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Review Article

Terpenoids as Natural Allelopathic Compounds in Plants

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ABSTRACT

Terpenoids, are derived from the alteration of basic metabolites through various major processes. They are chemicals not important for plant growth and expansion, but essential for plant of secondary metabolic processes.

Mono- and sesquiterpenoids are among the most common volatile organic compounds. These substances may exist in non- volatile form in some plants, Monoterpene glycosides are volatile in some plant species, an example is that water decomposes into volatile forms when tissues are damaged, since plants do not have the ability to move and extend from their opponents. In turn, it has the ability to form a variety of secondary compounds, such as terpenes that improve its protection from microbes, diseases, insect pests and weeds. The aim of the study presents a definition of terpenes, and its relationship to allelopathic phenomenon,and how manufacturing works to keep plants safe from microbiological and insect pests. allelopathic plants release secondary metabolites, they cause negative or positive effects on nearby plants.

Keywords: Terpenoids, Allelopathy, biosynthesis, Weeds, allelochemicals.

INTRODUCTION

Terpenoids, often known as terpenes, one of the biggest family of chemicals found in plant products and have most structural diversity. Terpenes are the most common natural compounds with a wide range of structural variations that include linear hydrocarbons and carbocyclic skeletons. Over 23,000 known terpenoid molecules, such as carotenoids, tocopherol, phytol, steroids and hormones, have been studied previously (Pattanaik and Lindberg, 2015), plants kingdom contains thousands of terpenes, but only a small number of them can be produced by each species.

The name terpene comes from the Latin term turpentine (*Balsamum terebinthinae*), It was coined by Dumas in 1866, when chromatographic and spectroscopic methods were developed. Terpenes are widely distributed in higher plants including Eucalyptus, conifers, and citrus., and are widely distributed in leaves, flowers, stems, and roots. Isopentenyl diphosphate (IPP) unit and its isomer, dimethylallyl diphosphate (DMAPP), are the met abolic precursors of terpenes. Terpenoids are involved in a variety of biological processes, including respiration, electron transport chains, cell wall and membrane production. Terpenoids are additionally widely utilized in medications, and agricultural chemicals (Tholl, 2015).

Terpenes classification is based on Wallach's, 1887 proposed isoprene units (C5H8), a 5-carbon compound that forms terpenes backbones (Brahmkshatriya and Brahmkshatriya, 2013). Terpene compounds are unsaturated hydrocarbons that are primarily generated from the isoprene unit (CH2=C(CH3) CH=CH2), whose chemical pattern is (CH2=C(CH3) CH=CH2). Fig. (1).

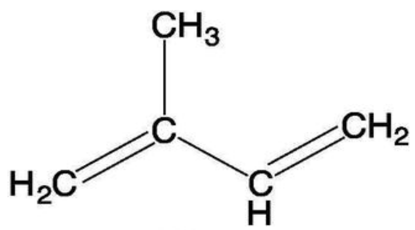

Fig. 1: Structure of one isoprene unit (Withers and Keasling, 2007).

Terpenoids have molecular formulas that where (n) is the number of connected isoprene units, which are multiples of that (C5H8), also known as the C5 statute; depicts Isoprene's chemical composition unit isoprene unit can be connected or organized into rings. Isoprene units can be connected to hemiterpenes, monoterpenoids, sesquiterpenoids, diterpenes, sesterterpenes, triterpenes, and tetraterpenes are all different types of terpenes that depend on the amount of isoprene units they contain, are produced successively to produce diterpenes, sesterterpenes, triterpenes, sesquiterpenoids, monoterpenoids, and hemiterpenes.

Table 1: Terpenoids are divided according to the number of isoprene units they contain

No.	Type of classification	Number of isoprene units	Structure formula	Example
1	Hemiterpenes	Single	C_5H_8	Prenol and isovaleric acid
2	Monoterpenoids	Two	$C_{10}H_{16}$	Geraniol, limonene, terpineol and myrcene
3	Sesquiterpenoids	Three	$C_{15}H_{24}$	Humulene, caryophyllene, and farnesol
4	Diterpenoids	Four	$C_{20}H_{32}$	Cafestol, kahweol, cembrene and taxadiene and phytol
5	Sesterterpenoids	Five	$C_{25}H_{40}$	Geranylfarnesol
6	Triterpenoids	Six	$C_{30}H_{48}$	Sterols
7	Sesquarterpenoids	Seven	$C_{35}H_{56}$	Ferrugicadiol and tetraprenylcurcumene
8	Tetraterpenoids	Eight	$C_{40}H_{64}$	Cyclic lycopene, carotenoids
9	Polyterpenes	More than eight	—	Natural rubber

(Table 1) contains the many isoprene unit categories and examples of the compounds related to each classification. The number of isoprene units in a terpene molecule can be utilized to describe it and necessary to construct the molecule. (Withers and Keasling, 2007). As determined by mechanism and kind of primary metabolites all the following secondary plant metabolites are produced by primary plant metabolites, tetra terpenes based on the quantity of isoprene units (1).

Biosynthesis of Terpenoids

Terpenoids, are synthesis primarily derived from the alteration of basic compounds through various major routes, which also cause the main metabolites' synthesis. metabolic routes for auxiliary metabolites are far too many to be simple to determine. Nonetheless, the production of key classes of these chemicals follows a few common pathways. The shikimate pathway is a significant system used by plants, as well as other organisms such as bacteria and fungi, to manufacture primary metabolites, which serve as the foundation for a variety of Flavonoids and phenols chemicals (Ghasemzadeh and Ghasemzadeh, 2011; Maeda and Dudareva, 2012).

Depending on the quantity of isoprene units included within the structure of molecules, the route of the shikimate containing numerous isoprene units (C5H8) connected in a head-to-tail arrangement can manufacture - terpenoids (Köksal *et al*., 2010). Terpenoids may additionally be made by the isopentenyl the diphosphate route developed from an intermediary substrate such as mevalonic acid (MVA) via the mevalonate pathway and the MEP/DOXP (methylerythritol phosphate deoxy-D-xylulose 5-phosphate) stands for methylerythritol phosphate/deoxy-D-xylulose 5-phosphate pathway. The production of terpenoids is depicted in Fig. (2). (Cheng *et al*., 2007; Varshney and Sondhia, 2008).

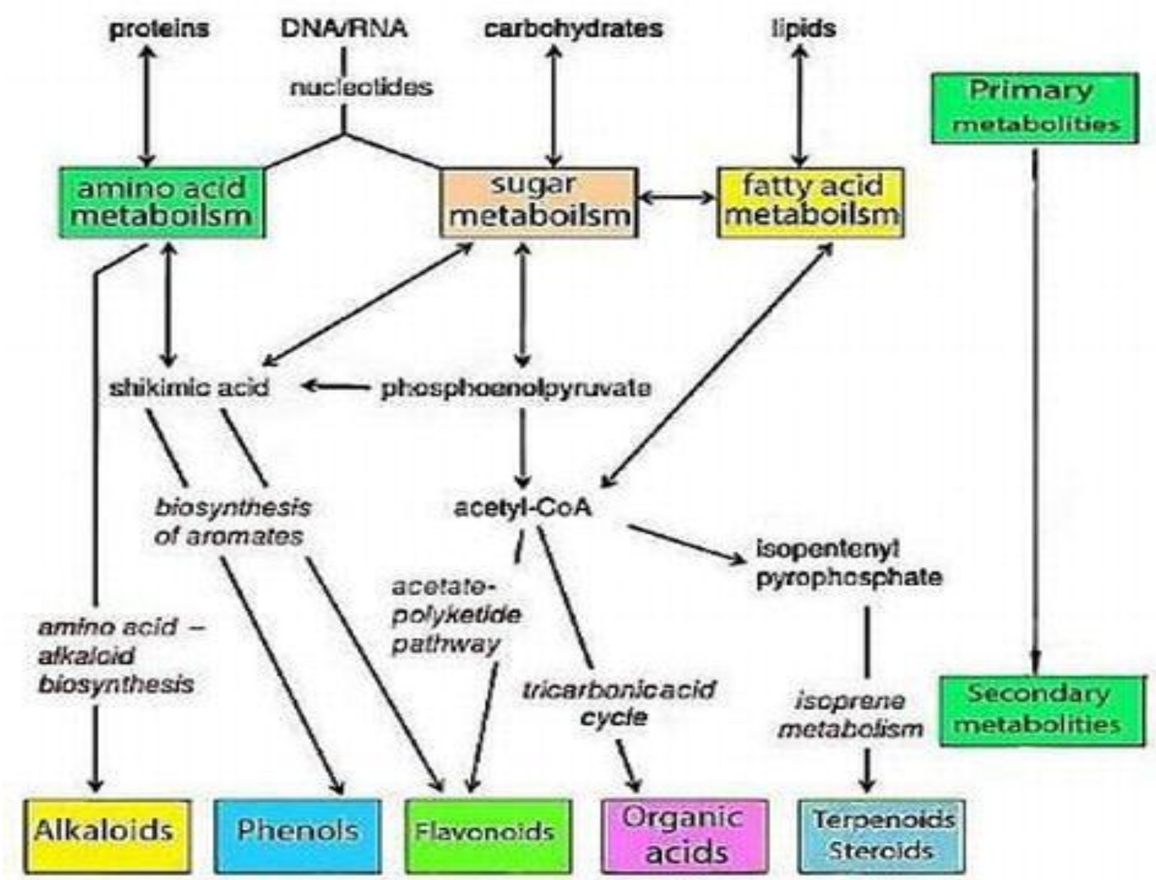

Fig. 2: general schematic metabolic routes that result in terpenoids and other significant secondary metabolites (Gunsolus and Curran, 1991)

The most terpenoides –producing plants families are those that produce resine and turpentine and especially the family Coniferaceae (Pinaceae) (monoterpenoies) (Breitmaier, 2006), in addition to four xerophytic plants, 60 species belong to Grindelia of the family Asteraceae like *Gridella camporum* which produce a mixture of non- volatile terpenoides and insoluble in water, also *Flourensia cernua* which belong to the family Asteraceae as a good producer of the terpenoides. The family Zygophyllaceae (monoterpenoides, sesquiterpenes) also one of the most important like *Larrea tridentate***,** in addition to family Simaroubaceae and medical plant *Commiphora wightii***,** Anacardiaceae, Burseraceae, Hammamelidaceae, Fabaceae, Rubiaceae (monoterpenoid), Genkgoaceae (diterpenes), Lamiaceae (monoterpenoides) Apiaceae (triterpenoides) (Hao and Xiao, 2020).

Relation between Terpenoids and Allelopathy

Allelopathy is one of the alternate strategies (Scavo *et al*., 2019), allelopathic plants transmit secondary metabolites (allelochemicals) to other plants nearby which is mediated by allelochemicals emitted into the environment, is the direct or indirect negative as well as positive effect of one plant on another because there is less competition for available resources, host plants may get more of the nutrients, water, and/or light.

Primary metabolites are classified allelochemicals into 10 categories, based on their structures and properties: (Iqbal and Fry, 2012). Namely:

(1) water -soluble organic acids, straight chain alcohols, aliphatic aldehydes and ketones.
(2) simple lactones
(3) long-chain fatty acids and polyacetylenes.
(4) quinines. (5) phenolics.
(6) cinnamic acid and its derivatives.
(7) coumarins. (8) flavonoids.
(9) tannins. (10) steroids and terpenoids.

The soprenoid or shikimate routes, that are accountable for the generation of vital oils, generate a vast spectrum of these biochemical (Maeda and Dudareva, 2012).

Terpenoids have Many Applications

The goal of plant protection is to protect plants from weeds, diseases, and insects. Pest biological management has been used for some time. The BIOCAT database exposes different insects and their agriculturally useful natural enemies. The most extensively utilized substances as antimicrobials and cosmetics are monoterpenoids and sesquiterpenoids, which are the most readily available chemicals in secondary plant metabolites.

Plants produce monoterpenoids and sesquiterpenoids as protective compounds against insects, fungus, and other nearby plants. Fig. (3). (Withers and Keasling, 2007; Ninkuu *et al*., 2021).

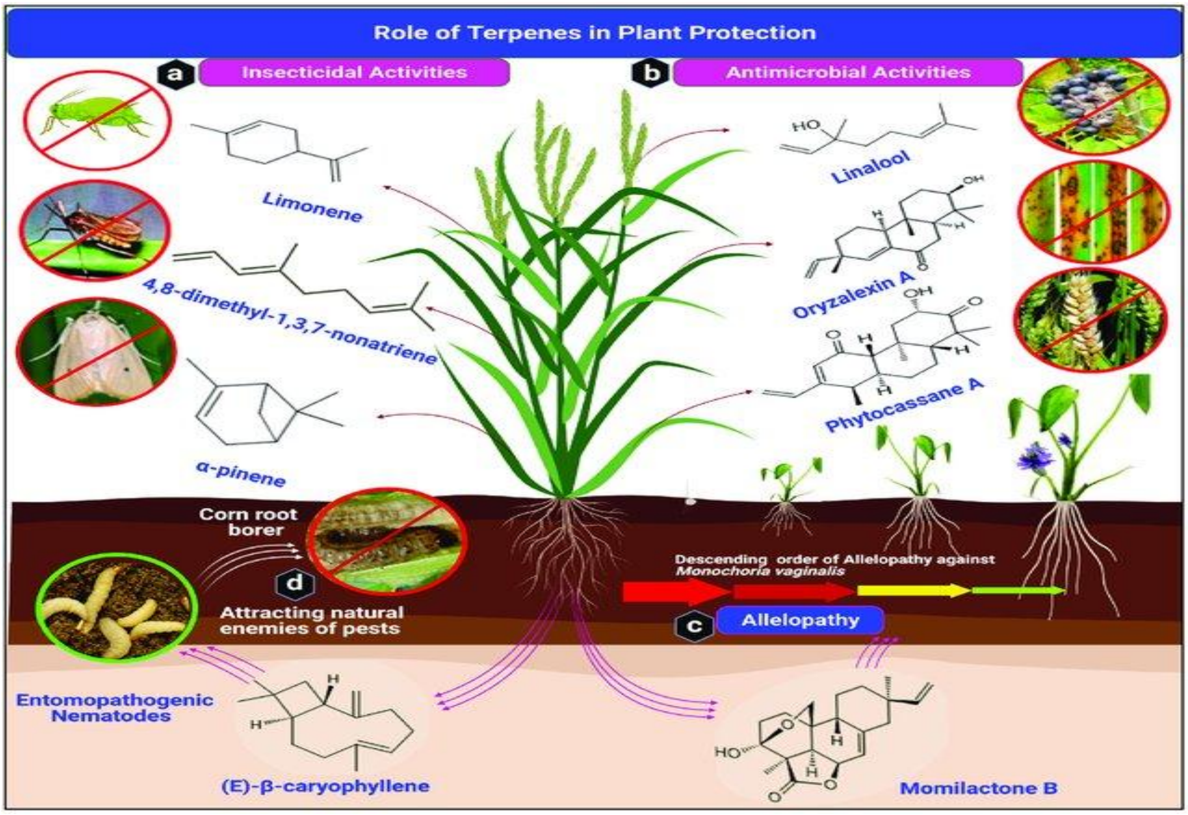

Fig. 3: Terpenes' role in plant protection. Four critical functions of terpenes in plant protection: (a) insecticidal role of terpenes, (b) antimicrobial activities of terpenes against rice blast disease and Fusarium head blight, and (c) allelopathy of root exudates of plants. Momilactone B inhibits the growth and development of *Monochoria vaginalis*. (d) Terpenes indirectly attract natural enemies of pests, e.g., (E)-β-caryophyllene attracts entomopathogenic nematodes on corn root borer. (Structures were drawn and analyzed with Chem Draw software, version 20.0.0.41, and uploaded on BioRender.com to create the illustration) (Ninkuu *et al*., 2021)

1- Role of Terpenoids in Plant Germination and Growth

Terpenoids in secondary metabolism, are essential to promote plant survival. This allows these plants to protect their own environments, which may include natural adversaries, competitors, and friends, among other things.

There are numerous uses for the terpenoids made by particular kinds of plants. Most of these factors are regulated by creator or donated plants and the environment around them, such as aroma to tempt particular animals and insects, help with blooming, provide defense or function repellents, store energy, speed up the repairing of wounds, limit water evaporation. Different plant parts, including wood, bark, seeds, rhizomes, roots, fruits, and leaves, can be used to make essential oils (Fornari *et al*., 2012), capability for allopathy on target or recipient plants can manifest as reduced (Jefferson and Pennacchio, 2003).

They make up a large portion of the essential oils found in many trees, which give certain tree s their distinctive scent. By vaporizing or being slightly leached by water, they are released into the atmosphere. When emitted, these substances stunted the growth of nearby plants and made other iss ues worse (Azimova *et al*., 2012). The terpenoids compounds include, Volatile monoterpenes, Squiterpenes were discovered in tomato leaf extracts of type VI glandular t-richomes, including -terpinene, limonene, caryophyllene, humulene, and element (Schilmiller *et al*., 2009). Since monoterpenes are lipophilic substances, they may expand plant cell membranes as a result of monoterpene buildup, causing harm to the membrane's structure (Xu *et al*., 2012). Terpenoids' interactions with plant cell membranes are depicted Fig. (7) (Poonpaiboonpipat *et al*., 2013).

Monoterpenes found among volatile oil also decoupled photophosphorylation via oxidation (transform ADP to form ATP using the energy of sunlight). Monoterpenes reduce cellular respiration as a result, which interferes with ATP synthesis.

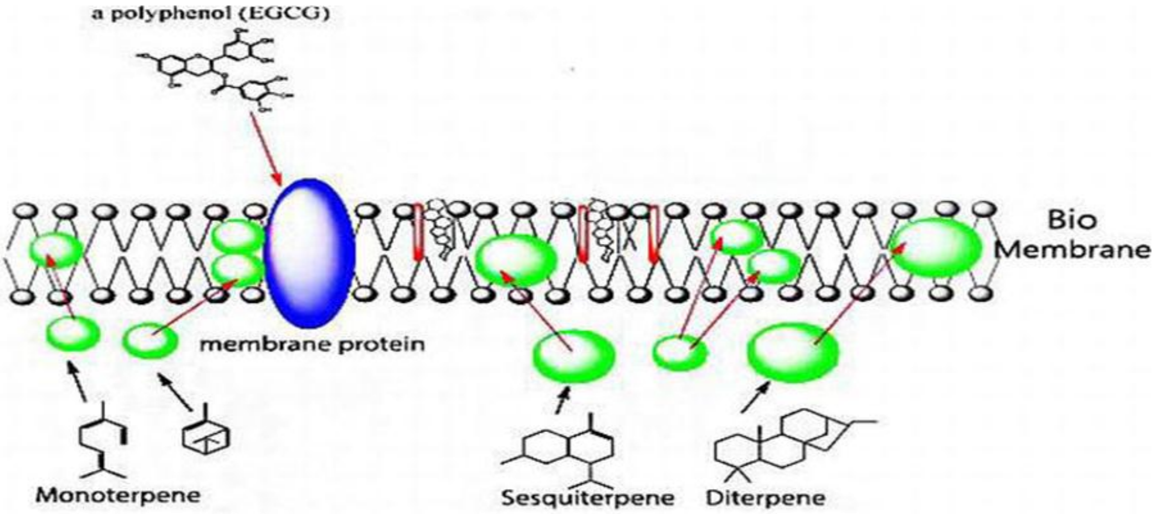

Fig. 7: Terpene connections with plant cell membranes (Poonpaiboonpipat *et al*., 2013).

Sharifi-Rad *et al*. (2014) Benzyl isothiocyanate, cubenol, 1-butenyl isothiocyanate, and dimethyl trisulfide were found to have a greater impact than other chemicals on the effects of *S. arvensis* essential oils.

The essential oils from *S. arvensis* may have allelopathic effects. According to this brief analysis, terpenoids may be crucial for plant evolution and ecological communication. Plants gain from terpenoids that are kept inactively, such as glycosylated Premature ventricular contractions PVOCs, and only need to be hydroxylated in emergency situations

2- Terpenoids as Herbicide in Nature

Allelochemicals are poisonous organic root exudates that have the potential to have a deleterious physiological effect on nearby plants.

Weeds' respiration, germination, ion uptake, and photosynthesis are all inhibited by these compounds. Allelochemicals also impair activation of the stoma, transpiration, enzyme action, hormone levels. Inhibition gene activity, inhibiting signal transmission, reducing cell membrane permeation are additional effects of allopathic activities (Scognamiglio *et al*., 2013).

Sharifi-Rad *et al*. (2015) and Alfatemi *et al*. (2015) noticed that terpenoids play roles to remove a variety of weed species because they are less specific secondary metabolites that target a variety of proteins by creating hydrogen, hydrophobic, and ionic bonds. Terpenoids are a novel sustainable agricultural metabolite that should be taken into consideration if weed losses are to be reduced and to protect the location from the dangers of artificial herbicides. Monoterpenoids, which are main constituents of essential oils, demonstrated the highest phytotoxicity when compared to sesquiterpenoids. Dudai *et al*. (1999) and Angelini *et al*. (2003) found that *S. herbacea* seed and leaf extracts did not affect the medicinal plants *Hyssopus officinalis* and *Nigella sativa*, but had negative impacts on the weeds *Taraxicum officinale* and *Amaranthus retroflexus*.

Essential oils can be used to suppress weed germination and growth because of the terpenoids and allelochemical substances they contain. The most significant class of allelochemicals, terpenoids, has demonstrated effective phytotoxic against a variety of weed kinds by inhibiting germination and limiting growth. The advantages of phytotoxicity impacts of several terpenoid elements which make up significant portion of essential oils, on diverse weed species, as well as their potential applications as natural weed killer. (Almarie, 2020).

Terpenoids assist trees in self-defense. Chemical ecology places a lot of emphasis on the compounds' movement in the air, soil, and water. (Yu *et al*., 2022) PVOCs released into the air destroyed by herbivores interact with nearby, unaffected plants, warning a potential for injury from herbivores and improving their fitness (Arimura and Pearse, 2017).

The most phytotoxic substances that fully inhibited the germination and root development of stiff ryegrass, according to the authors, were trans-anethole and linalool. Additionally, Linalool and trans-anethole have allelopathic suppressive influence on a variety of microbes in addition to higher plants.

Semerdjieva *et al*. (2022) showed several factors that inhibit weed seeds were seen by three EOs that were utilized in the experiment. The *M. officinalis* seeds' germination energy was increased by the tested juniper EOs. With increasing EO application rate, germination energy increased by up to 70- 100 percent in comparison the germination energy of (control) treatment of 15%. El-Rokiek *et al*., 2021; Semerdjieva *et al*., 2022).

2- Role of Terpenes as Antibacterial

Terpenoides demonstrated antibacterial, antifungal, and other activities Wheat plant growth shows that when sprayed with *C. sativum*, height, leaf count per plant, fresh and dry weight all significantly increase. 40 days after seedling with *C. sativum* waste oil predominated in all concentrations compared to the untreated control. Jankovský and Landa (2002); Ali and Neda (2011) when compared to the untreated control, all growth parameters showed a maximum significant increase after the use of waste *C. sativum* oil at a rate of 4%.

When *A. fatua* weed competition with wheat declined resulting in more nutrients being taken by the target plant (wheat). As a result, rising in wheat growth was compared to the unwedded control, the plant's height, number of leaves, fresh weight, and dry weight/plant all rose. The results show that spraying *C. sativum* waste oil at concentrations (2-4%) over the lonely control significantly increased spike length, spike number per plant, and spikelet number/spike.

Agricultural waste from coriander plants is being recycled in studies as a potential source for the manufacture of aromatic oils since the results indicated using mustard waste oil as a bioherbicide alternative to dangerous chemicals and save the environment. The only variation between the two was in the proportion of the constituents with some extra novel compounds in the dry coriander plant. The essential oil of this species has antimicrobial assets. In addition, *H. officinalis* is used to treat asthma, bronchitis, herpes, and digestive issues (Benarab *et al*., 2020).

4- Terpenes' Function in Insect Modulation

For chemotactic and landing efficiency the majority of feeding insect host identification is based on either visual, physical, or both cues. (Benarab *et al*., 2020).

The majority of the C5, C10, and C15 isoprene chain terpenes used as olfactory signals are created in the epidermis's glandular trichomes of the host plants to protect them from insects. These substances have a property called antixenosis, which disturbs an arthropod's way of life or unintentionally draws in its predators

The majority of terpenes are defense related substances, with gibberellins and brassinosteroids playing major responsibilities in development and progress. Terpenes are substances that act as alert compounds, protective pollution, wayfinding signs, and antifeedant deterrent compounds. Terpenes are utilized to defend against insects and dangerous bacteria since they contain over 25,000 volatile Organic Compounds in varied quantities and toxicities causes proteins, amino acids, and nucleic acids to become denaturized.

By reducing plant nutrients, Iris plant can also prevent insects from making prostaglandins and leukotrienes, which will stop them from growing and developing Iridoid decreases insect development and survival rates *in vitro* settings and prolongs the larval stage

(Rassaeifar *et al*., 2013; Taban *et al*., 2013; Ulukanli *et al*., 2014), known as pyrethroids, flowers and leaves produce monoterpene esters that modulate neurotoxins. This terpene is poisonous to moths, beetles, wasps, and bees Pyrethroid is one of the active chemicals in the majority of commercial pesticides since research has demonstrated that it is safe for the environment. The housefly, drugstore beetle, rice and bean weevils, as well as other insects, are also deterred by the essential oils of Gaultheria (Ericaceae) and Eucalyptus (Myrtaceae). Additionally, the rice diterpenoid momilactone A guarded against white-backed planthopper infection (Pinheiro *et al*., 2015; Arora *et al*., 2015). Biopesticides based on terpenes have been in use for a while. Some people use neem extracts, essential oils derived from *Chenopodium ambrosioides*, diversity active components from orange or citrus oils (Saharkhiz *et al*., 2016).

Juniper essential oils (EOs) offer medicinal qualities such as anti-inflammatory, antioxidant, antibacterial, antifungal, antiseptic, repellent, and insecticidal actions be cause they contain terpenoids, particular classes of oxygenated monoterpenes, and sesquiterpenes hydrocarbons. (Zheljazkov *et al*., 2017)

CONCLUSION

Plants produce over 300,000 secondary metabolites. secondary metabolites are created by pla-nts, primary metabolites play a function in cellular survival and reproduction. The goal of plant protection is to protect plants from weeds, diseases, and pests. Pest biological management has been used for many years. It is well known that plants produce terpenes to protect themselves from biotic (pathogenic bacteria, herbivorous, pests and weeds) and biotic (salt, light, water, temperature) difficulties. Terpenes have been studied as an ingredient in drugs because of their low risk to the environment and to people's health. pesticide and herbicide formulation has experienced a widespread revival.

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التربينويدات مركبات طبيعية في النباتات

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الملخص

التربيونيدات مشتقة من تغيير المستقبلات الأساسية من خلال عمليات رئيسية مختلفة، التربينويدات عبارة عن مواد كيميائية غير ضرورية لنمو النبات وتطوره ولكنها اساسية لاستمرارية النبات في عمليات التمثيل الغذائي الثانوية.

تشكل أحادي وسداسي تربينويدات من أكثر المركبات العضوية المتطايرة المشتقة من النبات شيوعا قد توجد هذه المواد في شكل غير monoterpene glycosides متطاير في بعض الأنواع النباتية، مثال على ذلك هو تتحلل بالماء إلى أشكال متطايرة عند تلف الأنسجة، ونظرًا لأن النباتات ليس لها القدرة على التحرك والهروب من خصومها. بالمقابل لها القدرة على تكوين مجموعة متنوعة من المركبات الثانوية، مثل التربينات التي تحسن من دفاعها ضد الأمراض الميكروبية، والآفات الحشرية، والأعشاب الضارة. تناولت هذه المقالة مقدمة للتربينات وعلاقتها بظاهرة الاليلوباثي، وأنواعها، والتركيب الحيوي، ودورها في الدفاع عن النباتات ضد الالتهابات الميكروبية، والآفات الحشرية. حيث ان بعض النباتات تحرر مركبات اليلوباثية مسببة تأثيرات سلبية او ايجابية على النباتات المجاورة.

الكلمات الدالة: التربينويدات، الاليلوباثي، التخليق الحيوي، الادغال، المركبات الاليلوباثية.