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PROSPECT OF ANTIFEEDANT SECONDARY METABOLITES AS POST HARVEST MATERIAL

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Abstract: Pest control agents using plant-based material have been proposed and used as alternatives to synthetic chemicals for integrated pest management. Phytochemicals have been known to have little or no harmful effects on pose humans or the environment as they are safe and mostly biodegradable in nature. The bioactivity of plant-based compounds has been widely reported in numerous literature and is a subject that is gaining more relevance by the day. The antifeedant technique for control of post harvest pest have been studied extensively though mostly at laboratory level and only very few plant-based compounds or formulations have actually been used in agricultural post harvest processes. Plant-based antifeedants secondary metabolites are found among chemical compounds such as phenols, alkaloids, quassinoids, chromenes, saponins, polyacetylenes,, cucurbitacins, cyclopropanoid acids, terpenoids and their derivatives. This paper discusses some of these compounds and their effect against known storage pests.

Keywords: Antifeedants, Secondary metabolites, Plant species, Post harvest storage

I. INTRODUCTION

1.1 Antifeedants

Plants produce an enormous and diverse types of chemical compounds within their system but not all these compounds participate directly in the growth and development of the plant. These phytochemicals, also known as secondary metabolites are distributed largely within the plant kingdom and the plant physiological make-up. The complexity of their chemical structures and biosynthetic pathways are well noted and the phytochemicals have been investigated for their chemical properties extensively over a long period of time. The recognition of their biological properties have increased the current focus for the search of new drugs/medicines, antibiotics, insecticides, herbicides, and behavior-modifying chemicals. Literature reports have indicated that many of these compounds have important significance in protection against herbivorous nature and the phytochemical diversity of insect defenses in tropical and temperate plant families has also been significantly proven. [1]

From among these isolated plant metabolites, only a very few have been tested against a rather limited number of insect species thereby leading to the assumption that several effective compounds may still remain to be discovered. Researchers, when testing these isolated secondary metabolites or compounds from the plant extracts, use only a few or even only one species of a particular insect or pest for biological evaluation hence leading to the possibility of effective feeding deterrents to a particular insect species going undetected. A notable example is the case of a well-known antifeedant, azadirachtin, which has been tested against seven orthopterans spanning six orders of magnitude in the inter-specific differences. Compounds known as insect antifeedants usually have a more oxidized or unsaturated structure. However, molecular size and shape as well as functional group stereochemistry also affect the antifeedant activity of a molecule. Antifeedants have been found amongst all the major classes of secondary metabolites such as limonoids, quassinoids, diterpenes, sesquiterpenes, monoterpenes, coumarins, isoflavonoids, alkaloids and ellagitannins

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but it has been observed that the most potent antifeedants belong to the terpenoid group, which has the greatest number and diversity of known antifeedants compounds. The limonoids (a terpenoidal compound)
as chemical constituents from plants have been well studied and one of the most established example is the Azadirachtin A (Figure 1) from *Azadirachta indica* A. Juss of family Meliaceae, which has also been synthesized and is said to be a widely reported insect antifeedant [2]. Other known isomers of Azadirachtin have been reported to be active as antifeedants, but comparatively less than what has been reported for the Azadirachtin A. This compound has been reported to be effective against about 400 species of insects belonging to the following orders: Blattodea, Caelifera, Coleoptera, Dermaptera, Diptera, Ensifera, Heteroptera, Homoptera, Hymenoptera, Isoptera, Lepidoptera, Phasmida, Phthiraptera, Siphonoptera, and Thysanoptera.[3].

1.2 Post Harvest Technology

Post harvest technology is defined as an inter-disciplinary scientific technical procedure applied to agricultural produce after harvest for its safety, preservation, maintenance, processing, packaging, sharing, marketing, and utilization to meet the food and nutritional requirements of the people in relation to their needs. It was developed in agreement with the needs of each society to motivate agricultural production; prevent post-harvest losses, improve nutrition and add value to the products.

The Crop Production and Postharvest Technology involves the implementation of research projects on topics ranging from production and storage to the processing and marketing of agricultural products. These research activities include a collection of subjects from agronomy, plant protection (pest, disease, and weed control), agricultural mechanization, irrigation, drainage, cropping systems, food storage, postharvest technology, farm management, and agricultural economics. There is also the need to ensure there is assurance of improvement on the quality of products, the expiration period of these grains and the control of insects and microorganisms in these stored grains.

Agricultural practice is environmentally sensitive and there are many constraints to swift food production hence the need to develop techniques to reduce post harvest losses as well as to preserve and improve the quality, crispness, and nutritional value of agricultural produce until the products reach the consumer. This paper aims at discussing the prospect of using secondary plant metabolites which acts as antifeedant for this purpose.

II. SECONDARY METABOLITES AS DEFENSE IN POST-HARVEST STORAGE

Plant metabolites are formed in two main components - Primary metabolites and Secondary metabolites. The Primary metabolites comprises of all plant cells constituents that are directly involved in growth, development, or reproduction processes, these include sugars, proteins, amino acids, and nucleic acids. Secondary metabolites are those plant constituents that are not directly involved in the developmental process of the plant but in the physiological aspect including the plant defense system. Some are undoubtedly produced for easily appreciated reasons, e.g. as toxic materials providing defence against predators, as volatile attractants towards the same or other species, or as coloring agents to attract or warn other species, but it is logical to assume that all do play some vital for the well-being of the producer. These compounds usually belong to the chemical class of compounds such as alkaloids, phenols and terpenoids. Secondary metabolites with identified antifeedant activity among these classes of compounds are:

(a)Terpenes:

These are found in all plants and corresponds to the most significant class of secondary metabolites with estimated number of identified and isolated chemical compounds in the range of about 22,000. Among the Diterpenoids, Gossypol (Figure 2), produced by cotton (*Gossypium hirsutum*) has shown strong antifeedant, antifungal and antibacterial properties. The Triterpenoids have similar molecular structures to plant and animal sterols and steroid hormones, the Phytoectysones are mimics of insect molting hormones. When produced by plants such as spinach (*Spinacia oleracea*), they disrupt larval development and increase insect mortality. The fragrance from lemon and orange peels have been attributed to a class of triterpenoids called limonoids. Azadirachtin (Figure 1) belongs to this class of limonoid isolated from neem trees (*Azadirachta indica*) with an efficacy that indicates that some insects are repelled by concentrations as low as a few parts per million. An essential oil *Citronella* isolated from lemon grass (*Cymbopogon citratus*) also belongs to this class of compound and contains high limonoidal levels ensuring its efficacy and popularity as well as its low toxicity in humans and biodegradable properties making it an insect repellent of

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choice in the United States. Foxglove (*Digitalis purpurea*), another triterpenoid is the principal source of the cardiac glycosides Digitoxin (Figure 3) and Digoxin, which are used medicinally in small quantities to treat heart disease in people. Some herbivores have overcome the dangerous effects of cardiac glycosides and actually use these toxins for their own benefit [4]. Terpenoidal compounds, (-)-cubebol and (+)-2,7(14),10-bisabolatrien-1-ol-4-one with strong feeding activity against *Acusta despesta* have been reported. The compounds strongly inhibited feeding in the *A. despesta*, a snail

species well-known as a pest of many vegetables and crop. These compounds are among the best known sesquiterpenoids have played a large extensive role in plant defense.[5]

(b) Phenols: The phenolic compounds are another group of secondary metabolites found within plant tissues that serve as defense mechanism against pathogens, produced through the shikimic acid and malonic acid pathways in plant systems, they cover a wide range of defense-related secondary metabolites such as tannins, lignin flavonoids, anthocyanins, and furanocoumarins. The flavonoids comprise a very large group within the phenolic compounds, while the anthocyanins, colorful in nature, are responsible for the impartation of the beautiful colors observed in the flowers, fruits and leaves of plants known to produce water-soluble pigments that protect foliage from the damaging effects of ultraviolet radiation. Others such as Phytoalexins which are isoflavonoids have antibiotic and antifungal properties that are produced in response to pathogen attack. The active principles in these secondary metabolites disrupt pathogen metabolism or cellular structure. Examples of these phytoalexins include Medicarpin (figure 4) produced by alfalfa (*Medicago sativa*), Rishitin produced by both tomatoes and potatoes (the *Solanaceae* family), and Camalexin, produced by *Arabidopsis thaliana* family), and *Arabidopsis thaliana*. Quercetin, a flavonoid (Figure 5), isolated from *Bobgunnia madagascariensis* has also been reported to have antifeedant effect on *Tribolium casteneum* which is a maize and flour weevil ([4],[6]. Tannins show toxicity to insects through their action of binding to the salivary proteins and digestive enzymes including trypsin and chymotrypsin which results in protein inactivation in the organisms, this causes them to ingest high amounts of tannins but they fail to gain weight and become emaciated and may eventually die. Lignin, another phenolic conmpound is a highly branched heterogeneous polymer found in the secondary cell walls of plants, though the primary walls could also be lignified. Lignin consists of a large number of the phenolic monomers (in hundreds or thousands) and forms the primary component of wood. The insoluble, rigid, and virtually indigestible structural frame ensure lignin presents a strong barrier against insect attack.

(c) Alkaloids

Alkaloids are naturally-occurring organic compounds containing nitrogen moiety, and are usually heterocyclic in nature. Derived mainly from amino acid groups such as aspartate, lysine, tyrosine, and tryptophan, it had been observed that many of them play an extensive role in the physiological make up of these insect or pest species. The tobacco plants (*Nicotiana tabacum*) produces Nicotine (Figure 6) which is an alkaloid from its roots and transports it to leaves where it is stored in vacuoles. This is released when herbivores graze on the leaves and break open the vacuoles. Caffeine (Figure 7) also an alkaloid found in plants such as coffee beans (*Coffea arabica*), tea leaves (*Camellia sinensis*), and cocoa beans (*Theobroma cacao*) has shown toxic properties against both insects and fungi. High levels of caffeine produced by coffee seedlings have been reported to inhibit the germination of other seeds in the vicinity of the growing plants, a phenomenon called allelopathy. New alkaloidal compounds, (+)-11_-methoxy-10-oxoerysotramidine and (+)-10,11-dioxoerysotramidine identified in the seeds, seed pods and flowers of *Erythrina latissima* showed strong antifeedant activities against third-instar *Spodoptera littoralis* (Boisduval) larvae. The antifeedant effect of Erythrinaline alkaloids gives an indication of its usefulness in post harvest storage and crop protection. It was also observed that, farms with maize growing under the *E. latissima* tree were sparsely attacked by the stem borer. Since the tree is a widespread flowering plant, its seeds and flowers can be harnessed and utilized as a potential biopesticide or antifeedant in agricultural post-harvest processes [7].

Other plant metabolites with antifeedant effects include Cyanogenic glycosides, another secondary metabolite produced by plants also known to possess toxic nitrogenous compounds responsible for the decomposition hydrogen cyanide

(HCN) which stops cellular respiratory action in aerobic organisms. Plants that produce cyanogenic glycosides also produce enzymes that convert these compounds into hydrogen cyanide, including glycosidases and hydroxynitrile lyases, but they are stored in separate compartments or tissues within the plant; when herbivores feed on these tissues, the enzymes and substrates mix and produce lethal hydrogen cyanide [4]. Others include compounds belonging to the aliphatic ketones and aldehydes compounds of *Commiphora rostrata*, whose constituents have indicated great repellent action against *S. zeamais* in comparison to the synthetic commercial insect repellent N,N-diethyl toluamide [DEET] used in the study [8]. Essential oils of *Matricaria recutita* known to contain precocenes as an active constituent also interfere with insect glands that produce juvenile hormones resulting

in the suppression of insect growth while moulting [9]. It was also reported that the chemical compounds, 1-alpha terpenol and 2-dodecanone were the most repellent components of *Cleome monophylla* essential oil against *Rhipicophalus appendiculatus* and *S. zeamais.* The plant species release a variety of volatiles including various alcohols, terpenes, and aromatic compounds that serve as defense mechanisms against herbivores and pathogens. These constituents can deter insects or other herbivores from feeding, having direct toxic effects, or involved in recruiting predators and parasitoids in response to feeding damage. They may also be used by the plants to attract pollinators, protect plants from disease, or help in interplant communication ([9],[10]).

The use of green pesticides particularly for stored grain pests has come with high recommendations in recent times and the essential oils seem to be one of the best choice being suggested. Studies have shown that essential oils are readily biodegradable and less detrimental to non-target organisms as compared to synthetic pesticides [11]. Application of plant products especially essential oils is a very attractive method for controlling post harvest crop diseases. Production of essential oils by plants is believed to be predominantly a defense mechanism against pathogens and pests [12]. Essential oils are gaining considerable acceptance for use in post harvest storage, crop protection and fumigation because of the relative safety, biodegradable status and their exploitation for other multi-purpose uses. The problem of the development of resistant strains of fungi and insects may be solved by the use of essential oils of higher plants as fumigants in the management of storage pests because of synergism between different components of the oils ([13],[14]). Aromatic plants produce many compounds that are insect repellents or act to alter insect feeding behavior, growth and development, ecdysis (moulting), and behavior during mating and oviposition. Essential oils interfere with basic metabolic, biochemical, physiological, and behavioral functions of insects [15]. Some essential oils have larvicidal effects and the capacity to delay development and suppress emergence of adults of insects of medical and veterinary importance [16]. Thyme oil and monoterpenoids including thymol, anethole, eugenol, and citronellal combinations have been patented for pesticidal activity against cockroaches and the green peach aphid as reported by various literatures ([17-23].

III. SYNERGISM IN ANTIFEEDANT ACTION OF PLANT SECONDARY METABOLITES

Complex mixtures of secondary compounds in plant extracts contribute to a great deal for synergism, which enhances the joint action of active compounds against insect and reduces the rate of resistance development [24]. Mixtures of psoralen with xanthotoxin or bergapten resulted in reduced mortality of *Spodoptera exigua* reared on artificial diets mixed with linear and angular furanocoumarins and then exposed to UVB radiation, suggesting an antagonistic effect. In contrast, mixtures of similar composition, but at lower combined concentration where psoralen was the minor component, caused greater mortality in *S. exigua* than the sum of individual linear or angular furanocoumarins, suggesting a synergistic effect of psoralen [25].

The avermectins are a group of broad-spectrum pesticides with activity against a variety of arthropods [26]. Avermectin has shown high efficiency in controlling vegetable pests like *P. xylostella* L. and arthropods [27]. Furthermore, it has been successfully used as an essential part of integrated cabbage pest management in cabbage fields in Fuzhou, China, where it showed high efficacy in reducing pest species abundance while very low harmfulness to their natural enemies that caused higher overlaps between the predators and their prey as compared to methomyl, another synthetic compound [28].

Usually some secondary compounds isolated from plant show no bioactivities or attractiveness to insects, a feasible way to explore its potential is to mix these chemicals with some insecticide. Apigenin showed a strong attraction to DBM in this experiment, and resistance to avermectin was over 812-folds in *Plutella xylostella* population compared with the unselected parents. In order to delay the resistance to avermectins in DBM, avermectin was chosen for the blend containing the feeding stimulant apigenin. The result show that the high mortality of insect was caused by the mixture of apigenin and avermectins [29].

Essential oils are a complex mixture of components including minor constituents, in contrast to synthetic pesticides based on single products, and they act synergistically within the plant as a defense strategy [24]. Formulated pesticides from essential oil have found use as as mono-products against some pests, especially soft-bodied and sucking insects as well as mites. They have also been used in rotation or in combination with other crop protectants, including conventional (synthetic or microbial) pesticide products. Some of the essential oils effectively controlled pests that are resistant towards synthetic pesticides. Essential oils have limited efficacy against large chewing insects, as lepidopterans, coleopterans, and they can be phytotoxic if misused (e.g., applied at rates exceeding that recommended on the product label). The disadvantages of limited persistence and phytotoxicity could be lessened through microencapsulation of essential oils when formulated [30]. Some of these research findings suggest further work is needed to reveal the complexity of physiological activity exerted by mixture of secondary constituents on insect pests with antifeedant activities and also to ensure the possibility of synthesizing these compounds.

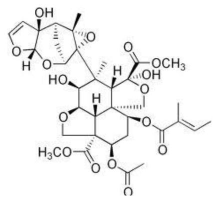
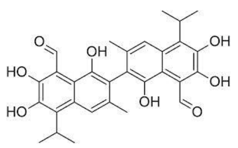
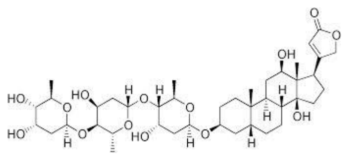
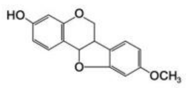

Figure 1. Azadirachtin Figure 2. Gossypol Figure 3. Digoxin Figure 4. Medicarpin

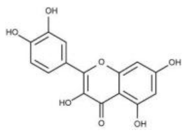
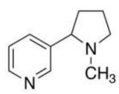
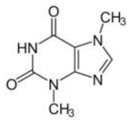
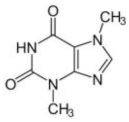

Figure 5. Quercetin Figure 6. Nicotine Figure 7. Caffeine Figure 8. Theobromine

Examples of Chemical Structures of Some Secondary Metabolites

IV. NANO TECHNOLOGY AND ITS ROLE IN POST HARVEST ACTIVITIES.

Nanotechnology is an evolving subject in the area of scientific studies in biology, chemical sciences and physics. The possibility of experimentation in bio-based synthesis of nano-metals using leaf extracts and microorganisms such as bacteria and fungi are currently ongoing [31]. Biosynthesized Nanoparticles (NPs) are used in antimicrobial, anti-viral and antihuman immunodeficiency virus (anti-HIV) studies [32]. Using plants for NP synthesis can be advantageous over other biological processes because it can be suitably scaled up for large-scale NP synthesis[33]. Nanotechnology has become one of the most promising new technologies for pest control and emerging new trends in pest management are taking considerable interest in it. Nanoparticles help to produce new pesticides, insecticides, and insect repellants[34]. Nanoencapsulation is a process through which a chemical is slowly but efficiently released to a

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particular host for insect pest control. Release mechanisms include diffusion, dissolution, biodegradation, and osmotic pressure with specific Ph [35]. These processes also deliver DNA and other desired chemicals into plant tissues for protection of host plants against insect pests. Nanoparticles embodied with essential oils extracted from garlic bulbs are effective against *T. castaneum* Herbst, a stored product pest of maize and maize flour products [30]. Syngenta, an Agrochemical Corporation has embarked on research involving the use of nanoemulsions in its pesticide products. Encapsulated product from Syngenta delivers a broad control spectrum on primary and secondary insect pests of cotton, rice, peanuts, and soybeans. Marketed under the name Karate® ZEON, a quick release microencapsulated product containing the active compound lambda-cyhalothrin (a synthetic insecticide based on the structure of natural pyrethrins) which breaks open on contact with leaves. The encapsulated product "gutbuster" only breaks open to release its contents when it comes into contact with alkaline environments, such as the stomach of certain insects. This new technology has improved pesticide and fertilizer delivery systems which can lead to environmental changes, especially in the controlled release manner (slowly or quickly) of substances in response to different signals e.g. heat, moisture, ultrasound, magnetic fields, etc. In recent times, nanotechnology has been widely accepted publicly because it has not yet been linked to any toxicological and ecotoxicological risks. Research on nanoparticles and insect control has been directed toward production of faster and ecofriendly pesticides to deliver into the target host tissue through nanoencapsulation. This is to further control pests efficiently, prolong the protection time, and improve the Agricultural sector. ([30],[36-38]).

V. CONCLUSION

Secondary metabolites from plant tissues are an important source for biopesticides and the development of antifeedants. Extensive use of synthetic pesticides and their environmental and toxicological risks have generated increased global interest in the development of alternative sources of chemicals to be used in safe management of plant pests. Currently, research activities in different parts of the world are focusing attention on possible exploitation of higher plant products such as novel
chemotherapeutics for plant protection because they are mostly non phytotoxic and easily biodegradable[39]. It is also been considered that some secondary metabolites isolated from plant that have been shown to have no bioactivities or antifeedant properties against insects, could be explored for their potentials by mixing these isolated constituents with some insecticide.

The use of Botanicals help in preventing the dumping of thousands of tons of pesticides on the earth since they are safer to the user and the environment because of the biodegradable nature, as they have the capability to break down into harmless compounds within hours or days in the presence of sunlight. Although botanical antifeedants may not be too helpful in controlling many agronomic crops, they are promising alternatives to conventional pesticides in the developed world where a premium is placed on human and animal safety for controlling pest of medical and veterinary importance (at homes, schools, restaurants, hospitals, and garden) and in developing countries where they constitute an affordable tool for crop and post harvest protection [40].

Currently, different botanicals have been formulated for large scale application as biopesticides and antifeedants in eco-friendly management of plant pests and are being used as alternatives to synthetic pesticides in crop protection and post harvest usage. These products have low mammalian toxicity and are cost effective. Such products of higher plant origin may be exploited as eco-chemicals and integrated into plant protection programs. Recent reviews of the main chemical classes of plant secondary metabolites that have been used in crop protection and post harvest have focused on the most recent advances in the chemicals disclosed, their mode of action and their fate in the ecosystem, their current use in pest management underlying registration procedures and commercialization potential. Antifeedants based on plant essential oils have also been given commercial potential while the use of rotenone appears to be waning. A number of plant substances have been considered for use as insect antifeedants or repellents, but apart from some natural mosquito repellents, only a little commercial success has ensued for plant substances that modify insects or pests behavior but with the advent of nanotechnology there is a new light at the end of the tunnel.

Several factors appear to limit the success of botanicals, most notably regulatory barriers and the availability of competing products (newer synthetics, fermentation products, microbials) that are cost-effective and relatively safe compared with their predecessors. In the context of agricultural pest management, botanical antifeedants are best suited for use in organic food production in industrialized countries but can play a much greater role in the production and postharvest protection of food in developing countries. Therefore, there is urgent need to bioprospect the pesticidal property of different plant constituents as well as essential oils from some of these plants and detailed *in vitro* and *in vivo* investigations are required for their recommendation of their practical application as pesticides for the control of post harvest biodeterioration of food commodities and thereby enhancing shelf life of the commodities [39][41].

Botanicals are incorporated in integrated pest management programs as products in crop protectant rotations. Currently, botanicals are facing fewer competitions in organic food production, which estimated to be growing by 8% to 15% per annum in Europe and in North America[42]. Recently, the use of microencapsulation for the essential oils has allowed slower release rates of oils to be achieved, thus prolonging protection time. Using gelatin-arabic gum microcapsules maintained the repellency of citronella up to 30 days on treated fabric stored at room temperature (22°C) [43].

There is a wide scope for the use of plant-based pesticides in the integrated management of different insect pests. Production of botanical antifeedants would reduce the high cost of importation in developing countries.

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