

Review Article

Promising Natural Products in Crop Protection and Food Preservation: Basis, Advances, and Future Prospects

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The increase in demand for agricultural produce necessitates the continuous search for affordable, ecofriendly, readily available crop protectors, and food preservatives. Historically, the use of various chemicals was employed in controlling plant diseases and to maintain food quality. In the past few decades, several natural product-based alternatives have been discovered and projected as better alternatives to synthetic pesticides and other synthetic agrochemicals. Recent studies focusing on the application of different botanicals in crop protection and food preservation were carefully selected and reviewed. The application of plant extract in the biogenic preparation of nanoparticles was also reviewed. This review confirms that several natural products can be used as a safe replacement for synthetic agrochemicals. Different plant extracts have also served as feed for the synthesis of nanoparticle, which is increasingly applicable in crop protection and food preservation.

1. Introduction

The ever increasing population of man has continued to fuel the global urge for producing cash and food crops. The recent breakthrough in food production is partly due to the discovery and usage of synthetic agrochemicals and food preservatives, which significantly resolved several issues [1]. The resulting abundance of high-quality agricultural produce has subdued concerns associated with food scarcity in developed nations [2]. However, environmental and health concerns associated with the consumption of these agricultural products massively led to the search for safer and cheaper agrochemicals and food preservatives from natural products.

The innovative approach to enhance global food productivity is achievable through applications of sustainability channels. In advanced countries, agrochemicals are applied not only to preserve foods but also to mitigate pest invasion leading to unbroken food supply [3, 4]. In recent times, pesticides are observed to interact with the plant genome and the ecosystem. They eventually get metabolized in

organisms' tissues leaving disastrous end-products [5, 6]. These end-products (or metabolites) are adjudged to pose serious threats to target organisms, man, and the ecosystem [7]. Although consumption of fruits and vegetables is encouraged by Food and Agriculture Organization (FAO) and World Health Organization (WHO), however, the uptake of pesticide residues in most farm products (including vegetables and fruits) creates daunting aftermaths [8]. FAO and WHO have published recommended limits of organophosphates, carbamates, and organochlorine pesticides both in food and cash produce. Table 1 presents the maximum residue limits of various pesticides in fruit and vegetable.

The table was developed from FAO and WHO data [9, 10].

The intake of organophosphate residue in food was found to cause antiandrogenic effects and interfere with semen production, ejaculation, and total sperm count in male organisms [11–13]. Pyrethroid pesticides such as trans-3-(2, 2-dichlorovinyl)-1-methylcyclopropane-1, 2-dicarboxylic acid and 3-pherooxybenzoic acid were linked to abnormal morphology and low sperm motility [14, 15].

TABLE 1: Maximum residues' limits of pesticides in fruits and vegetables.

Class of pesticides Examples	Maximum residue limit (MRL) in mg/kg						
	Carbamate		Dithiocarbamates			Pyrethroid	
	Benomyl	Carbaryl	Carbosulfan	Mancozebthiram	Cypermethrin	Deltamethrin	Fenvalerate
Sweet corn		1.0			0.05		0.1
Cucumber		3.0	0.5	2.0			
Watermelon		1.0	0.2	1.0			
Brassica vegetables		1.0	0.5		1.0	0.1	2.0
Peppers chili	2.0	0.5	0.5	2.0	2.0	0.1	
Mango	2.0	1.0		2.0	0.7	0.2	1.5
Potato		0.2	0.05	0.2			0.05
Citrus fruits	3.0	7.0	0.1	2.0	0.3		
Grapes	3.0	5.0		5.0	0.5		
Spring onion	0.5					0.3	2.0
Tomato	3.0			10.0	0.2	0.1	
Shallot	2.0		0.5	0.5	0.1	0.05	
Onion, bulb				0.5	0.01		
Okra			0.5	0.2	0.5		
Egg plant			0.03	0.2	0.03	2.0	
Kale				15.0			
Pumpkins				0.2		2.0	
Cabbage							3.0
Papaya					0.5		
Class of pesticides Examples	Organophosphate		Organochlorine		Bipyridyliums	Triazine	
	Chlorpyrifos	Dimethoate	Malathion	DDD	Paraquat	Atrazine	Ametryn
Cabbages	1.0		8.0	0.02	0.07		
Sweet corn			0.02			0.1	
Spinach	0.5			0.2	0.07		
Banana	2.0						
Okra	0.5						
Cauliflower		0.2	0.5				
Spring onion			5.0		0.05		
Broccoli			5.0		0.07		
Kale			1.0		0.07		
Peppers chili	3.0		0.1				
Tomato		2.0	0.5		0.05		
Citrus fruits		5.0	7.0		0.02		
Shallot		0.5	1.0				
Onion, bulb	0.2	0.5	1.0		0.05		
Potatoes	3.0				0.05		
Cucumber	1.0				0.02		
Pineapple						0.1	0.1

Recently, health defects such as nausea, headache, endocrine disruption, cancer, oligospermia, and azoospermia have been reported from the intake of pesticide metabolites in food [8, 16]. There have been major concerns about acts protecting the consumers of agricultural products in Africa. Certain farmers and marketers do not comply with these rules because of their selfish interest, while the improper usage of pesticides by others has been linked to a lack of awareness of the right adequate dose to be administered [3].

Crop protection and food preservation are indispensable entities in global food sustainability. Several methods of preservation have effectively prevented food spoilage caused by insect infestation, climatic conditions, and microbial attacks [17]. However, studies revealed vast health issues relating to applications of synthetic pesticides and

preservatives [6, 18]. This spurred the search for safe and economical materials without harmful or detrimental effects to the health of consumers and the environment at large. Several natural preservatives and pesticides have been formulated and applied in food, pharmaceutical, and agrochemical industries [1, 19, 20]. In a broad sense, plant metabolites constitute the basic unit of life, protect plants from ultraviolet radiation, attract insect pollinator, promote hormone production, and enhance plants' survival. Phytochemicals such as alkaloids, phenylpropanoids, polyketides, terpenoids, carbohydrates, amino acids, lipids, and nucleic acids are essential materials in the production of several pesticides, herbicides, insecticides, and virucides [21–23]. This review is focused on appraisals of natural agrochemicals with promising protection and preservative potentials on crop and food products. It also explores the basis, advances,

and potential prospects of natural preservatives and pesticides. This will enlighten farmers, marketers, government agents, and stakeholders on the potential threats accompanying indiscriminate usage of pesticides and food preservatives, thus promoting good health and environmental sustainability.

2. Crop Protection: An Overview of Current Methods

In the past two decades, the production and distribution of crop and food products have been severely affected due to the invasion of drug resistance microbes, pests, and other external influences [24]. Particularly, pests have significantly affected the socioeconomic aspect of most developing countries by causing depletion and extinction of most crop species. The impact of pests on agriculture is evidenced in the reduction of crop yield, production capacity, plant density, and plant development [25]. In advanced countries, several measures have been designed to counter pests' attacks on crops and crop products. The most efficient method is the use of pesticides, which are classified into insecticides, fungicides, herbicides, virucides, bactericides, nematocides, molluscicides, and rodenticides based on the target species [4]. Biopesticides, which include naturally occurring pesticides in plants and genetically modified plants, have continued to gain much attention [6, 26]. Research has revealed that pesticides are vital in the protection of plants from pest invasion before the product gets to the final consumers [27]. This review focuses on insecticides, herbicides, fungicides, and virucides [3, 25]. Majorly, target organisms come in contact with the pesticides when applied directly by spraying on plants or indirectly. Certain applications of pesticides cause physical and biological damage to the target organisms by destroying key organs and interfering with some life processes such as photosynthesis, cell mitosis, and reproduction [6, 28, 29].

2.1. Current Methods of Crop Protection

2.1.1. Herbicides. Over the years, herbicides have been seen as an agent, which control the growth of unwanted plants in a sustainable way. Synthetic herbicides are widely engaged and are made available to farmers at cheaper prices [1, 30, 31]. Based on the mode of interaction, there are selective or nonselective herbicides. Nonselective herbicides affect a wide variety of plants alongside the target weed and are engaged in clearing large areas such as construction sites and fallow grounds, while selective herbicides work majorly by restricting the growth of targeted plants [31]. Certain herbicides are taken up through foliage, and they either function as inhibitors, disruptors, or regulators of various biosynthetic pathways [31, 32]. Examples of synthetic herbicides are glyphosate, imazapyr, hexazinone, paraquat, and picloram [30, 33], while examples of organic herbicides include corn gluten meal, D-limonene citrus oil (plant-based), and monocerin (fungi-based) [1].

2.1.2. Fungicides. Fungal growth (spores), which affect the growth and well-being of plants, can be successfully inhibited by the utilization of fungicides [29]. Based on their mode of activity, fungicides are categorized into three types: systematic, contact, and translaminar fungicides [34]. Systematic fungicides are redistributed by the xylem vessels after been absorbed, thereby blocking mitosis and cell division. Contact fungicides, however, works only on places sprayed and are not absorbed by plant tissues [34, 35]. Translaminar fungicides help in even distribution of fungicides from the upper parts of the plants to the lower parts [36]. Synthetic fungicides such as azoxystrobin, prochloraz, or thirame are mostly employed in crop protection, while examples of natural fungicides include rosemary oil, tea tree oil, and jojoba oil among many others [37–39].

2.1.3. Insecticides. Insecticides are applied to depopulate or eliminate the pests, which cause qualitative and quantitative damages to plants and farm produce [40, 41]. Insecticides have been successfully applied to increase mortality rates of insects, while ovicides and larvicides have successfully targeted the insect eggs and larvae stages, respectively [42, 43]. Several insecticides are utilized in agriculture, medicine, and households to prevent the activities of insects. Chemical compounds such as carbamates, nicotinoids organochlorine, organophosphate, and pyrethroids are the major constituents of insecticides [27, 41]. The two major classes of insecticides are systematic and contact insecticides [44]. Systematic insecticides are applied to plants (which the insects will consume and die), while contact insecticides are applied directly to the insect. Upon contact, the insect dies [44]. The mechanisms by which insecticides exert their activity have been investigated. Several chemical classes of insecticides act as either inhibitors, agonists, antagonists, regulators, or neurotoxicants based on the target site in the nervous system such as acetylcholine receptors, acetylcholinesterase, and voltage-gated sodium channels across the nerve membrane [41, 45]. Insecticides can be categorized as synthetic (inorganic and organic) and natural insecticides. Inorganic insecticides lack carbon in their structure and contain metals, e.g., copper sulfate, ferrous sulfate, and copper, while organic insecticides are carbon-containing compounds such as captan, carbamate, and glyphosate. Natural insecticides include nicotine and pyrethrum amongst others [1, 43, 45, 46].

2.1.4. Virucides. Viruses are infectious agents that can only replicate in living cells of a particular host such as plants, and they are linked to several damages and wastage of crop produce [47, 48]. In the treatment of viral diseases, virucides and antiviral agents have been effectively and successfully utilized for this effect. Virucides are known to completely eradicate viruses, while antiviral agents hinder the replication of viruses in cells and stop the transfer of viruses. Antiviral agents do not destroy the virus [47, 49]. Furthermore, the antiviral agents come in contact with the plant through foliar, get absorbed by the stomata, and move into the tissues of the plant. The resulting outcome is the

inhibition of the activity of the viral nucleic acids (DNA and RNA), which causes replication of viral cells [47, 49, 50]. Examples of synthetic antiviral agents are bavistin, benlate, and ribavirin, while antofine, duflin, glucan, and ningnanmycin are examples of natural antiviral agents commonly used [47, 50, 51].

2.1.5. Other Methods of Pest Management. Other methods include the use of natural predators or parasites such as lacewings, lady beetles, wasps, and hoverfly larvae, which feeds on a wide range of insects such as aphids, scale insects, spider mites, whiteflies, and many others [52]. Microbes such as *Trichoderma* spp., which help in protecting and keeping the plants healthy can be introduced [53]. Physical barriers such as scarecrows, traps, nets, or nearness to farmstead contribute to terrifying birds and scaring animals away [54]. Cover crops such as red clover, common vetch, daikon radish, or sweet clover are also utilized in controlling weed and help to fix nitrogen in the soil [55, 56]. Interestingly, the advent of cross-breeding and modification of genes in some plants has been employed to boost their disease/insect resistance traits [57, 58], unique dietary combinations, high protein content, resistance to herbicides [59], and drought and saline tolerance [60].

2.2. Negative Effects of Current Methods in Crop Protection. Inappropriate use of synthetic pesticides has led to pollution of a diverse kind in the environment, which is detrimental to man and his environment. The chemicals are applied directly to crops to protect them from attacks by insects, and this has been known to cause unsolicited problems [32, 46, 61]. Extensive and uninformed use of pesticides available in the market often leads to resistance from pests. The use of synthetic pesticides has helped greatly in crop protection. However, after a while, they accumulate and contaminate the environment moving from one medium to another. They particularly affect drinking water or penetrate the food chain [3, 25, 46]. Certain pesticides that are used for postharvest preservation are expected to disintegrate into nonharmful products after some time. However, these chemicals are not allowed to disintegrate before crop products are sold to consumers, and this has caused food poisoning for some families [62]. The use of toxic pesticides is still prominent, as farmers continue to make use of banned products, which engender environmental challenges and affect the well-being of farmers. Farmers who are exposed to arsenic poisoning are potentially at risk of occupational skin cancer and Bowen's disease [63]. The use of protective suits by farmers is on a decline, and farmers are stricken by various diseases as a result [63, 64]. Several reports covered the effects of pesticides on male hormonal function, while few have considered its effects on female hormonal function [61]. Certain studies have been able to ascertain the correlation between the menstrual cycle and pesticide exposure. Some irregularities such as long menstrual cycles, intermenstrual bleeding, and missed periods have 60–100% chances of occurring in people with pesticide exposure compared with women not exposed to pesticides [65, 66].

The environmental effects of pesticides have been studied and found to be caused by the percolation of pesticide constituents into water bodies via mechanical media such as wind or rain. Over time, the accumulation of pesticide residue in water bodies can threaten the growth, survival, and reproduction of aquatic organisms [3, 27, 46]. Aquatic organisms interact with pesticides by direct absorption through the skin, through the gills, and the mouth. Unsuspecting consumers such as pregnant or nursing mothers are prone to health issues after consuming contaminated fishes [67]. Even though pesticides disintegrate through processes such as photodecomposition, thermal degradation, and microbial decay, the processes are slow. The resulting exposure of aquatic animals to pesticides such as aldrin, dieldrin, DDT, malathion, endosulfan, dichlorvos, pyrethroid, methyl parathion, and chlordane were reported to cause an increased hemoglobin content [68], endocrine/hormonal imbalance, histopathological changes in the liver and gills, hematopoietic tissue, genetic defect, hyperactivity [69], hyperstimulation [70], and impairment of metabolism in fish, vertebral deformities, and behavioral disorder. Specifically, these exposure results in blindness, loss of appetite, induced sterility, decrease in fertility, interference with natural defense mechanisms, and eventually death [71–73]. The life cycle of salmon is affected by the exposure to specific pesticides that alter their ability to swim, get food, maintain a position in the river, avoid predators, and define territories. Furthermore, the transition state is impaired in salmonids, while spawning is delayed in adult salmon. There is also a change in behavior, blockage of sex hormones, and poor bone development [74]. Also, the effect of pesticides on soil microorganisms has been reported. It was observed that some mycoflora were inhibited by the addition of fungicides. However, the soil mycoflora soon overcame the effect of the fungicides [39]. Another important use of herbicides is the control of plants that block pipelines in houses and industries. Herbicides that have been used to control the unwanted blockage of sewer pipelines by cottonwood tree roots include triclopyr (5.22 mg/L), penoxsulam (0.83 mg/L), and dithiopyr (1.15 mg/L). Although a high concentration of these herbicides inhibit nitrification in wastewater treatment and slow down the removal of organic carbon in activated sludge, the use of highly diluted herbicides does not lead to such an unwanted activity [75]. Besides, it has been found that some herbicides stay longer in the soil and affect the growth of other crops on rotation [76].

2.2.1. Challenges with Other Methods of Pest Management. Different methods have been engaged in the control of the pest attack. However, there are some setbacks associated with their uses. For example, making use of natural predators does not ascertain complete eradication of the target pest, and the absence of target pest when natural predators are introduced can cause damages to crops. Likewise, the introduction of these natural predators can be time-consuming, especially if the farm is large [77]. Cover crops have been successfully applied to prevent loss of water from the soil. However, during winter, it causes reduction in soil

water [55]. Genetically modified (GM) species have provided a solution to several challenges related to crop protection over the years. However, whenever these GM plants are found in unwanted places on the farm, removing them becomes a challenge since they are herbicide-resistant [78, 79]. Even though scarecrows have been used on the farm to chase birds away, they are not efficient, and over time the bird gets used to the still images [54]. A summary of the negative effects of the current methods used in crop protection is shown in Table 2.

2.3. Natural Products in Crop Protection. Several studies have examined the application and efficacy of plant extracts in the fight against various diseases affecting plants. Solvent extracts from various plants have exhibited great potential in combating weeds invasion and microbial attacks.

2.3.1. Natural Products as Herbicides. Weeds are becoming resistant to conventional herbicides such as glyphosate, and natural products are serving as good alternatives [85]. Plants and microorganisms are major sources of secondary metabolites, which have found diverse application in agriculture. Plants that release chemical substances that affect the growth, nutrient uptake, and reproduction of other organisms are said to be allelopathic. Studies have shown that plants with the strong allelopathic activity are used in weed control. In recent times, crude extracts from different plant parts have been used effectively to hinder weed germination and growth [86]. *Melaleuca cajuputi* extract contains active compounds such as caryophyllene, eugenin, humulene, which are responsible for its medicinal properties and herbicidal potential [87]. Root extracts from *Mikania micrantha* afforded four novel thymol derivatives, which were discovered to have allelopathic properties [88]. Nine active compounds were discovered from the ethanol extracts of five *Amaranthus* species leaf. Amongst these, coumarin and saponins were responsible for the observed allelopathic effect against lettuce [89]. Biochanin A, an important isoflavone, exhibited a phytotoxic effect against both dicotyledon and monocotyledon weed species such as *Amaranthus caudatus* L. and *Echinochloa crusgalli* L. species. Interestingly, the degradation product of biochanin A is phytotoxic to the same weed species [90]. Similarly, two furanocoumarins (chalepin and chalepentin) were isolated from root and aerial parts of *Ruta graveolens* and taproots of *Hortia oreadica*. They effectively inhibited the growth of *Allium cepa*, *Lepidium sativum*, and *Lycopersicon esculentum*, thus showing greater impact than those of synthetic herbicides [91]. Furthermore, aqueous extracts from *Nerium oleander* L., *Olea europaea* L., and *Ricinus communis* L. leaves and synthetic herbicides (tibenuron) were applied to inhibit the growth of *Cyperus rotundus* L. [32]. Worth of note is the fact that *N. oleander* extracts gave the highest inhibitory effect compared to the other two extracts and the synthetic herbicide. Although the active compounds in the extracts were not isolated/characterized, phytochemicals such as phenolic compounds, flavonoids, terpenoids, and

alkaloids were generally found to be responsible for the allelopathic activity of the extracts [32].

Asides from plants, several organisms such as bacteria, fungi, and viruses have also been known to produce phytotoxic substances. For instance, certain microorganisms have been established as sources of bioactive secondary metabolites. An example is the new strain of *Lasiodiplodia pseudotheobromae*, from which the bioherbicide, mellein, was extracted and chromatographically purified. Mellein exhibited a notable activity on *Setaria italic*, *Cyanoclon dactylon*, *Axonopus compressus*, and *Valerianaceae* [92]. Similarly, *Pseudomonas aeruginosa* produced a bioherbicide (2-(hydroxymethyl) phenol), which inhibited the growth of pigweed and sorghum [93], while two herbicidal compounds were isolated from a strain of *Streptomyces* and were successfully used to inhibit the growth of *Digitaria sanguinalis* and *Sorghum bicolor* among other grasses [94]. Furthermore, a fungal strain from *Trichoderma polysporum* was employed in inhibiting the growth of *Pisum sativum* and *Vicia faba* L. [95], while *Trichoderma koningiopsis* caused 60% foliar damage on *Euphorbia heterophylla* (Mexican fire plant) [96]. A worthy note is that 1D and 2D NMR as well as mass spectrometry were employed in the characterization of most of these phytotoxic compounds. Structures of these herbicidal compounds are shown in Figure 1.

2.3.2. Natural Products as Fungicides. Several plant extracts have been successfully employed as fungicides. Examples include *Azadirachta indica* leaf extract [97], peels of *Ipomoea batatas* Lam [98], *Curcuma longa* leaves [37], *C. papaya* leaves [38], and thyme and lemongrass extract [99]. The activity of *Azadirachta indica* leaf extract can be attributed to the presence of compounds such as dibutyl phthalate, phytol, nonanoic acid, tritriacontane, and 1,2-benzenedicarboxylic acid in the crude extracts [97]; Similarly, three compounds namely stigmasterol, 3-friedelanol, and urs-13(18)-ene-3 β -yl acetate were identified in the peels of *Ipomoea batatas* Lam. with a reasonable activity against the growth of *Sporothrix schenckii* and *Trichophyton metagrophytes* fungi [98]. Thyme and lemongrass extract successfully reduced sheath blight disease in rice by attacking *R. solani*, thereby enhancing crop growth and yield of grains [99]. These activities are a result of the essential oils, saponins, tannins, flavonoids, and other phenolic compounds that were present in the extracts [100, 101]. Furthermore, extracts from *Curcuma longa* leaves have been found to possess impressive minimum inhibitory concentrations of 6.25 $\mu\text{g/ml}$ against *Aspergillus fumigatus* and 12.5 $\mu\text{g/ml}$ against *helminthosporium spp.* [37]. Furthermore, a soilborne disease, which is also known as pink root disease (initiated by a fungus—*Pyrenochaeta terrestris* (Hansen)), constitutes a problem for onions in the nursery. However, extracts from *A. indica* and *C. papaya* leaves were compared well with synthetic fungicides in the inhibition of this fungus disease. Therefore, *A. indica* and *C. papaya* leaves can be engaged as a cheap, readily available, and environmentally friendly alternative in the antifungal therapy [38].

TABLE 2: Negative effects of current methods of crop protection.

Methods	Examples	Disadvantages	References
Herbicides	Dimethylarsinic acid diuron, imazapyr, and picloram	Dizziness, headache, vomiting, fall in blood pressure, convulsions, and general paralysis Cancer	[62, 80] [33]
Fungicides	Mancozeb, malathion thirame, and fenarimol	Inhibition of hormone synthesis, developmental defects, menstrual cycle irregularities, impaired fertility, and spontaneous abortion/ stillbirths	[61, 81, 82]
Insecticides	Spinetoram	Minimal or mild eye irritation	[83]
	Diazinon	Lymphoma	[44]
	Aldrin	Liver diseases and lung cancer	[54]
	DDT	Chronic liver damage, reproductive disorders, cytogenic effects, and breast cancer	[61]
Genetically modified species	GM maize and soybean	Higher level of severe inflammation in stomach and lower glucose levels	[78, 79, 84]
Use of cover crops	Common vetch, daikon radish, and sweet clover	Soil water depletion	[55]
Natural predators	Lacewings, lady beetles, and trichodrema	The introduction of predators at the wrong time causes more damage to the plants	[77]
Use of scare crows	Mannequin or decoy	Not always effective in scaring birds and animals away	[54]

The direct application of pure organic compounds has similarly been reported. Five phenolic compounds namely alkylresorcinols (AR), ferulic acid, quercetin, phlorizin, and resveratrol were directly used against the phytopathogenic fungi *Botrytis cinerea*. Ferulic acid was most effective against several fungal isolates and resistant strain of *B. cinerea* [102]. Another study successfully used lauric acid to eliminate *Rhizoctonia solani*, *Pythium ultimum*, and *Blumeria graminis* growth on barley seedlings [103]. Interestingly, these emerging natural products are getting commercialized. An example is a product called “Plant tonic,” which contains alfalfa, humic acid, kelp, and vitamin B₁. This product has been used to inhibit mycelial growth and conidial germination of rice blast disease [104].

In the same vein, certain microbes have been found to produce secondary metabolites that have been successfully applied in crop protection. For instance, alteramide B, which has a broad spectrum against phytopathogenic fungi such as *Alternaria alternata*, *Colletotrichum gloeosporioid*, *Magnaporthe oryzae*, and *Valsa ambiens*, is an active component in *Lysobacter enzymogenes* [105]. Similarly, a novel strain of bacteria such as *Bacillus velezensis* has been found useful in the inhibition of *Verticillium dahliae*, soilborne fungi that affect tomatoes [106] and olives [107]. The antifungal compounds produced by this bacterium include tetradecane, benzaldehyde, and 1-decene amongst many others [106]. Likewise, *Ochrobactrum intermedium* was used in the treatment of *Colletotrichum falcatum*, which is responsible for red rot in sugarcane [108]. Also, a novel strain of fungi such as *Trichoderma erinaceum* was applied in boosting the growth of rice crop and inhibiting the growth of *Rhizoctonia solani*, *Sclerotium oryzae*, and *Sclerotium rolfsii* [109]. Liquid fermentation of brown sugar containing *Bacillus megaterium* has also been employed in controlling *Alternaria japonica*, which affects broccoli [110]. Relevant structures of some fungicidal compounds are shown in Figure 2.

2.3.3. Natural Products as Insecticides. In the search for safe, cheap, and sustainable means to control insect infestation, some selected botanicals have been successfully investigated. Crude extracts from different plant parts have displayed notable insecticidal properties. These include *Carica papaya* seed extract [111], polar and nonpolar extracts of seeds, peels, and pulp of *Persea americana* Mill [42], stem and leaf extract of *Clausena lenis* [112], *Callistemon citrinus* leaf extract [113], ethanolic extract of *Annona mucosa* seeds [114], citrus essential oil [115], *Azadirachta indica* seeds, *Phytolacca dodecandra* seeds, and *Schinus molle* seeds [43]. The active constituents in some of these extracts with insecticidal value are not hidden. The phytochemicals in these extracts are directly responsible for observed activities, and their mechanisms of action have been investigated. The neem tree has several products obtainable from its leaf, bark, and seed extracts [116, 117]. In particular, neem seeds contain azadirachtin as its major component. Azadirachtin whose insecticidal property has been well established operates by interfering with feeding, growth, synthesis, and distribution of molting hormones (ecdysteroids) leading to sterility in adult female insects and incomplete molting in the young insects [118, 119]. This compound is also effective against aphids, beetles, borers, caterpillars, whiteflies, mealy bugs, and weevils and considered as mild against vertebrates or beneficial insects such as ladybugs, bees, and spider [118, 120]. The wide range of activity observed in azadirachtin led to the various brand of organic insecticides (Agroneem, Azatrol EC, and Ecozin), which have emerged from the neem tree [118]. Similarly, ethanolic extract from *A. mucosa* seeds owes its insecticidal activity to acetogenins, which are potent against arthropods. Acetogenins exert their action by inhibiting the enzyme of the cellular plasma membrane and mitochondrial electron transport systems of target arthropods [114].

Another example is *C. papaya* seed extract, which contains an active component “Papain” [111]. This extract has been reported to be toxic against mustard aphid [121],

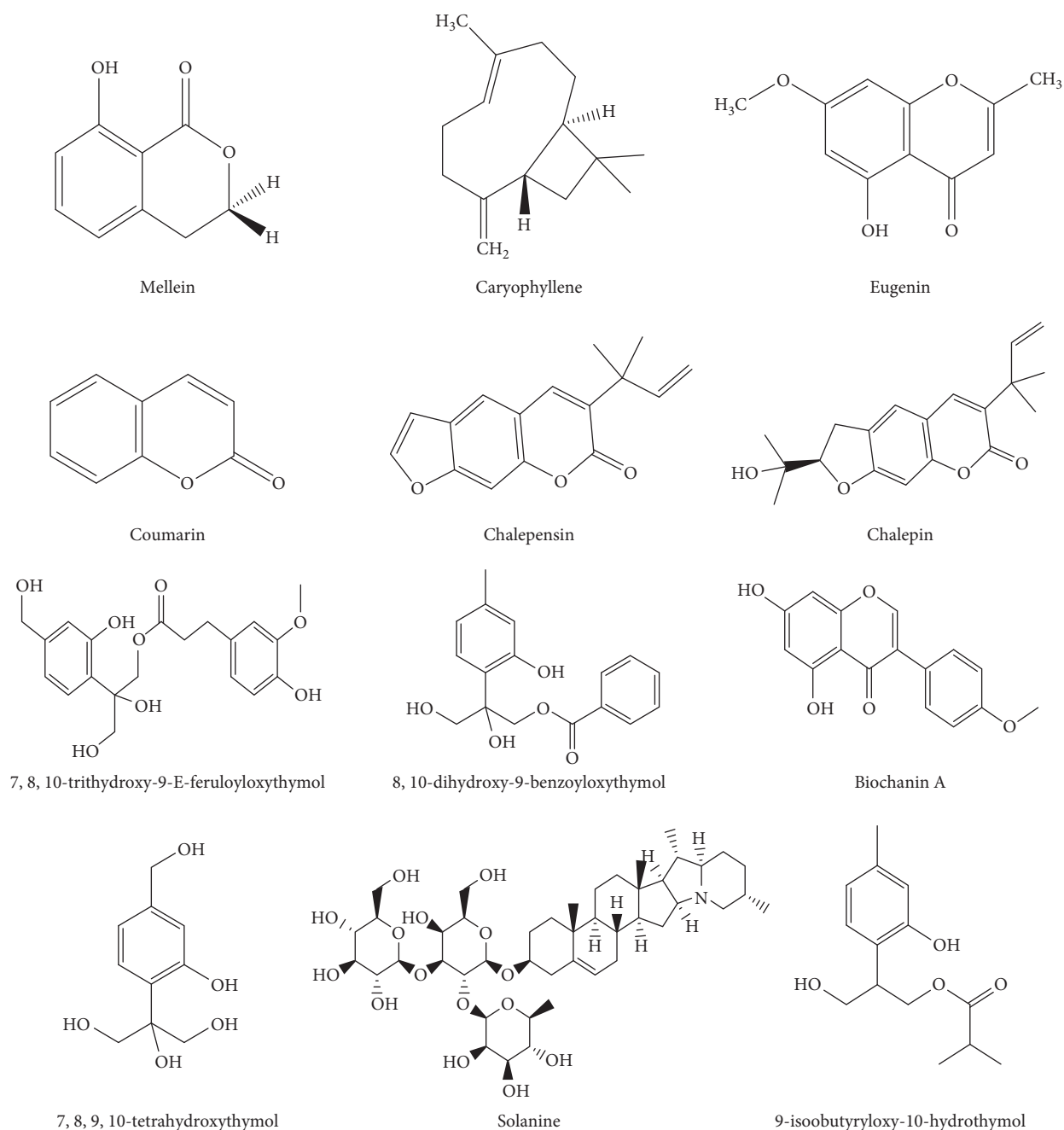


FIGURE 1: Relevant natural herbicidal molecules.

Sitophilus zeamai [122], cotton aphid, flea beetle, spotted bollworm, and whitefly [123]. Furanocoumarins were identified in *C. lenis* extract, which possesses insecticidal [112], phytotoxic [91], and antiproliferative [124] properties. Similarly, the active ingredient in citrus essential oil, “D-limonene”, increased the mortality rate of the three species of vineyard mealybugs [115], while bis(2-ethylhexyl) benzene-1, 2-di-carboxylate in ethyl acetate fraction of the *Tetraena mongolica* stem had a strong larvicidal activity on *Pieris rapae* larvae (cabbage white) [125]. Studies showed that bruchid-resistant cowpea cultivar powders were successfully used to protect harvested cowpea seeds from insects

such as *Callosobruchus maculatus* [126]. Generally, polar and nonpolar extracts from *C. citrinus* leaves and *P. americana* fruits owe their antibacterial, antimalarial, anti-diabetic, anti-inflammatory, antiviral, anticancer, anti-asthma, antifungal, larvicidal, and insecticidal activity to phytochemicals such as alkaloids, flavonoids, tannins, triterpenoids, saponins, polyphenolic (catechins and trans-3-O-caffeoylquinic acid), and unsaturated steroids [42, 113, 127, 128]. Furthermore, aqueous seed extracts from *A. indica*, *S. molle*, and *P. dodecandra* were most active against fall armyworm (FAW) larvae of maize [43]. Most synthetic insecticides have developed resistance to FAW,

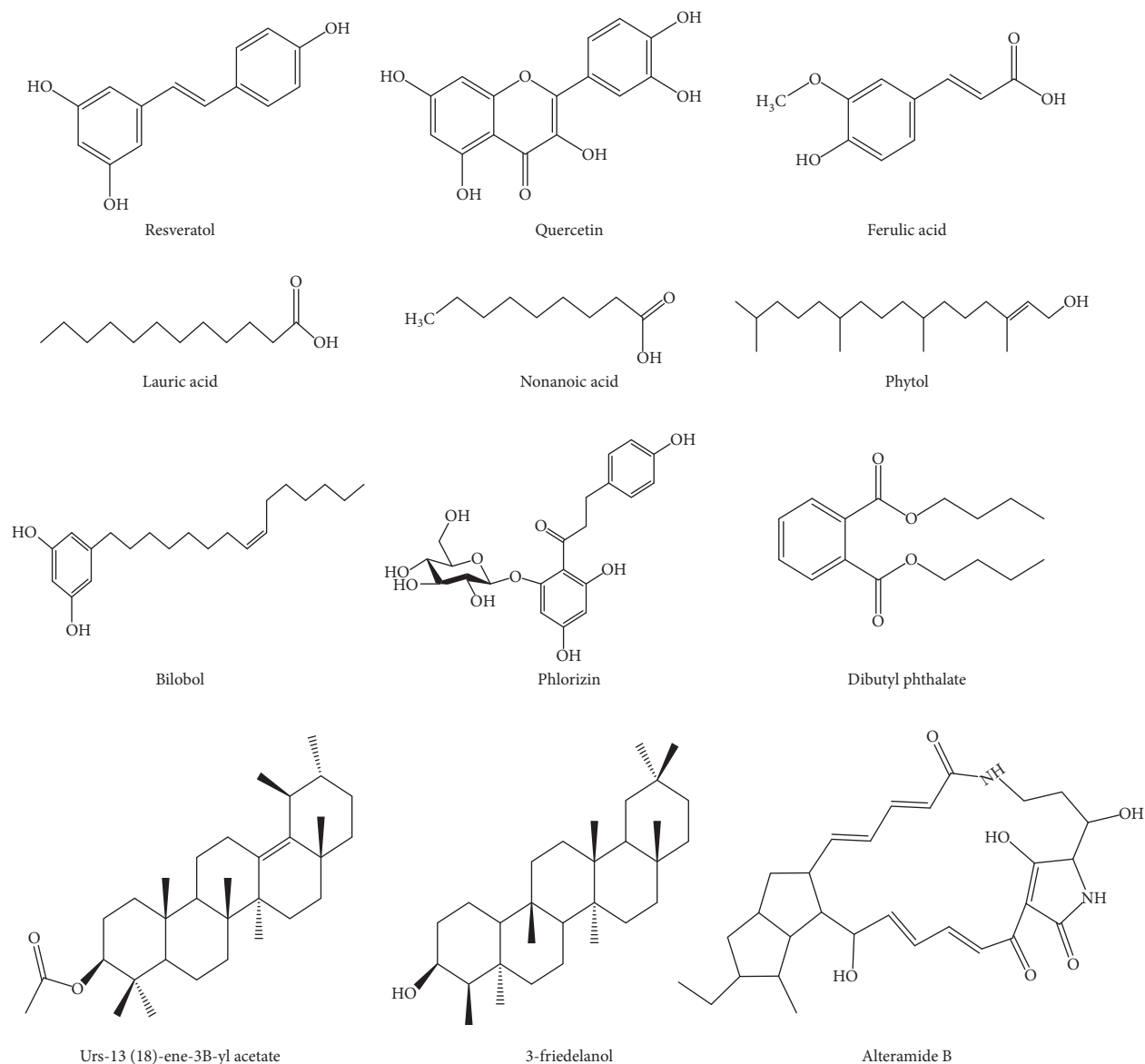


FIGURE 2: Relevant natural fungicidal molecules.

which necessitated the search for natural botanicals [129]. In summary, the use of seed extracts is more prominent alongside the use of other plant parts for their insecticidal activity. However, this is a subject for future investigation.

Furthermore, certain microbes have also demonstrated insecticidal potential in recent times. An emulsifiable concentrate of fungus *Metarhizium rileyi* was successfully used to control the infestation of maize by fall armyworm [130]. Similarly, entomopathogenic fungus, *Beauveria bassiana*, was able to significantly increase the mortality rate of both nymphs and adult forms of tomato/potato psyllid. If not controlled, this tomato/potato psyllid affects bell pepper, eggplant, potato, and tomato, while secondary metabolites such as oosporeins, bassiacridin, and bassianin were responsible for the high mortality rate [131, 132]. In the same vein, methanol extracts from *Cladosporium cladosporioides* and *Purpureocillium lilacinum* have been used to effectively control the population growth of *Aphis gossypii* and cotton

aphid. The major constituents in the extracts were identified as linoleic acid and palmitic acid [133]. Another example is *Metarhizium anisopliae*, which caused 98% and 87.1% mortality effect in two-spotted spider mites (*Tetranychus urticae* and *Tetranychus cinnabarinus*), respectively [134]. Entomopathogenic bacterium, *Bacillus thuringiensis*, exhibited insecticidal activity against *Plutella xylostella* larvae (diamondback moth) and also protects *Brassica campestris* (field mustard) from sclerotiniosis [135]. Relevant structures of some insecticidal compounds are shown in Figure 3.

2.3.4. Natural Products as Virucides. Several studies have shown that there are thousands of plant viruses, but the available treatment is not sufficient in eradicating these infections. This has led to a continuous search for sustainable alternatives. Interestingly, some plants naturally resist virus

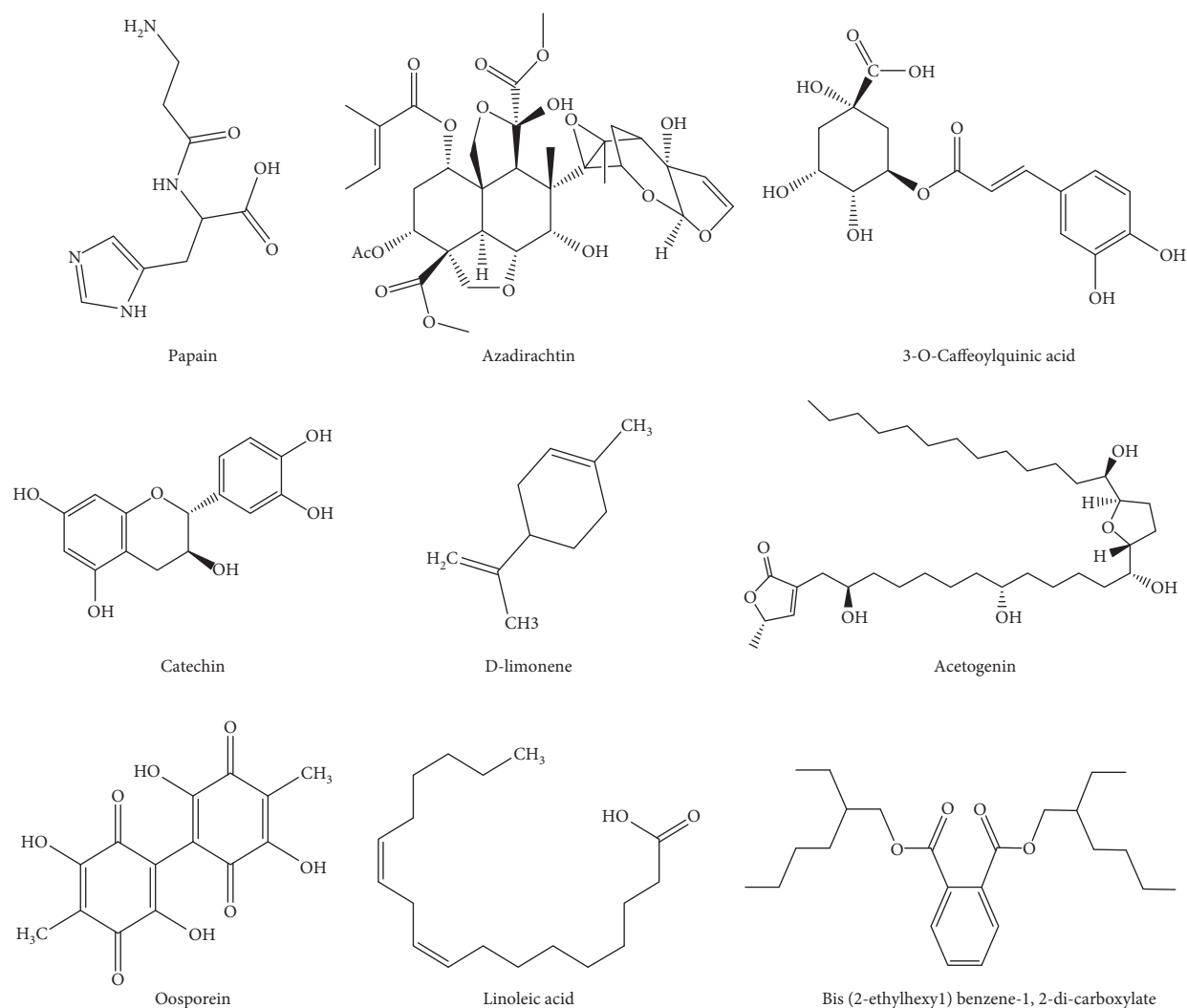


FIGURE 3: Natural insecticidal molecules.

replication in their cells, while some natural extracts resist virus replication when applied to other plants [47]. A rich review has been carried out on the use of antiviral agents from natural sources against the tobacco mosaic virus (TMV), which is common among tobacco, cucumber, pepper, and ornamentals [51]. Some of these botanicals include *Picrasma quassioides* [136], *Glycyrrhiza glabra* L. [137], *Arundina graminifolia* [138], *Tithonia diversifolia* [139], *Cephalotaxus sinensis* [140], *Actinidia chinensis* [141], and prickly pear [142]. Similarly, *Salix alba* [48], *Tanacetum vulgare* [143], *C. sinensis* [140], prickly pear [144], and *A. chinensis* [141] showed an antiviral activity against cucumber mosaic virus (CMV) isolated from cucumber and watermelon. *Strophanthus speciosus* and *T. vulgare* were also effective against potato virus Y (PVY) in tobacco and tomato plants, respectively [143, 145]. *Thuja orientalis* extract was effective against eggplant blister mottled virus (EBMV) isolated from eggplant [146], fig leaf mottle-associated virus-1 (FLMaV-1) was identified in fig trees [147], and watermelon mosaic potyvirus (WMV) and zucchini yellow mosaic virus (ZYMV) were common to watermelon [148, 149]. Prickly pear has also

exhibited a notable antiviral activity against zucchini yellow mosaic virus (ZYMV) and squash mosaic virus (SqMV) isolated from zucchini (*Cucurbita pepo* L.) [142].

Different classes of phytochemicals have been implicated in the foregoing antiviral activities of plant extracts. These include alkaloids, coumarins, flavonoids, phenolics, and terpenoids amongst others. Alkaloids: 1-methoxycarbonyl- β -carboline from methanolic extract of *P. quassioides* wood [136], drupacine and cephalotaxine from methanolic extract of *C. sinensis* leaves and branches [140], Opuntin B from aqueous extract of prickly pear cladode [142, 144]; flavonoids: Liquiritin from methanolic extract of *G. glabra* root [137, 150]; phenolics: gramniphénol C from a chromatographic fraction of *A. graminifolia* whole plant extract [138] and salicylic acid from aqueous extract of *S. alba* leaves and bark [48]; terpenoids: 1 β -methoxydiversifolin-3-0-methyl ether and tagitinin C isolated from methanol extract of *T. diversifolia* whole plant part [139], rhodoxanthin from ethanol extract of *T. orientalis* leaves and fruits [151, 152], spathodic acid-28-O- β -D-glucopyranoside and 5-methoxycoumarin-7-O- β -D-glycosidase (coumarin) from ethyl

acetate extract of *A. chinensis* root bark [141]; and a variety of phytochemicals have been detected in methanol extract from *T. vulgare* flower [143] and ethanol extracts of *S. speciosus* leaves and fruits [145].

The use of microbes as effective producers of antiviral agents has also been exploited in the eradication of plant viruses. An example is the application of *Bacillus amyloliquefaciens* in the treatment of tobacco streak virus (TSV) in cotton plants [153] and broad bean wilt virus (BBWV), pepper mild mottle virus (PMMoV), and CMV in pepper [154]. Similarly, polysaccharides extract from *Penicillium chrysogenum* successfully inhibited the spread of TMV. In the same vein, secondary metabolites were isolated from *Brucea javanica*, namely brucein B and bruceantinol, had the highest inhibitory activity against pepper mottle virus (PepMoV) [155]; ningnanmycin, the first antiviral agent to be isolated from *Streptomyces noursei* var-*xichangensis*, showed a notable activity against TMV [156]; an active constituent in *Streptomyces hygroscopicus*-cytosinpeptidomycin exhibited a potent antiviral activity against southern rice black-streaked dwarf virus (SRBSDV) and TMV [154, 157]. Figure 4 presents a summary of relevant virucidal molecules.

3. Food Preservation: An Overview of Current Methods

The need to maintain dietary value, composition, flavor, colour, pH, and texture of a particular food product over long time is the reason behind food preservation [24, 158]. Spoilage in food is attributed to activities of microorganisms, which cause food degradation and oxidation, which leads to rancidity and browning of food. The ripening process which is caused by enzymes present after harvesting or slaughtering (in the case of animals) is the third cause of food spoilage. Several techniques have been employed in handling and conserving food to reduce wastage [24]. The different farm products such as meat, fish, fruits, vegetables, roots, and tubers are not preserved in the same way since they are of different composition. In food preservation, physical processes such as salting, drying, and boiling are employed, while chemical processes involve the use of different types of chemicals [158, 159]. Historically, approaches such as bagging, cooling, curing, drying, fermentation, heating, jelling, salting, and smoking were employed. However, in recent times, modern industrial techniques such as freeze-drying, pasteurization, irradiation, vacuum packing, artificial food additive, and high-pressure food preservation are in vogue [24]. Generally, some microorganisms are harmful, while others are beneficial. The beneficial ones have been intentionally employed in the preservation of food products [160, 161]. Drying and smoking involve the removal of water from the farm produce, thereby reducing the possibility of spoilage. Techniques such as sun drying, oven drying, roller drying, vacuum drying, spray drying, tunnel drying, and freeze-drying can be explored [24, 162]. Irradiation combines sterilizing and drying of products such as fruits and vegetables to meet quarantine requirements for export. However, this process is not widely accepted by consumers due to uncertainties about health safety associated with the

technology [24, 163, 164]. Majorly preservatives can be classified as antimicrobials or antioxidants preservatives. Antimicrobial preservatives inhibit the growth of spoilage organisms, which could be bacteria, fungi, or yeast. Examples include sodium benzoate, sodium nitrate, and potassium sorbate [165]. On the other hand, antioxidant preservatives hinder or slow down oxidation processes or inhibit factors that cause ripening/browning of farm produce after harvest. Examples include sodium succinate and ascorbic acid [19, 165].

3.1. Pitfalls of Current Methods in Food Preservation. The pitfalls observed in the current methods of preservation include a reduction in nutritional quality, unpleasant side effects, and diseases such as cancer in extreme cases. Prolonged drying/smoking and irradiation lead to loss of colour, flavor, aroma, texture, and vitamins [24, 163, 166], while the use of sulfites in fruits have resulted in side effects such as headaches and allergies. Unexpected chemical interactions also occur between certain preservatives. For instance, sodium benzoate and ascorbic acid interact to produce carcinogens, thereby causing life-threatening diseases [158, 167, 168]. Similarly, nitrites and nitrate mostly which are used in meat product undergoes some reactions when consumed and turn into nitrous acid, which results in stomach cancer, brain tumors, and leukemia [169]. Studies on fermented and nonfermented soy foods revealed that the risk of gastric cancer development was associated with high consumption of fermented soy foods, while the high consumption rate of nonfermented soy foods reduced the risk of gastric cancer [170, 171]. A summary of the negative effects of the current methods used in food preservation is shown in Table 3.

3.2. Application of Natural Products in Food Preservation and Their Advantages. The nature of food usually determines the kind of preservative to be employed [18]. Antioxidant preservatives are applied to oily food, while antimicrobial preservatives are applied to food containing an appreciable amount of water. However, both preservatives are required for food containing both oil and water, e.g., bread and sausages [174, 175]. While antimicrobial agents inhibit the growth of microorganisms, and antioxidants hinder unwanted oxidation of oily content in food [18]. Examples of such natural antimicrobial preservatives are tea tree oil, turmeric oil, lemon balm extract, and neem oil, while ascorbic acid, tocopherols, and rosemary oil are popular examples of antioxidants preservatives [19, 20, 175].

3.2.1. Antimicrobial Preservatives. Several plant extracts have been investigated for their ability to serve as preservatives agents against foodborne pathogens. Recently, the antibacterial activity of pure compounds isolated from plant extracts has been reported. The potency of stigmaterol, an isolate of ethyl acetate fraction of *Congea tomentosa* stem against the growth of *Aspergillus flavus*, *Aspergillus niger*, *Bacillus subtilis*, *Escherichia coli*,

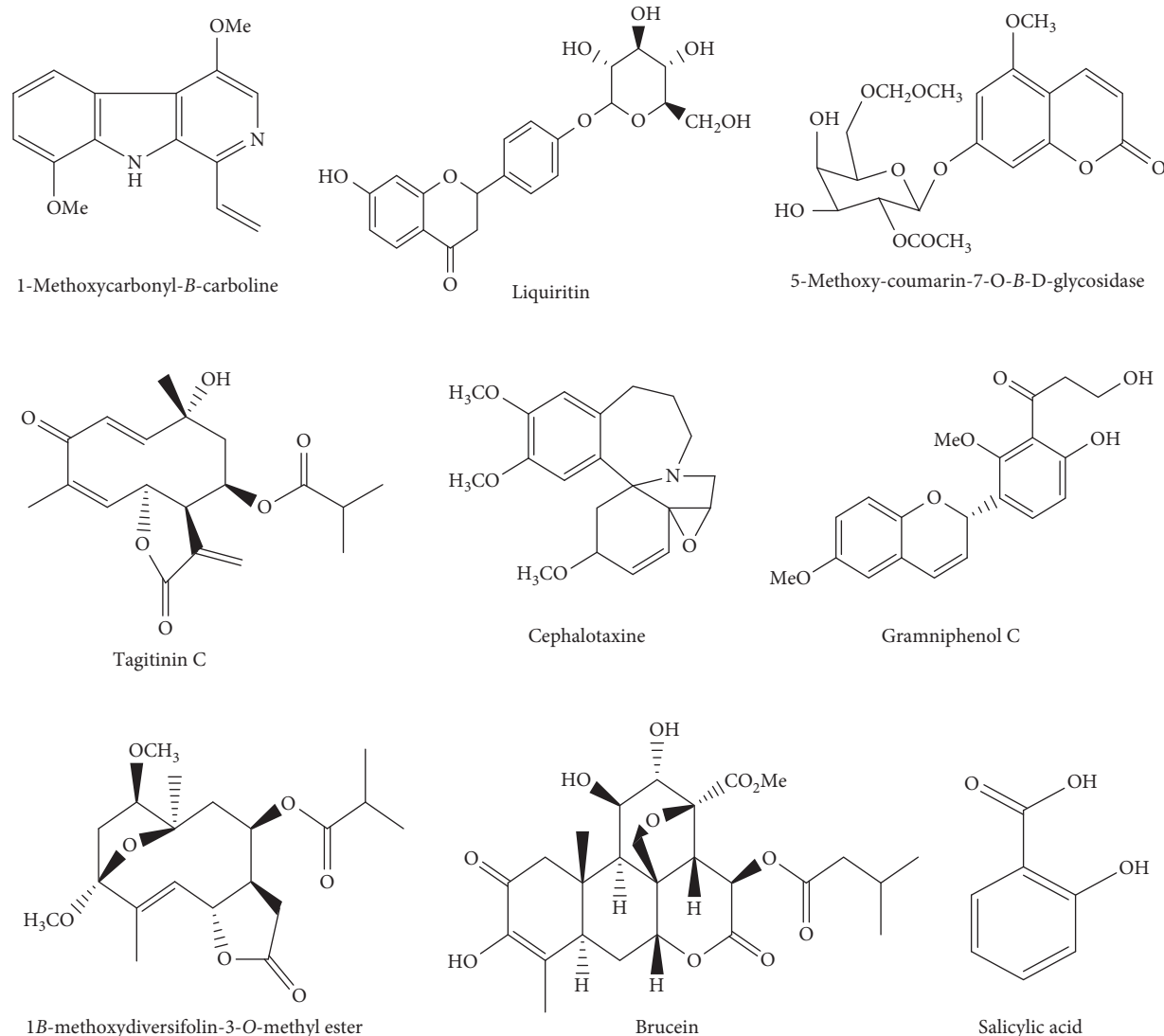


FIGURE 4: Natural virucidal molecules.

TABLE 3: Pitfalls of the current methods in food preservation.

Methods	Examples of food preserved	Disadvantages	References
Drying, smoking, freezing irradiation, boiling	Fish, tobacco leaves, and various products	After a long period time, the food starts losing its colour, flavor, aroma, and vitamins	[24, 162, 163]
Fermentation	Dairy products and wine	Increased risk of gastric cancer	[170, 171]
Salting	Meat and fish products	When in excess, it causes high blood pressure and kidney stone	[158, 172]
Artificial food additives, e.g., sodium bisulfite,	Fruits, vegetables	They cause side reactions such as headaches and allergies	[166]
Sodium benzoate	Carbonated drinks, fruit juice, and pickles	Hyperactivity, leukemia, and other cancers	[158]
Potassium sorbate	Flavoured drinks, fine bakery wares, bread, and rolls	Not yet established	[173]
Nitrite or nitrate	Meat products	Suspected to cause stomach cancer, brain tumors, and leukemia	[169]

Penicillium digitatum, and *Serratia liquefaciens*, has been reported [176]. Similarly, dalpanitin and vicenin-3 isolated from ethyl acetate fraction of *Derris scandens* leaves

effectively inhibited the growth of *Staphylococcus aureus*, *Bacillus cereus*, *Pseudomonas aeruginosa*, and *E. coli* [177].

Second, several extracts have been proven as potent against the activity of *S. aureus* isolates and their resistant strains (MRSA), *P. aeruginosa*, *E. coli*, *Listeria monocytogenes*, *Salmonella typhimurium*, *Bacillus subtilis*, *Proteus mirabilis*, *Klebsiella* sp, *Salmonella typhi*, *Enterobacteriaceae*, *A. niger*, *A. flavus*, *Candida albicans*, *Penicillium notatum*, and *Rhizopus microspores*. Examples of such botanical extracts include extracts from *Cymbopogon citratus* leaves [178], *Garcinia brasiliensis* leaves [179], *Lepechinia meyenii* leaves [180], cranberry pomace [181], *Persea americana* seeds [182], *Siegesbeckia orientalis* L. whole plant part [183], *Chrysophyllum albidum* seeds [184], *Ferula caspica* aerial parts [185], *Azadirachta indica* leaves [116, 186], red prickly pear fruit [187], and *Citrus aurantium* L. flower [188]. Also, essential oil from leaves, stem, fruit peels, cloves, flowers, rhizomes, and seeds of several plants such as *Hymenaea cangaceira* leaves [189], *Vitex gardneriana* leaves [190], *Dalbergia pinnata* stem [191], *Citrus* sp. fruit peels [192, 193], *Allium sativum* cloves, and *Sesamum indicum* L. seeds [194] showed antibacterial activities.

Although the active antimicrobial agents in these natural sources were not isolated before use, the activity of the extracts is a result of the inherent phytochemicals, which may be working together in synergy. The antimicrobial, antioxidant, and cytotoxic properties of the extracts have been attributed to phytochemicals such as citral, aspilactonol B, and 8-methyl-6-prenylquercetin (found in *C. citratus*) [178], fukugetin and fukugiside (found in *G. brasiliensis*) [179], carnosic acid, carnosol, and rosmanol (found in *L. meyenii*) [180], and morin, myricetin, and rhamnetin (found in Cranberry) [181], while a wide range of phytochemicals such as alkaloids, cyanogenic glycosides, flavonoids, phenols, saponins, and tannins was found in *P. Americana* seed extract [182]. In the same vein, the ethyl acetate fraction of *S. orientalis* contained compounds such as 16 β , 17, 18-trihydroxy-ent-kauran-19-oic acid, 16 β -hydro-ent-kauran-17, 19-dioic acid, 16 α , 17-dihydroxy-ent-kauran-19-oic acid, and 17, 18-dihydroxy-ent-kauran-19-oic acid [183], germacrene D, (E)-caryophyllene, α -guaiene, and β -elemene (found in *H. cangaceira*) [189], caryophyllene oxide, 6,9-guaiadiene, and cis-calamenene (found in *V. gardneriana*) [190], elemicin, methyl eugenol, and 4-allyl-2,6-dimethoxyphenol (found in *D. pinnata*) [191], and limonene (found in citrus oil) [192].

Some food products require preservatives because they are fragile and more susceptible to spoilage caused by microorganisms. Tomato fruit, an important example, was preserved using aqueous extracts of *Moringa oleifera* seed; the extract successfully inhibited three species of bacteria and five species of fungi [195]. Similarly, aqueous extracts from *Carica papaya* seed and *Xylopi aethiopia* pod elongated the shelf life of tomatoes and pepper [196]. Additionally, the ethanolic extract of *Lippia citriodora* leaves sufficiently prolonged the shelf life of strawberry fruit [197]. Studies by Choi et al. established the efficacy of aqueous extract from *Camellia sinensis* (L.) seed as a natural preservative in soy sauce and inhibited the growth of *C. albicans* and *Zygosaccharomyces rouxii* [198]. Another

good example is rice puddings, a type of dairy product that was preserved using the methanolic extract of *Citrus aurantium* L. flower [188]. Fruit and vegetable smoothies are enriched with nutrients and vitamins but have a short life span. To prolong their shelf life, hydroethanolic extracts from *Beta vulgaris* L. (beet) leaves and stem, which also exerted inhibitory properties against the growth of *Listeria innocua*, *Saccharomyces cerevisiae*, and *E. coli* [199], were required.

The foregoing extracts exhibited both antimicrobial/antioxidant properties due to the presence of certain alkaloids and carpine in *C. papaya* [200]; eugenol, sarbiene, benzoic acid, and camphor in *X. aethiopia* [201]; assamsaponin A, assamsaponin B, and heasaponin E1 in *C. sinensis* [198]; quinic acid, linoleic acid methyl ester, and pentadecanoic acid in *C. aurantium* [188]; and vitexin-2-O-rhamnoside and vitexin-2-O-xyloside in *B. vulgaris* [199]. Also, salmon fish was preserved using aminoethyl-phloretin (AEP), a phloretin derivative from a flavonoid (phloretin) extracted from apples and 2-bromine ethylamine [202]. Furthermore, in a bit to establish the efficacy of the natural extracts as preservatives, Soumya et al., compared natural extracts from lemongrass (LG), clove, and cinnamon (CC) leaves with a synthetic antimicrobial preservative (calcium propionate). The synthetic and natural preservatives were incorporated in muffin batter and both LG and CC elongated the shelf life from 16 to 24 days [203]. Furthermore, Ribeiro et al. investigated the activity of *Artemisia dracuncululus* (Tarragon) as a preservative for pizza dough. Antitumor and antimicrobial activities were observed in addition to the antioxidant activity of *A. dracuncululus* extract. Hence, the use of *A. dracuncululus* extract as a preservative is more beneficial than the use of ascorbic acid, since it would not require an additional (antimicrobial) preservative [204]. Hence, employing certain natural preservatives comes with additional benefits such as nutritional and medicinal fortification.

Apart from the use of plant extracts and phytochemicals, microbes have found increasing applications in the food industry. An active compound reuteri was isolated and purified from *Lactobacillus reuteri*, a probiotic microbe, and was used to inhibit the growth of food pathogens such as *L. monocytogenes*, *Salmonella* spp., and *E. coli* [205]. Also, a strain of *Lactobacillus plantarum* significantly inhibited the growth of food pathogens such as *Aspergillus flavus*, *Aspergillus parasiticus*, and *Penicillium expansum* in fresh cheese [206, 207]. Similarly, chitosan from *Aspergillus brasiliensis* was used in preserving and enhancing the quality of fish sausage, and it also has a complementary antimicrobial activity against yeast and molds, *E. coli*, *Enterobacteriaceae*, and *S. aureus* [208]. Furthermore, a strain of *Enterococcus mundtii* coupled with chitosan and sodium lactate remarkably inhibited the growth of *Listeria innocua*, *Shewanella putrefaciens*, and psychrophilic flora in fish [209]. Besides the use of plants, microbes have been employed as sources of preservative because they are easy to produce and generally nontoxic. The structures of these antimicrobial preservatives compounds are shown in Figure 5.

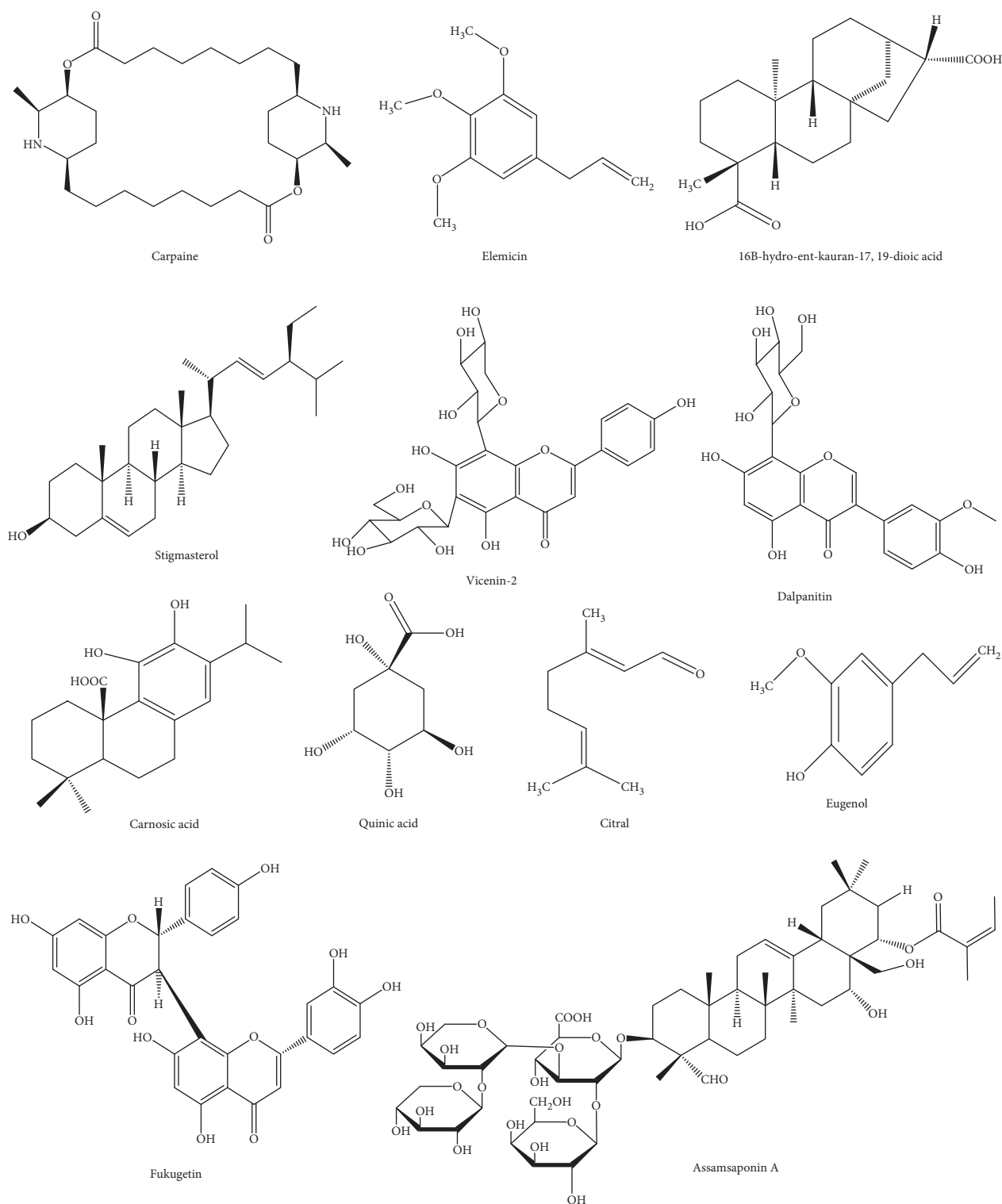


FIGURE 5: Natural antimicrobial-preservative molecules.

(1) *Mechanism of Action.* Studies have shown that different phytochemicals exhibit different biological activity based on substituent groups within their chemical structure. Generally, different ways through which antimicrobial agents exert their activity include inhibition of nucleic acid synthesis, inhibition of cytoplasmic membrane function, inhibition of

energy metabolism, bacterial toxin production, and biofilm formation [210, 211].

Polyphenols make use of their hydroxyl group to attack the phospholipid bilayer of bacterial cell membranes, disrupting enzyme systems, which result in a limited supply of essential iron required for the growth of the microbes

[212–214]. They also exert their activity via prooxidant damages to the cell membrane. For example, cinnamic acid ester and 3-p-trans-coumaroyl-2-hydroxyquinic acid (CHQA) disrupts the bacterial cytoplasmic membrane and interactions with membrane proteins and lipids. Also, CHQA inhibits DNA synthesis of the bacteria through the groove binding mode and reduces intracellular ATP [215–217]. Syringic acid, (+)-catechin, and vanillic acid function by inhibiting the formation of biofilm [218], while quercetin acts by inhibiting DNA gyrase. However, the presence of the hydroxyl group at C-5 in ring A, at C-4 in ring B, and the methoxyl group at C-3 and C-8 in the A ring increases the inhibition [210].

Phytosterols such as stigmasterol have been known to mimic endogenous sterols based on their structural similarity. This gives them the ability to replace the hormone, thus disrupting the cell membrane. In the same vein, certain steroids suppress the ability of certain microbes to resist antibiotics by disrupting the multiple drug efflux pump proteins in multidrug-resistant microbes [176, 219]. The presence of vinyl and peroxide moiety in steroids leads to an enhanced antibacterial activity [176, 220]. A different mechanism of action has been observed for different types of alkaloids. An example is isoquinoline alkaloids, which act by inhibiting type I topoisomerases. Indolizidine and isoquinoline alkaloids exert their activity via the inhibition of nucleic acid synthesis, while polyamine alkaloids act by affecting the outer and cytoplasmic membranes [221]. Also, some evidence show that saponins owe their antimicrobial activity to the alteration of cell wall permeability [222, 223].

Furthermore, a variety of plant extracts have been found to successfully inhibit biofilm formation from various microbes mentioned earlier; such extracts which can be used as preventive coatings include *V. gardneriana* leaves [190], the aqueous extract of black grape residue [218], ethyl acetate fraction of *Orostachys aponicas* [224], methanol extract of *Zingiber officinale*, chloroform extract of *Myristica fragrans* [225], ethanol extract of *Fraxinus angustifolia* leaves and barks [226], and cardamom essential oil [227], while isolates such as (+)-nootkatone from the essential oil of grapefruit [228], and pulverulentone A from methylene chloride-methanol fraction (MME) of *Callistemon citrinus* leaves [229] can be used as a good alternative for preventing biofilm formation.

3.2.2. Antioxidants Preservatives. Natural extracts with antioxidant capacity have been employed in different food products ranging from meat, fruits, yogurt, and biscuits. Apart from microbial suppression/elimination, parameters that are used to assess the efficacy of preservatives include antioxidant capacity, external appearance, nutritional profile, pH, and individual fatty acids. Various crude extracts have been applied to some of these examples. In meat preservation, extracts from *C. citratus* effectively increased the shelf life and improved the quality of chicken sausage [178], while ethanol extract from cranberry pomace and methanol extract from citrus coated on polyethylene terephthalate (PET) trays inhibited lipid oxidation in pork and

cooked Turkey meat, respectively [181, 230]. Also, Tayengwa et al. incorporated extracts from grape pomace (GP) and citrus pulp (CP) into diets of steers, and results showed that diets with GP extract extended the shelf life of the beef after slaughtering compared to CP extracts [212]. Similarly, studies showed that extracts from *Terminalia arjuna* bark [231], red prickly pear fruit [187], and *Cucumis melo* L. seeds [232] were successfully employed to elongate the shelf life of beef. Phytochemicals such as alkaloids, coumarins, flavonoids, tannins, and terpenoids were identified in hydroalcoholic extracts of *C. citratus* leaves [178] and extracts from *T. arjuna* bark, fruits, stem, and leaves [233], while fifteen phenolic compounds including naringenin-7-O-glycoside, gallic acid, vanillic acid, and 4-hydroxybenzoic acid were identified in *C. melo* L. seeds [232]. These extracts contribute to nutritional, organoleptic, anticancer, anti-inflammatory, antimutagenic, antimicrobial, and antioxidant properties of foods to which they are applied [234–236]. In a related development, *Aloe vera* gel was utilized as a fruit coating in the preservation of *C. papaya*, raspberry, and *Manilkara zapota* L. fruit. *A. vera* gel reduced weight loss, suppressed fungal growth, maintained a high level of antioxidant capacity, and other parameters in the coated fruit during storage [237–239].

Similarly, a natural pigment found in tomatoes, “anthocyanin,” whose production is usually enhanced by contaminations from pathogens and stress conditions were augmented in purple tomatoes to slow down ripening and vulnerability to *Botrytis cinerea* [240, 241]. Apart from this application, anthocyanin is a good antioxidant agent, which protects against chronic human disorders, cardiovascular diseases, and certain cancers [242, 243]. Lemongrass can be applied either as an antioxidant or antimicrobial preservative agent. It was recently incorporated into herbal cookies to produce a variety that was not only nutritious but also possessed antioxidant, anticancer, anti-inflammation, and antidiabetic properties [21]. Also, *Cucumis melo* L. seeds powder was incorporated into bakery products to improve their functionality [232]. The chloroform and ethyl acetate extract of *Ferula caspica* aerial parts displayed a reasonable antimicrobial/antioxidant activity due to the presence of sesquiterpene derivatives, phenylpropanoid (laserine/2-epilaserine), steroid, flavonoids, and a benzoic acid derivative [185]. Based on the fact that potato could recover from wounds by healing itself, its peel has proven to be a bio-resource with great antioxidant [244]. The compounds which are produced when a potato is wounded include feruloyl quinic acid, ferulic acid, iso-feruloylputrescine, and coumaroylputrescine [245]. Decoctions from *Matricaria recutita* L. (chamomile) and *Foeniculum vulgare* Mill. (Fennel) leaves have been applied in the preservation of yogurt and biscuit. The chamomile decoction presented a higher antioxidant activity than potassium sorbate (E202) as shown by the observed parameters [246, 247]. The structures of these antioxidant compounds are shown in Figure 6.

(1) Mechanism of Action. Antioxidants are known to reduce oxidative stress by providing the stability required in biologically generated free radicals. Different phytochemicals

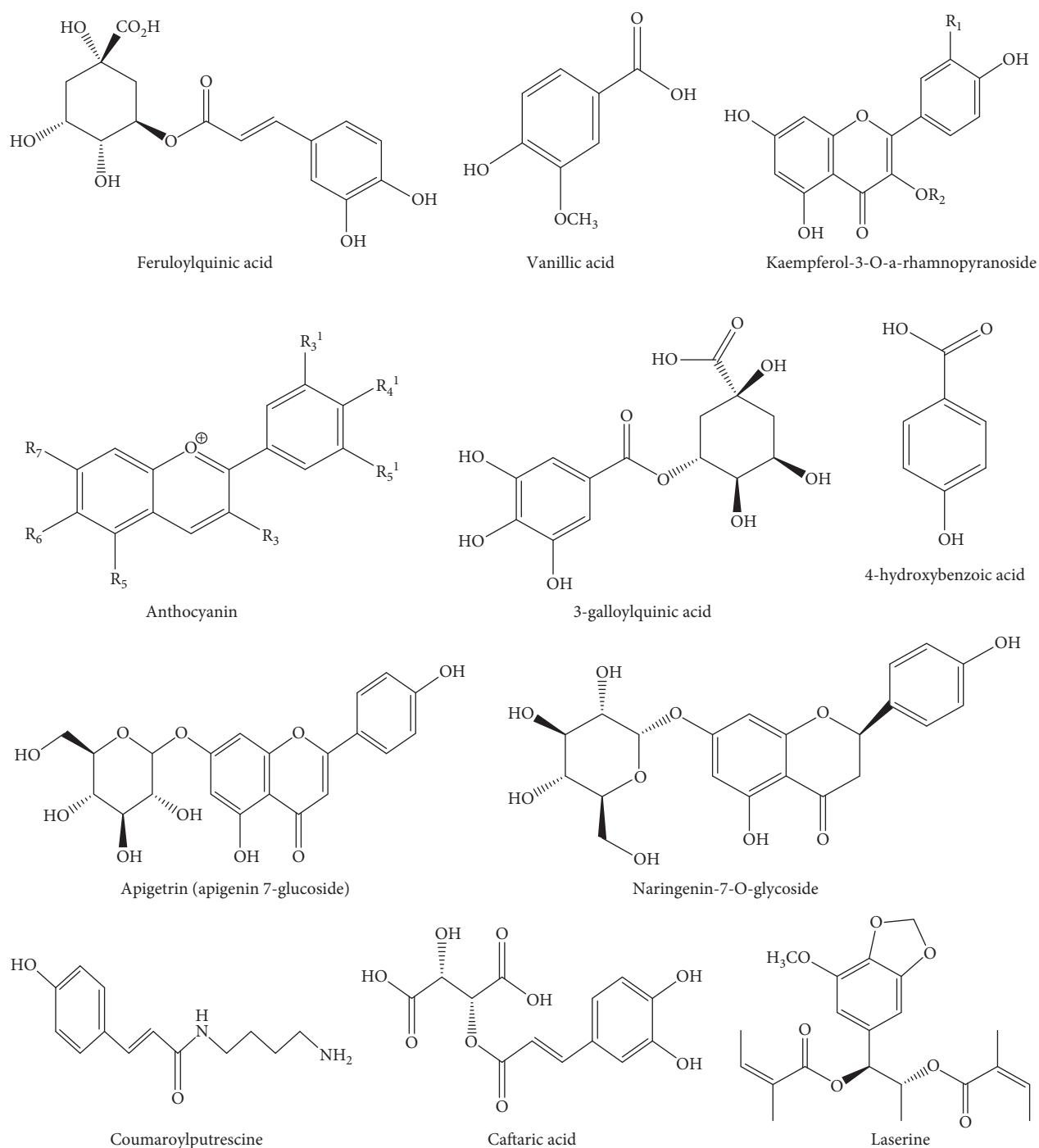


FIGURE 6: Natural antioxidant-preservative molecules.

have been found to exert their antioxidant activity through pathways such as reactive species scavenging (free radicals, nonradicals, and transition metals), chelating effect, binding effect, and inhibition of lipoxygenase [248–250]. Typical examples are polyphenols such as flavonoid and phenolic compounds, which have a good antioxidant capacity and inhibit oxidative processes by either acting as a reactive species scavenger [183, 237, 251], lipoxygenase inhibitor [212, 231, 252], or as reducing agents for metmyoglobin [178, 187]. Salicylic acid acts by stimulating enzymes, such as

superoxide dismutase, catalase, and peroxidase, while citric acid inhibits oxidative processes by binding to metals using its hydroxyl and carboxyl moiety [230]. Generally, alkaloids interact with reactive species by trapping them with hydroxyl groups in their structure, while their chelating effect on ferrous ions can be attributed to the presence of nitrogen moiety [253]. Particularly, indole, isoquinoline, isosteroid, and nicotine alkaloids act by scavenging free radicals and by reducing iron and molybdate [254–257]. Terpenoids reportedly exert their activity by inhibiting lipid oxidation and

reducing oxidative stress [258]. Although not as much as other phytochemicals, saponins from different plant extracts have also been found to inhibit the formation of reactive oxygenated species [259–261].

3.3. Challenges Associated with the Use of Natural Extracts in Food Preservation. The benefits associated with the use of natural extract cannot be overestimated. However, some demerits are involved in the use of botanicals for food preservation.

3.3.1. Poor Thermal Stability. During extraction, the use of hot extraction techniques is expected to facilitate extracts production. However, this leads to thermal decomposition of vital phytochemicals responsible for the antimicrobial activity and antioxidant activity, thus rendering the extract impotent and forcing industrialists to source for sustainable alternatives [262–264]. These explain the fact that not all techniques are appropriate for the extraction of certain compounds. Studies have shown that thermo-labile components decompose or become unstable at high temperatures [265, 266]. Flavanol and anthocyanins, for example, are affected by high temperatures [265]. Consequently, green techniques such as ultrasonic-assisted extraction, pressurized liquid extraction, natural deep eutectic solvent, and supercritical fluid extraction are suitable for extracting alkaloids, phenolic compounds, flavonoids, essential oils, terpenoids, saponins, and lipids in high yield [266–270]. Factors such as temperature, light, oxygen, and pH, which affect the activity of various compounds, should be considered when choosing a particular technique for extraction.

3.3.2. Toxicity Effect of Unrefined Crude Extracts. Most crude extracts obtained from plants contain a mixture of compounds, which are used directly without any further purification. Thus, the active compounds are not separated from the inactive/toxic ones, which are responsible for crude extract toxicity [271, 272]. Hence, isolation of the active compounds which exert the antimicrobial/antioxidant activity helps to eradicate the toxic compounds, which are not needed in such therapeutic mixtures. Though the process of fractionating and isolating these bioactive compounds are often expensive, energy, and time consuming [273]; bio-assay-guided fractionation of active compound is advised to reduce the complication that might arise [176, 177, 198, 213].

3.3.3. Low Yield of Pure Compounds. After extraction, quantification of the resulting natural product isolates usually reveals a low percentage yield. Hence, synthesizing these components becomes crucial. During synthesis, the stereochemistry of the compounds to be synthesized is very important because a wrong configuration can give rise to unsolicited outcomes. Apart from synthesizing natural products, there are various avenues via which the yield of natural products can be enhanced. Chromatographic methods such as countercurrent chromatography can give a reasonable amount of bioactive compounds [274].

Furthermore, via gene expression, the percentage presence of certain phytochemicals could be boosted to afford an increase in the percentage yield of the compound of our interest. Overexpressing certain genes in plants such as α -amyrin synthase in *Ipomoea batatas Lam* can give rise to increased yield of urs-13(18)-ene-3 β -yl acetate [98], just as glucosyltransferases, which can stimulate the production of anthocyanin diglucoside in *Solanum tuberosum* [240]. Squalene synthase in *Panax ginseng* increased the yield of triterpene saponins and phytosterols [275], while endo-protease enhanced the production of isoflavone and peptides in soy pulp by-product [276].

3.3.4. Unpleasant Effects on Sensory Properties. In addition to the foregoing, some crude extracts may sometimes have a particular odor, taste, colour, flavor, which affect the sensory properties of food even at low concentrations [203]. Many extracts have been found to rather enhance the sensory properties of the food product [187, 199, 246, 277]. However, there are a few expectations. Studies showed that extracts from goji berry by-product were used as substitutes for flour in baking cookies and muffin to different extents (0, 10, 20, 30, and 40 g/100 g). It was observed that at a substitution extent of 40 g/100g, the pastries had a bitter aftertaste and a displeasing texture, while at lower substitution rate, it gave appreciable results [278]. Similarly, the use of *O. ficus-indica* mucilage in bread production increased the antioxidant capacity of the bread. However, higher crust colour and more intense odor also accompanied the new products [279]. The chemical composition of the various extracts should be taken into consideration as different phytochemicals react differently with several food components. A proper analysis should always precede natural product applications in food preservation to avoid undesired chemical interactions' unpleasant results.

4. Plant Extracts as Feed for Silver Nanoparticle Production

Apart from the direct application of plant extracts in crop protection and food preservatives, several plant extracts, fractions, and isolates have served as reducing agents and stabilizers in the preparation of nanoparticles [280–282]. Since the advent of nanoparticles, different kinds of materials have been employed in their synthesis. Nanoparticles could be carbon-based, metal-based, lipid-based, ceramic, semiconductors, or polymeric nanoparticles [283]. Among the numerous examples of metal-based nanoparticles, silver nanoparticles (AgNPs) have received a lot of attention because of the simplicity of its synthesis and its notable antimicrobial activity [167, 284, 285]. There are two main approaches to the synthesis of nanoparticles: top-down and bottom-up. In the top-down approach, nanoparticles are synthesized from macroscopic materials. This approach is expensive, slow, and not suitable for large scale production when compared to the bottom-up approach. The top-down approach involves processes such as evaporation/condensation, laser pyrolysis, and ionic/electronic irradiation.

TABLE 4: Green synthesized silver nanoparticles from plant and their applications in crop protection and food preservation.

Plants material	Extracts	Possible applications	References
<i>Tithonia diversifolia</i> leaf	Aqueous	As an antimicrobial agent in the pharmaceutical and food industries	[293]
<i>Musa paradisiaca</i> midrib	”	Nano-ice for the preservation of fish and other food products	[297]
Oolong tea	”	As a fruit coating to preserve postharvest qualities of fruits, e.g., cherry tomatoes	[280]
<i>Melia azedarach</i> leaf	”	As an antifungal agent against <i>Verticillium dahliae</i> in eggplants and edible fruit coating to preserve	[298, 299]
<i>Zea mays</i> L. corn flour	”	For cancer treatment and radical scavenging agent	[300]
<i>Sesame cake</i> oil	”	As an antibacterial and antitumor agent	[301]
Belladonna mother tincture	”	Antimicrobial agent and anti-inflammatory agent	[302]
<i>Acalypha indica</i> leaf	”	As a fruit coating, antioxidant, and good antifungal agent.	[303]
<i>Phyllanthus emblica</i> fruit	”	As an antimicrobial agent against <i>Acidovorax oryzae</i> strain	[281]
<i>Annona reticulata</i> leaf	”	As larvicidal agent against dengue vector (<i>Aedes aegypti</i>) and antimicrobial activity	[304]
<i>Camellia sinensis</i> leaf + polyethylene glycol (PEG)	”	As an antimicrobial agent against food pathogens	[305]
Grape pomace and orange peels	”	”	[306]
<i>Persea americana</i> seeds	”	”	[307]
Cocoa pod	”	Growth enhancer for root and shoot elongation for more nutrient absorption, a good antioxidant, prolongs shelf life, high tolerance level against fungi, and nematodes	[308]
<i>Euphorbia tirucalli</i> latex	”	As nematicides against <i>Meloidogyne incognita</i> in tomatoes	[309]
<i>Suaeda maritima</i>	Ethanol	As biopesticides to fight against <i>Aedes aegypti</i> and <i>spodoptera litura</i>	[310]
<i>Lindera strychnifolia</i> roots	Aqueous and ethanol	Antioxidants wound healing and anticancer agents	[311]

Currently, the most utilized top-down approach is the photolithography, which finds application in the manufacture of computer chip-sand. However, in the “bottom-up approach,” the applied principle is different, and the nanoparticle synthesis is less expensive [286, 287]. Physical, chemical, and biological methods are utilized in the bottom-up approach. The build-up of nanostructure molecules in the physical method includes several techniques amongst which chemical vapor deposition is most popular [288, 289]. The techniques in the chemical method could be classified under the following categories: colloidal, sol-gel processing, microemulsion of oil–water, hydrothermal synthesis, polyol, sonochemical synthesis, and electrodeposition [290]. The chemical method is carried out using wet chemistry, ion implantation, and product functionalization routes. Wet chemistry routes remain the most widely explored among the chemical reduction methods used in the synthesis of silver nanoparticles, which involves the use of sodium borohydride, reducing sugars, citrate as reducing agents, silver mirror reaction, N, N-dimethylformamide (DMF), and polyol process seed-mediated growth [291–293]. Researchers, in the search of the improved method, have identified biological methods as economically friendly and environmentally benign without any reported known toxicity. The biological route mainly involves the use of microorganisms and plant extracts [294, 295]. Green synthesis of silver nanoparticles has been widely employed because it is cheaper, safer, and ecofriendly [284, 296]. Interestingly, nanoparticles usually display a higher antimicrobial activity when compared with the plant extracts, which executes the reduction of the metallic ions and serves as the capping agents. Recent and notable examples of such green synthesis and their application are captured in Table 4.

As nanoparticles application continues to expand, concerns have begun to emerge about the possible toxicity of the materials [283]. However, these nanoparticles do not pose serious threats as seen in other methods [312].

5. Conclusion

The foregoing review shows that natural product has gained reasonable ground in crop protection and food preservation. Various extracts from different plant sources execute protective and preventive properties via known classes of secondary metabolites that they contain. Several studies directly employed crude extracts, while some studies fractionated the extract into less complex forms before application. A few in-depth studies, however, isolated the active constituents, which were responsible for the activities under review. Although the active natural molecules are usually present in little quantities, they have proven to be better alternatives compared to their synthetic counterparts, which have been hitherto employed. There is a widely spread notion that natural remedies are safer than synthetic chemicals. Hence, the growing interest of scientists in authenticating the efficiency of natural products in crop protection, food preservation, and other medicinal applications. Although various crude extract have given impressive results in this direction, isolating the phytochemicals such as flavonoids, alkaloids, tannins, and saponins could provide better solutions to various agro-related challenges. This approach deserves more scientific attention in the future. An interesting development is the application of plant extract for the green synthesis of nanoparticles, which tend to proffer impressive results. Particularly, silver nanoparticles (AgNPs) have been applied in crop protection and food preservation.

However, the rising toxicity and environmental concerns about AgNPs are also worthy of further research [312]. Government policies should be put in place to encourage the commercialization of natural-based agrochemicals, and farmers should be enlightened about the benefits of these health and environment-friendly products.

Abbreviations

AHAS: Acetohydroxyacid synthase
 AR: Alkylresorcinols
 CC: Clove and cinnamon
 CMV: Cucumber mosaic virus
 EPA: Environmental Protection Agency
 FAW: Fall armyworm
 FAO: Food and Agriculture Organization
 GM: Genetically modified
 HPLC: High-performance liquid chromatography
 LG: Lemon grass
 AgNPs: Silver nanoparticles
 TMV: Tobacco mosaic virus
 WHO: World Health Organization.

Data Availability

The data used to support this review article are available in major scientific databases such as Scopus, Google scholar, PubMed, Science Direct, and other relevant sources. Keywords such as crop protection, food protection, natural products, pesticides, insecticides, herbicides, and natural food preservative will assist in obtaining these articles.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

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