart from restored beans. This study unfolds the biosynthesis pathway of vanillin [48].