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Plant Secondary Metabolites, Their Classification and Biological Roles: A Review

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ABSTRACT

Metabolism represents the primary and essential biological phenomenon occurring within the living cell, encompassing the synthesis of crucial biomolecules and their subsequent breakdown to liberate the requisite energy for diverse cellular functions. Two distinct forms of metabolism exist: primary and secondary, the primary one, facilitating the production of fundamental organic substances to support growth, reproduction, and other biological processes, including proteins, carbohydrates, lipids, and nucleic acids. Plants constitute an indispensable reservoir of chemical compounds possessing diverse biological attributes that can be exploited by humans for their benefit. These substances primarily emerge through chemical transformations of secondary metabolism includes terpenes, alkaloids, phenolic compounds, saponines, steroids each group possesses unique traits and attributes that set it apart from other groups, and each of these categories fulfills crucial and indispensable functions within the majority of living cells.. These secondary metabolites are synthesized in minute amounts that are sufficient to fulfill specific plant needs in response to particular environmental factors. These compounds possess unique properties that enable them to play important biological roles not only in the life of plants, but also in the life of other living organisms, including humans.

Introduction

Plants, are autotrophic organisms, possess a secondary metabolism and primary metabolism, both processes are present in all living organisms. This process of secondary metabolism enables these organisms to build and synthesize a wide range of chemicals. These substances, known as secondary metabolites, are derived from the secondary metabolism of plants [1]. Secondary metabolites are organic compounds that do not possess a direct function in the process of photosynthesis, growth, and development. Nevertheless, they indirectly contribute to the survival of the plant by fulfilling various crucial roles. For instance, these compounds may serve as signaling molecules, aid in herbivore prevention, or exhibit antimicrobial properties. The current advancements in technology have facilitated the isolation and characterization of secondary metabolites from raw plant extracts [2].

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Secondary metabolites are a derived from various primary metabolite compounds. The distribution of compound within each organism is not uniform. The variation in their chemical structure is influenced by the advancements in organic chemistry and the interplay between composition and effectiveness. The physiological functioning of these metabolites is intricately connected to their chemical composition and associations [3]. Examination of physiological activities and the composition of secondary metabolites holds significant significance due to the fact that based on this understanding, their application in various sectors has been made feasible [4]. This review elucidates the categorization of secondary metabolites derived from plants and their applications in everyday existence, in addition to their significant therapeutic attributes. The primary emphasis of this review centers on five pivotal classifications of secondary metabolites, specifically terpenes / terpenoids, alkaloids, phenol compounds, saponins, , and steroids.

Synthesis of secondary metabolites by plants:

Plants possess a remarkable ability to produce various secondary metabolites that constitute the majority of their metabolism [5]. There are approximately four hundred thousand plant species capable of producing huge numbers of active compounds, the functions, composition and use of which have not yet been fully discovered [6].This compound functions as an organism and serves as a highly efficient mechanism of protection against both biotic and abiotic pressures that plants encounter [7]. Due to demographic, climatic, and cultural variations, different civilizations plants have developed their own distinctive traditional medicinal systems, which encompass the identification and utilization of specific plants along with their various applications [8]. The commencement of the extraction of active compounds from medicinal plants was initiated during the nineteenth century, marking a significant milestone in pharmacognosy progress with the identification of quinone as a pivotal element in Cinchona trees [9]. From that time, numerous botanical specimens employed in traditional medicine have been transported to the laboratory for the purpose of scrutinizing their active components. The leaves of Digitalis as a source of digitoxin, morphine drawn from opium poppy latex, Aspirin, an offshoot of salicin originating from *Salix alba* bark, Pilocarpus leaves as a source for pilocarpine, Cinchona bark for quinine production, and all serve as prominent illustrations of plant-derived compounds harnessed in early medicinal practices that continue to be utilized in clinical contexts to this day [10]. Some instances include certain botanical specimens, which serve as a significant reservoir for several potent constituents. Include: *"Ephedra sinica* (Ephedraceae), *Rauwolfia serpentina* (Apocynaceae), *Catharantus roseus* (Apocynaceae), and. *Catharantus roseus*, known as *Vinca rosea* " [8]. From the plant extract, 150 natural products had been characterized including vincristine and vinblastine, two bisindole alkaloids, which have been proven extremely valuable as drugs for treating "lymphomas and childhood leukemia" respectively. *"Rauwolfia serpentina* (Apocynaceae)" rhizome and roots were recorded in traditional medicine of India and Africa [8]. The ancient Chinese used *Ephedra sinica* (Ephedraceae) to treat severe colds. Ephedrine that acts to decongest the nose, this compound used for synthesis salmetrol and salbutamol which are antiasthma agents [11]. In the year 2001, a significant proportion of the medications dispensed globally were derived from botanical sources. Furthermore, it is worth noting that 11% of the 252 vital medications cataloged by the World Health Organisation (WHO) were exclusively derived from plants, and a substantial quantity of medications were synthesized from natural product lead compounds [10,11] sorghum is known to possess various SM, specifically terpenes, flavonoids, tannins, alkaloids, phenols, saponins and steroids [12]. The genetic, environmental, and cultivation factors exert a strong influence on the nature, properties, amount, and content of secondary metabolites in plants [13].

Secondary Metabolite Characteristics

Normally, compounds derived from plants are categorized into primary and secondary metabolites based on their role in the existence of plants. Primary metabolites are essential for the overall well-being of cell plant generated uniformly from plants, while secondary metabolites are frequently unique to certain plant families. These metabolites enable successful plants survival under particular ecological conditions [14]. Primary metabolism is responsible for the modification and synthesis of carbohydrates, fats, proteins, and nucleic acids. On the other hand, secondary metabolism is responsible for secondary metabolites production, which are typically with smaller size and lower molecular weight (less than 3000 Da.) [8]. Secondary metabolites exhibit a greater degree of structural complexity and possess a larger number of side chains when juxtaposed with primary metabolites [15]. The demarcation between primary and secondary metabolism lacks clarity: furthermore, these two classifications are interconnected due to the fact that primary metabolism furnishes the initial substrates that serve as foundations for the secondary metabolic pathways (Figure 1) [16] Secondary metabolites possess distinctive characteristics due to their limited production and varying construction. The abundance of chemical structures exhibited by secondary metabolites is remarkably extensive, with a significant portion displaying exceedingly intricate compositions [17].

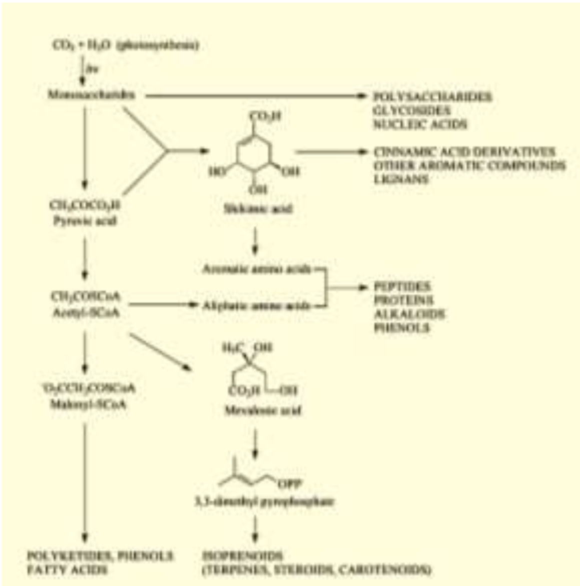

Figure1. Primary metabolites and their links to secondary metabolism [16]

Biological role of secondary metabolites

The utilization of plant metabolites commenced as early as 2600 BC, and over subsequent four thousands years, plants secondary metabolites were principally utilize in medicinal, toxic, in addition to nutritive purposes. Morphine, originating from "opium poppy (*Papaver somniferum*)" was initially isolated in 1806, signifying a groundbreaking epoch in secondary metabolite investigation [18]. Secondary plant metabolites exhibit a wide array of ecological functions in the natural world. These compounds play a vital role in all interactions between plants and their surroundings, and are essential for both defense mechanisms and reproductive processes [14]. plants possess the ability to synthesize secondary metabolites in order to defend themselves against a variety of pathogens such as viruses, bacteria, fungi, and other harmful agents. It is intriguing to show that certain secondary compounds have a significant part in determining the nutritional and sensory types of different plant-based products. Diverse features exhibited by these multifunctional organic compounds enable their application in the development of body care products, immune support formulations, and medical treatments, including analgesics, antioxidants, and blood pressure regulators. Additionally, they can be utilized as dietary supplements, bio-indicators, and in various other domains [18]. Bustos-Segura and Foley,[19] mentioned that the repertoire of these metabolites encompasses, for instance, substances that allure pollinators, substances that repel and deter herbivores, substances that counteract the growth of microorganisms during pathogenic invasions, or substances that safeguard against non-living stressors. Although these compounds confer substantial ecological benefits to the plant organism, there exists an expansive capacity to harness the biological activity of plant metabolites for human utilization. Secondary metabolites have a great importance in medicine, cooking spices , fragrances, and dyes [12]. they also function as allelopathic agents which exert an influence on the growth, viability, and procreation of neighboring flora. Moreover, additionally, they serve as a means of adapting to abrupt fluctuations in environmental conditions such as temperature, humidity, light intensity, and periods of drought [20]. Several of the secondary metabolites found in plants exhibit potent properties. These isolated compounds, such as alkaloids, have various applications. For instance, codeine as an antitussive, papaverine as a phosphodiesterase inhibitor, reserpine as an antihypertensive, morphine is commonly used as a pain killer, ephedrine as a stimulant, quinine as an antimalarial, ajmaline as an antiarrhythmic, Cocoa flavonols (coronary artery disease), caffeine as a stimulant, galanthamine as an acetylcholine esterase inhibitor, pilocarpine for glaucoma , scopolamine as a treatment for travel sickness, berberine for psoriasis, , capsaicin for rheumatic pains, colchicine for gout, yohimbine as an aphrodisiac, and various types of cardiac glycosides. Flavonoids such as Naringin (anti osteoporotic), cardamonin (anti-cancerous), anthocyanins (antidiabetic) helps in treating various diseases [21]. Most of the secondary metabolites that have been utilized in pharmaceutical production are derived from plants and their various components. These encompass primarily alkaloids, glycosides, flavonoids, volatile oils, tannins, resins, and so forth [22]. Epidemiological investigations have demonstrated that the consumption of plants abundant in poly phenolic compounds can lower the incidence of conditions such as "cancer, gastrointestinal tract disorders, heart disease, liver disease, atherosclerosis, neurological disorders and obesity". Flavonoids, which belong to the phenolic compounds, exhibit noteworthy potential as antioxidants, surpassing the efficacy of carotenoids and vitamins C, E, in certain instances. Antioxidants are thought to play a role in mitigating oxidative stress, a contributing factor in the development of chronic degenerative ailments such as cancer, premature aging and heart disease. Alkaloids, characterized by the presence of aromatic nitrogen, find application in the healthcare realm as antitumor agents, antipyretics, analgesics, nervous system stimulants, blood pressure regulators, and combatants against microbial infections [12]. The secondary metabolites can be classified into the following main compounds (Figure 2):

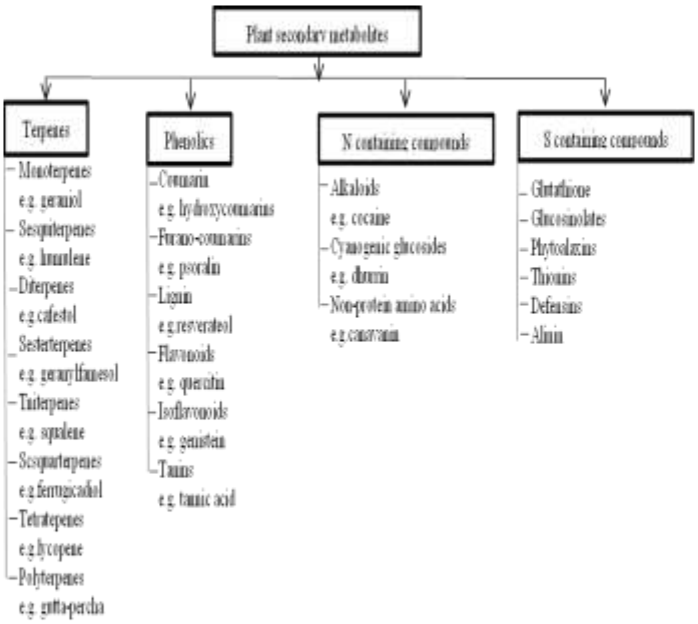

Figure 2. The four major types of secondary metabolites

1. Terpenes

Terpenes, as the constituents of essential oils, represent a myriad of organic, chemical compounds and stand as one of the most heterogeneous natural products found in plants, particularly with regard to their structural composition. This class of compounds is synthesized by a vast number of plant species, and their aromatic properties are attributed to their high volatility. It is well-established that terpenes derive their fundamental structural unit from isoprene (2-methyl-1,3-butadiene), a relatively straightforward hydrocarbon molecule, which is also prevalent among numerous other secondary metabolites in plants. 'Terpenoids bear resemblance to terpenes, albeit with a subtle distinction; terpenoids are the byproducts of terpenes that have undergone denaturation through oxidation, thereby possessing an additional oxygen atom within their chemical framework. These two terminologies exhibit a considerable similarity and are commonly employed interchangeably [23]. They are formed meanwhile mevalonic acid metabolic pathway (Figure 3) [12]. They form the most extensive category of secondary metabolites in plants, in which over 40,000 distinct molecules are distributed [24]. The compounds are also recognized as "isoprenoids" due to isoprene molecule being the fundamental building block that constitutes them [25]. They are categorized based on the quantity of isoprene units they encompass. The most uncomplicated group among them is hemiterpenes, which consist of a single unit of isoprene and a structure comprising 5C. The widely recognized hemiterpene is isoprene, a volatile substance produced by photosynthetically active tissues. The terpenes, divided into "monoterpenes" with two units (C_{10}), "sesquiterpenes" with three units (C_{15}), "diterpenes" with four units (C_{20}), "triterpenes" with six units (C_{30}), "tetraterpenes" with eight units, and "polyterpenes" with more than ten ones, comprise the remaining two groups [26]. Numerous botanical organisms possess terpenes within their blossoms and fruits, characterized by amalgamations of evaporative substances that yield distinctive aromas. Notable examples include "lemon, mint, eucalyptus, ginger, and basil" [27]. Terpenes fulfill numerous biological roles and participate in the primary as well as secondary metabolic processes of botanical organisms. Within the central metabolism, they fulfill various roles such as being photosynthetic pigments "carotenes" acting as electron carriers "ubiquinone and plastiquinone" regulating plant growth and development "giberilins, strigolactones, brassinosteroids" constituting cell membranes "phytosterols" and participating in protein glycosylation [25]. Terpenes function as toxic compounds, food deterrents for insects and defense molecules. Additionally, certain plants utilize terpenes as attractants for pollinators or as dispersers [28, 29, 30].

2. Alkaloids

They are constitute a category of nitrogenic compounds that are predominantly present in flora, albeit not exclusively. Over 27,000 distinct alkaloids have been identified thus far, with 21,000 originating from various plant species. The composition of alkaloids involves the presence of one or more nitrogen atoms in the configuration of primary, secondary, or tertiary amines. These nitrogen atoms confer alkaloids with fundamental characteristics, allowing them to exist as water-soluble salts following interaction with acids. Additionally, alkaloids containing quaternary nitrogen atoms can be observed in nature [12]. Even in cases where there lacks a standardized categorization for alkaloids, numerous standards have been utilize for the purpose of organizing them. These include their biosynthetic origin, the existence of a fundamental heterocyclic nucleus within their structure, their pharmacological attributes, and their distribution among various plant families [31]. Alkaloids can be observed in diverse plant components such as foliage, branches, bark and seeds. Nearly all naturally occurring alkaloids exhibit specific physiological actions. While certain alkaloids possess toxicity, others serve as valuable medicinal agents [32]. The physical characteristics of alkaloids are typically colorless and exhibit optical activity. They are primarily found in crystalloid form. For instance, "quinine and nicotine" possess a melting point ranging from one hundred to three hundred ºC. Generally, alkaloids contain one nitrogen atom, with exceptions such as Ergotamine, which contains five nitrogen atoms. These nitrogen atoms can exist as primary, secondary, or tertiary amines, all of which possess basic properties. The extent of basicity is contingent upon the molecular structure and functional group. Although the presence of alkaloids is not indispensable for the plant, there exists evidence that suggests the functions which these compounds fulfill in vegetables. Initially, they were considered as byproducts of nitrogen metabolism and nitrogen reservoirs in the plant, as well as growth regulators. However, it is currently widely acknowledged that their primary function is to safeguard the plant against insects and herbivores due to their toxicity and deterrent properties. While certain alkaloids act as plant protectant against predators or microorganisms through their toxic or repellent characteristics, others achieve this by competing with other plant species in a specific habitat through allelopathic substances [33]. Plants create most of their alkaloids, which are harmful substances that act as defensive mechanisms against other living things. Basic in nature, alkaloids, primarily originating from plant sources. Numerous advantageous characteristics of alkaloids are well-known. such as anti-plasmodic, anti-psychotic, and anti-inflammatory as well as some alkaloids' potential anti-neoplastic properties. Spokesperson [34]. They are derived from one of more prevalent amino acids: "lysine, tyrosine, and tryptophan". Plants have been found to contain over 12,000 alkaloids, belonging to more than 150 families, with approximately twenty percent of flowering plants possessing alkaloids. In the plant kingdom, these compounds generally exist as salts of organic acids, such as "acetic, malic, lactic, citric, oxalic, tartaric, tannic, and other acids". Certain alkaloids with weak basic properties, like nicotine, are naturally occurring. Additionally, presence of specific alkaloids are in the form of sugar glycosides, such as "glucose, rhamnose, and galactose" such as solanum alkaloids "solanine". Alkaloids can also exist as amides "piperine" and as esters "atropine, cocaine" of organic acids [35]. True alkaloids, protoalkaloids, polyamine alkaloids, peptide and cyclopeptide alkaloids, and pseudoalkaloids are the four main categories into which all alkaloids can be divided. There may be some exceptions to this, such as galantamine, which is thought to be linked to isoquinoline alkaloids despite lacking an isoquinoline building block. The acetate or shikimate pathways (Figure 4) may yield the remaining alkaloids' building blocks. Alkaloids contain a broad range of biological functions, which makes them valuable from a pharmacological perspective [36]. Since they are mainly soluble in aqueous solutions, protonating the nitrogen in water makes it easy to extract them. Known for their anxiolytic, analgesic, and hallucinogenic properties [37], During the process of plant development, there occurs a modification in both physiological and chemical aspects, resulting in alterations in alkaloid structure as well as deposition sites. An example of such modification can be observed in Macleaya cordata, where the benzylisoquinoline alkaloid protopine undergoes rearrangement, leading to the formation of sanguinarine. Furthermore, it is noteworthy that sanguinarine tends to accumulate in the leaves during the vegetative growth phase, while in times of seed formation, it is predominantly found in the fruit shells [38]. this group contains some of the most well-known and notorious substances, including morphine, caffeine, nicotine, and cocaine. These chemicals also frequently have physiological effects on the central nervous system. Alkaloids make about 50% of medications derived from plants, while being a minor group of metabolites. Some plant families like "nightshades (Solanaceae) and the poppy family (Papaveraceae)" particularly, are rich in different alkaloids. In other cases, certain plant species present the occurrence of a typical alkaloid e.g. "Coffea sp. / caffeine, Conium maculatum / coniine" [39].

3. Phenolic compound

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Phenolic compounds are a very varied collection of secondary metabolites, these are substances that have an aromatic hydrocarbon and a hydroxyl group immediately bonded to them. In terms of chemistry, the most basic example of this class is phenol [40]. The categorization of phenols relies on the determination of the quantity of Carbon atoms and aromatic rings present in the molecules (ranging from 1 or 2 benzene rings to a multitude of polyphenols). The differentiation is dependent on the chemical composition and characteristics: "simple phenols, acidic phenols, acetophenones, and phenylacetic acids, hydroxycinnamic acids, coumarins, flavonoids, biflavonyls, benzophenones, xhantones, stilbenes, quinones and betacyanins. Lignans, neolignans, tannins, and phlobaphenes". The latter group of substances consists of polymers, which possess structures that are more intricate in nature [41]. All plant organs, including those of the "Gentianaceae, Theaceae, and Orchidaceae" families, produce and collect natural phenols, which make up two – three percent of all plant organic mass, and occasionally up to 10%. These substances have a significant impact on plant development, stem and root elongation, seed germination inhibition, wound healing, and cell division [42, 43]. The synthesis of phenolic substances takes place in the plant body through the participation of enzymes from three principal pathways of amino acid phenylalanine transformation [44]:

- "polyketide pathway elongated side chains of phenylpropanoids, flavonoids are formed C6 - C3 C6"
- "shikimatic pathway synthesis of phenyl-propanoid derivatives C6 -C3"
- "acetate-mevalonate pathway formation of aromatic terpenoids, in particular monoterpenes"

Gao *et al.*, [45] show more that phenolic compounds play a crucial role in determining the pigmentation of leaves, flowers, and fruits. Moreover, they actively contribute to plants reproductive and growth by participating in the defense mechanisms toward pathogenic microorganisms, parasites, predation ultraviolet radiation (UV-light). The synthesis of phenolic substances occurs when plant cells identify potential pathogens through the recognition of preserved pathogenic-associated molecular patterns, prompting a biological response. Consequently, infection development is impeded well before the pathogen can spread throughout of entire organism. Additionally, phenolic compounds are present in various plant-derived foods and beverages, including cereals, fruits, vegetables, legumes, tea, coffee and chocolate among others. Furthermore, these substances are responsible for therapeutic features found in plants, rendering them highly valuable in the fields of cosmetology, pharmacology, and medicine. The examination of specific phenolic contents provides a basis for distinguishing between plant species, thereby serving as a molecular taxonomy marker.

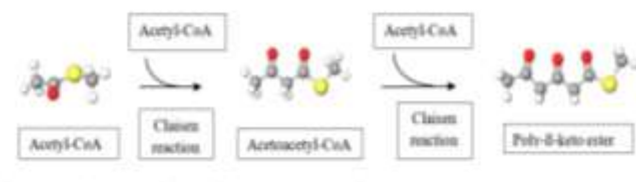

Figure 3. Melonate acetate formation pathway (modification) [8]

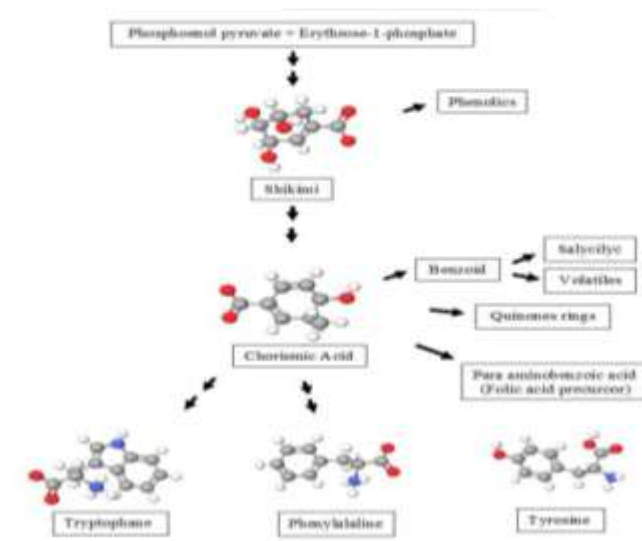

Figure 4. Pathway of shikimic acid formation from erythrose (modification) [46]

4. Saponins

Saponins exhibit a distinctive property in the form of froth, whereby upon interaction with water and agitation, an enduring foam is generated. Saponins possess high solubility in water while can not soluble in ether. Furthermore, they impart an induce sneezing and irritation of the mucous membranes and bitter flavor. These compounds possess the ability to eradicate erythrocytes or cause hemolysis, thus exhibiting toxicity towards ectothermic organisms. The term sapotoxins is commonly employed to denote saponins that are particularly harsh or toxic. Saponines chemical configuration consists of comprising aglycones and glycons to form a glycoside. "Glycon" component encompasses saccharide entities including glucose, fructose, and other forms of saccharides. The aglycone segment, on the other hand, is constituted by sapogenin. Natural elements containing saponins act as surfactants due to amphiphilic property of these substances. These surfactants are commonly utilize in the formulation of soap products. A surfactant is characterized by possessing both a lipophilic and hydrophilic group, thus enabling it to combine a mixture consisting of oil and water [47]. These compounds can act as reducing blood sugar levels, antibacterial and antiviral agents, augmenting vitality, enhancing the immune system, and mitigating blood clotting. As stated by [48], saponin compounds possess the capability to remedy various ailments.

5. Steroids

They are a collection of lipophilic compounds with low molecular weight, originating from diverse sources such as cholesterol, terrestrial organisms, marine organisms, and synthetic production. This group encompasses bile acids, several hormones secreted by the adrenal cortex and gonads, and a limited number of hydrocarbons [49]. The basic framework of steroids molecules consist of seventeen carbonic atoms collected from the combinations between 4 rings, 3 of which are cyclohexane and cyclopentane known to be a non-flat molecule with hexagonal C-rings. Steroidal compounds manifest themselves as crystals that exhibit needle-like shapes, revealing distinctive features encompassing hydroxyl groups, methyl groups, and unconjugated double bonds [50]. These steroids have numerous medicinal applications, despite their frequent association with detrimental effects on health. These steroids possess the potential for enhancing fat loss and promoting muscle growth, while also presenting a lower incidence of side effects. A considerable number of synthetic steroids have been extensively utilized as anesthetics, anticancer agents [49], anti-asthmatics [51], anti-hormonal medications [52], anti-inflammatory drugs, contraceptive agents, cardiovascular agents, and antibiotics [53].

Conclusions

Plants possess the capability to produce secondary metabolites as well as primary metabolites, and the production of such compounds varies among these plants. These compounds encompass terpenes, alkaloids, phenols, saponins, and steroids, all of which assume significant biological functions within diverse domains, notably the realm of medicine.

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مركبات الأيض الثانوية النباتية وتصنيفها وأدوارها البيولوجية: مراجعة

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الخلاصة:

يعد الأيض هي العملية الحيوية الأهم التي تجري على مستوى الخلية الحية وذلك لما تتضمنه من بناء جزيئات حيوية مهمة وكذلك هدمها لتحرير الطاقة اللازمة لإنجاز الفعاليات المختلفة. هنالك نوعين من الأيض، الأولي الذي تبنى من خلاله مركبات عضوية أساسية للنمو والتكاثر وغيرها كالبروتينات والكربوهيدرات والدهون والأحماض النووية. تعد النباتات مصدرا مهما من مركبات الأيض الثانوية التي تمتلك خصائص بيولوجية متنوعة يمكن للإنسان استغلالها لصالحه. تنتج هذه المركبات من خلال التحولات الكيميائية لعملية التمثيل الغذائي الثانوي تشمل مركبات الايض الثانوي هذه على التربينات والقلويدات والمركبات الفينولية والصابونينات إضافة الى الستيرويدات والتي لكل منها خصائص وصفات تميزها عن المجاميع الأخرى وكل نوع من هذه الأنواع له أدوارا حيوية مهمة في اغلب الخلايا الحية. يتم تصنيع مركبات الأيض الثانوية هذه بكميات صغيرة تكفي لتلبية احتياجات النبات المحددة استجابةً لعوامل بيئية معينة. وتمتلك هذه المركبات خصائص فريدة تمكنها من القيام بأدوار بيولوجية مهمة ليس فقط في حياة النباتات، ولكن أيضًا في حياة الكائنات الحية الأخرى، بما في ذلك الإنسان.

الكلمات المفتاحية: *مركبات الايض الثانوية، التربينات، القلويدات، الفيتولات، الصابونينات، الستيرويدات.*