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Application of Plant Products in the Synthesis and Functionalisation of Biopolymers

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Abstract: The burning of plastic trash contributes significantly to the problem of air pollution. Consequently, a wide variety of toxic gases get released into the atmosphere. It is of the utmost importance to develop biodegradable polymers that retain the same characteristics as those obtained from petroleum. In order to decrease the effect that these issues have on the world around us, we need to focus our attention on specific alternative sources capable of biodegrading in their natural environments. Biodegradable polymers have garnered much attention since they can break down through the processes carried out by living creatures. Biopolymers' applications are growing due to their non-toxic nature, biodegradability, biocompatibility, and environmental friendliness. In this regard, we examined numerous methods used to manufacture biopolymers and the critical components from which they get their functional properties. In recent years, economic and environmental concerns have reached a tipping point, increasing production based on sustainable biomaterials. This paper examines plant-based biopolymers as a good resource with potential applications in both biological and non-biological sectors. Scientists have devised various biopolymer synthesis and functionalization techniques to maximize its utility in various applications. In conclusion, recent developments in the functionalization of biopolymers through various plant products and their applications are discussed.

Keywords: Antibacterial and antiviral activity; Biomedical materials; Wound healing; Targeted and controlled drug delivery; Tissue engineering; Regenerative medicine

1. Introduction

Biopolymers are a type of polymers that is synthesized by living organisms. The origin of the term "biopolymer" can be traced back to the Greek terms "bio" and "polymer," which together symbolise the natural world and living organisms [1]. The term "biopolymers" can refer to either natural polymers, which are defined as any polymer that occurs naturally in the environment (such as cellulose or starch), or bio-based polymers, which are artificially produced from natural resources. They are long bio-molecule chains comprised of monomeric units repeating in a chain-like form and bonded together by covalent bonds. Examples of biopolymers include those with amino acids, sugars or nucleotides as their monomeric units, such as chitin, starch, cellulose, peptides, proteins, DNA, and RNA. Living things are capable of producing a mind-boggling variety of polymers, which can be categorised as follows: polysaccharides such as starch, cellulose, chitosan; poly amino acids and proteins; organic polyoxoesters such as poly(hydroxyalkanoic acids). It has been revealed that the biopolymers are both biocompatible and biodegradable, qualities that make them useful in a variety of applications. For example, in the food industry, they can be used as edible coatings, emulsions, and packing material. In the pharmaceutical industry, they can be used as drug carrier materials [2], medical prosthetics [3], dressing materials [4] and tissue scaffolds [1].

For example, Cyclodextrins are the cyclic oligomers used in drug delivery, food, as well as pharmaceutical industries and environmental engineering that are produced from natural polymer starch or its derivatives. Complexation of natural compounds such as dietry plant bioactives results in improved bioavailability, stability and bioactivity in various laboratory model organisms [5].

Recent years have seen a rise in public awareness of the dangers posed to the environment by the combustion of fossil fuels and the disposal of waste produced by the production of petrochemicals. Many studies have looked into potential renewable and biodegradable substitutes to petro products that could reduce environmental impact [5]. Biopolymers, which are primarily biodegradable materials made up of renewable raw materials, are one such viable answer. There could be significant environmental benefits to switching from synthetic polymers to biopolymers in commonly used products. Because biopolymers are derived from living organisms, they can be continuously replenished, so there is no danger of exhaustion. However, polymers are often derived from fossil fuels like oil and coal and hence have a limited resource capacity. Biopolymers offer the added benefits of being biodegradable and releasing fewer greenhouse gases during production, both of which can have a significant impact on our overall carbon footprint [6].

1.1. Classification of Biopolymers

There are numerous categories that can be applied to biopolymers, and each one applies to a different scale of evaluation. Origin is a key characteristic that can be used to differentiate natural, synthetic, and microbial biopolymers, as shown in Figure 1 [7]. Furthermore, these biopolymers can be categorised according to their biodegradability, polymer backbone, and the sort of monomers that are expressed.

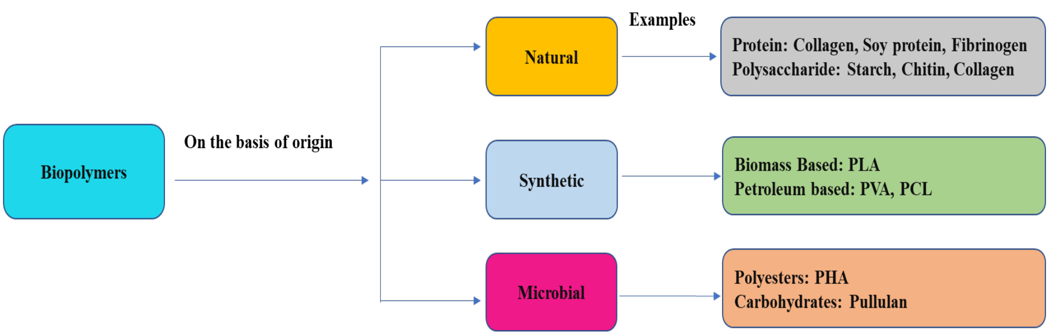

Figure 1. Classification of Biopolymers on the basis of origin.

1.2. Applications of Biopolymers

Biopolymers are useful in a wide variety of contexts and find extensive applications in many aspects of modern life. In addition, these materials constitute the basis for the production of hundreds of different items that we make use of in our everyday lives. In addition to this, they play a significant part in both the industry in which they operate and the overall economy. The production of biopolymers, which provide a more environmentally friendly alternative to plastic, is experiencing tremendous expansion. The most popular applications for biopolymers are in the packaging, agricultural, and medical industries [7]. The different application of biopolymers are shown in Table 1.

Table 1. Different types of plant derived biopolymers, along with their respective applications.

Biopolymers	Applications/Uses	Reference
Cellulose	Adsorption and Separation Materials, Thermal Insulation Material, Precursor of Carbon Aerogels, Biomedical Materials, Carrier of Metal Nanoparticles and Metal Oxides	[8]
Xylan	Coating and Film, Dairy products, Pharmaceuticals, Prebiotic, Antioxidant activity, Jam and Jelly, Bakery	[9]
Gum gum	In drilling fluid/hydraulic fracturing, Explosives, food additive in food industry, Polysaccharides based superabsorbent polymers in agriculture, film forming and thickening properties to the fabric in textile industry, Drug delivery, Medicinal and pharmaceutical, Dietary fibre, Cosmetics	[10]
Gum Arabic	Food additive, Microencapsulator, Cardio-, reno-, gut-, dental-protective, Anti-inflammatory agent and anticoagulant, Antimicrobial agent, Drug delivery agent, Sensor and tumor imaging, Shelf-life enhancer, Inducer of satiety and anti-obesity	[11]
Starch	Self-Healing polymeric materials, Application of starch in porous foam structures, Applications of starch in water treatment, excipient in the pharmaceutical industry, drug delivery using starch, Antimicrobial films and coatings based on starch	[12]
Zein	As a natural pharmaceutical excipient in drug-delivery systems, Zein-Based Nanoparticles in the Food Industry, Zein as a Carrier of Pesticides, Zein as a Potential Material for Bandages, Zein on Tissue Engineering	[13]
Latex	Biocompatibility in vitro, Tissue repair, Regeneration of bones and teeth, Proteins of the NRL serum: the proteins present in the NRL (natural latex rubber) serum have several interesting biological properties, such as angiogenic, anti-inflammatory, antimicrobial, osteogenic differentiation, and cell proliferation, NRL-based matrices as drug delivery system, as a delivery system for several peptides and proteins, used for delivery of plant extracts with medicinal properties	[14]
Xyloglucan (Tamarind xyloglucan)	Numerous applications such as thickening, gelling and stabilizing agents in food, to sizing and weaving in textiles, to adhesive and binding agents in industry, Antimutagenic activity, as dietary fiber, Antiviral activity, as a mucoadhesive, drug delivery, as extracellular matrix (ECM), as antioxidant and antitumor, as solid-phase diagnostics, as a biotic pesticide, as a surfactant, as a drilling fluid, as a flocculant	[15]

2. Molecular Farming

Molecular farming is the use of biotechnology to genetically modify crops for the aim of producing proteins and compounds for medical and industrial use. Most people in the underdeveloped countries can't afford treatments made with current technology because of how expensive they are. What we need to do create not only innovative therapeutics but also cost-effective alternatives to the current options. The need for biopharmaceuticals is expected to increase, and molecular farming may provide a solution. Therapeutics derived from plants are advantageous in many ways, including their low cost, lack of side effects, high yield, and convenience of storage [16]. Even as far back as the Neanderthal era (about 130 000 years ago), there is evidence that plants were utilised to treat ailments and speed up the healing process, specifically for wounds [17]. Roughly thirty percent of all contemporary drugs are derived from plants. The chronicles of medical history are replete with tales of plants that were transformed into medicines. Salicin, the active component of aspirin, was first extracted from the bark of white willow trees in the early 1800s. Even in the modern era, pharmaceutical companies continue to trawl rain forests in search of traditional cures for contemporary illnesses [17].

Molecular farming involves cultivating plants to generate recombinant proteins with added value, such like antibodies, subunit vaccines, and enzymes. Although several methods of molecular farming have been identified, commercial platforms are now focusing on just three: transgenic plants, cell and tissue cultures, and transient expression systems [18]. Utilizing plants as production facilities for biopharmaceuticals is a relatively new strategy made possible through genetic engineering. Tobacco plants engineered to produce human growth hormone were the first to express a pharmaceutically relevant protein [19]. Both bacterial and eukaryotic expression techniques have been used to produce recombinant proteins. When compared to the mammalian system, prokaryotic production is much more cost-effective and convenient [16]. However, the biological function of many mammalian proteins relies on posttranslational modifications, such as protein glycosylation, that cannot be carried out by prokaryotic production systems. Therefore, prokaryotic expression systems may not be as widely used as they formerly were. The costs associated with maintaining cell cultures and scaling up production when using mammalian cells are extremely expensive. Plants, on the other hand, share many similarities with the protein production and modification processes in animal cells, allowing for a level of protein modification that is equivalent to those seen in animal tissues [16]. Recombinant human proteins have been shown to include plant-specific glycans, which has been cited as a potential negative in the context of molecular pharming. The low immunogenicity risk of plant glycans is now widely acknowledged. The advent of numerous technologies for removing plant glycans and replacing them with human-like counterparts paved the way for the development of "bio-better" products with specific glycan profiles that improve their performance [20].

2.1. Different strategies for molecular farming

The expression techniques that are utilised for the synthesis of recombinant proteins in plants can either be stable expression or transient expression. Plant molecular forming (PMF) depends on the following methods for the expression of potential vaccine candidates: stable nuclear transformation, stable chloroplast transformation, or transient expression. Hydroponically grown plants are transformed in a stable manner using plant viral vectors, and the resulting recombinant proteins are harvested from the growth media. The different strategies are described in the Figure 2 [21].

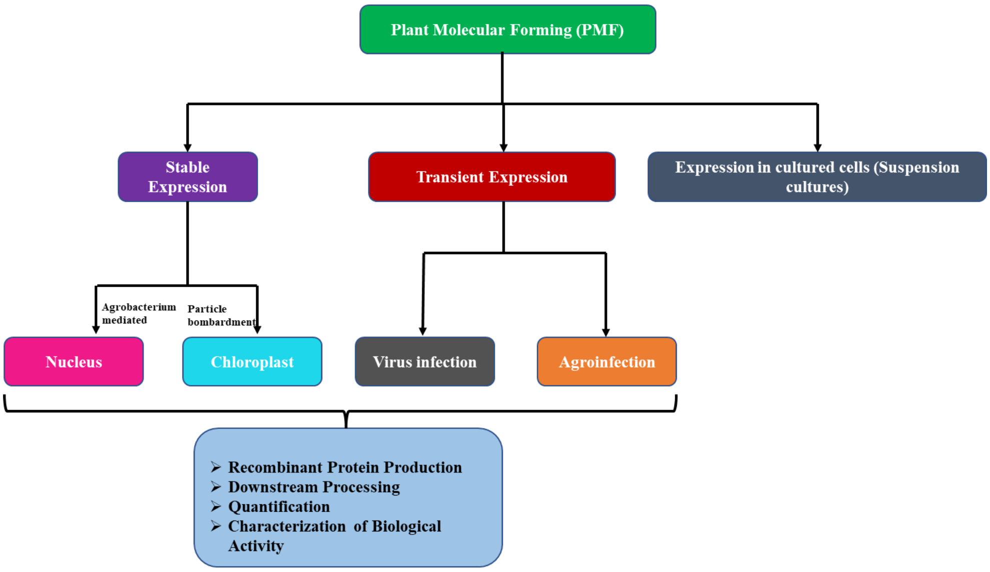

Figure 2. Critical summary of the methods used to modify plants to synthesize recombinant proteins for pharmaceutical and non-pharmaceutical applications.

2.2. Benefits, challenges and perspective of molecular farming

From a financial standpoint, plant-based biomolecule manufacturing is preferable to microbial and animal cell culture since it requires less expensive equipment, substrate, and electricity. By harnessing the energy from the sun, plants may create whatever protein or metabolite they need from carbon dioxide and inorganic substances [22]. Producing recombinant proteins in plants has several potential benefits, particularly in terms of the generation of biopharmaceuticals that are applicable to clinical medicine. To begin, industrial facilities that use fermentation or bioreactor systems are more expensive to operate than plant-based systems. Second, there is currently existing technology that can be used to collect and process enormous quantities of plants and plant products. Third, the necessity for purification can be eliminated if the plant tissue that contains the recombinant protein is employed in the production of a food product (edible vaccines). Fourth, plants can be coaxed into targeting proteins into intracellular compartments, where they will be more stable, or even into directly expressing those proteins in particular compartments (chloroplasts). Fifth, the amount of recombinant product that can be created is becoming progressively closer to being able to be produced on an industrial scale. Consequently, the potential dangers to human health posed by contamination with dangerous human pathogens or chemicals are reduced as much as possible [23].

Despite the tremendous advantages of plant-based production systems over traditional ones, they still have several drawbacks that make them less popular in society. Non-mammalian glycosylation and the issue of low yield, which can be caused by insufficient transcript expression or by the instability of the recombinant protein, are the two main obstacles that prevent plants from being fully utilised as alternative bioreactors to mammalian cell culture, in particular. It is also being given the proper attention to choose the host plant that will best accommodate any particular biomolecule as well as downstream processing [24]. Plants have their own set of benefits, but they can't compete with the well-established microbial and mammalian systems, which have good manufacturing and regulatory requirements already in place. The time it takes to get a therapeutic protein from the laboratory to the market remains long, despite the fact that years of study have demonstrated the feasibility of expressing many such proteins in plants. Therefore, in order to make progress, it is necessary to take advantage of the commercial viability and economic sustainability of technology by creating veterinary vaccinations, non-pharmaceutical diagnostics, cosmetic items, and industrial enzymes in plants. These types of products have a lower regulatory load when compared to therapeutic proteins [21].

3. Secondary metabolites

Secondary metabolites are organic compounds that are produced by an organism but play no role in its regular development. Secondary metabolites frequently play a crucial role in plant defence and are not essential for the immediate survival of the organism, in contrast to primary metabolites, which actively participate in photosynthesis and respiration and are therefore essential for the species' continued existence. A wide variety of organisms—from plants and fungi to bacteria and algae to animals—are responsible for synthesising these compounds [25]. Kossel is credited with introducing the idea of secondary metabolite to the field of biology. He pioneered the concept of secondary metabolites as distinct from primary ones. Czapek made a significant advance thirty years later when he devoted an entire volume to what he called "endproduckt" in his series of books titled "plant biochemistry". He hypothesised that secondary modifications, such as deamination, occurred in the course of nitrogen metabolism and gave rise to these compounds. These secondary metabolites quickly became characterised by their low quantity compared to the primary molecules produced by plants, often less than 1% of the total carbon, or by a storage mechanism that typically takes place in specialised cells or organs [26]. Secondary metabolism is sometimes seen as a way to safely store or eliminate "waste" metabolites that outcome from primary metabolism. These secondary metabolites are frequently produced at their highest levels throughout a switchover from active growth to stationary phase, and also the producer organism can grow without their synthesis, suggesting that secondary metabolism is not necessary, at least for short-term survival. According to a second viewpoint, the genes are involved in secondary metabolism serve as a "genetic playing field" on which natural selection and mutation can work together to fix new advantageous features through evolution. According to a different perspective, secondary metabolism is an essential component of cellular biology and metabolism; it depends on primary metabolism for the supply of the necessary enzymes, energy, substrates, and cellular machinery and aids in the producer's long-term survival [27]. These metabolites protect plants from biotic or abiotic stress. Secondary metabolites can be induced by stress. Primary metabolites support nutrition and reproduction. Secondary metabolites employed as medications, flavours, perfumes, pesticides, and colours have high commercial value. Such developments will broaden and improve the utilisation of higher plants as chemical sources, especially for medicines. The investigation of biological processes and the structure of secondary metabolites is crucial since it has allowed for applications in numerous fields. Numerous secondary metabolites are employed as flavour enhancers, insecticides, resins, gums, scents, and herbicides. Persistent and increasing work in this field should lead to biotechnological production of specialised, valuable, and undiscovered plant compounds. The therapeutic properties of plants are due to secondary metabolites, however these compounds are found only in small amounts in plants. Over the past 50 years, there has been an extensive research into the secondary metabolites of plants [28].

Due to the low concentration (in parts per million) at which many of these compounds occur in nature, massive harvesting is required to obtain sufficient quantities of the medication. Therefore, an environmentally friendly technique must be used to obtain complex chemical compounds biosynthesized by endangered plant species. There are no long-term options for meeting the market need other than growing medicinal plants or producing plant secondary metabolites in vitro. Plants are known to accumulate secondary metabolites after being exposed to numerous signal molecules or elicitors [29].

3.1. Classification of secondary metabolites and their use

Researchers have shown that secondary metabolites in plants are responsible for most of their medicinal efficacy and pharmacological effects, hence this class of compounds is becoming increasingly important to the field of natural products chemists. The classification of secondary metabolites has taken into account their chemical structure (such as the occurrence of rings or sugars), composition (such as whether or not they contain nitrogen), solubility in organic solvents or water, and metabolic process. The biosynthetic route has been the most often utilised criterion for classifying the secondary metabolites in plants. This suggests that terpenes, phenolic molecules, and alkaloids are the three main categories into which the secondary metabolites in plants can be subdivided [30]. The classification and examples of secondary metabolites are shown in the Figure 3 [31] and Table 2 respectively.

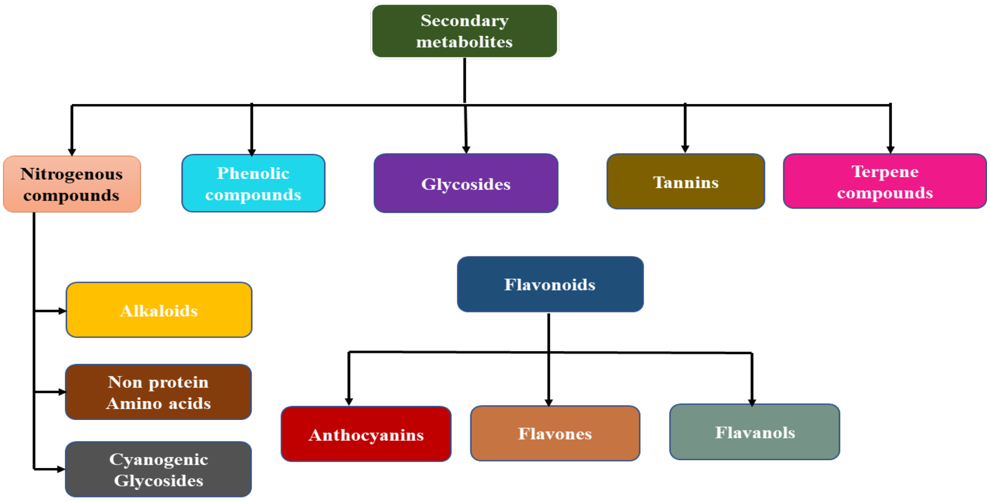

Figure 3. A general category for the secondary metabolites found in plants.

Table 2. Examples of plant secondary metabolites and its uses.

Compound	Source	Uses	Reference
Umbelliferone	Sweet potato	Sunscreen agent	[32]
Xanthone	Gentianaceae family	Hepatoprotective	[33]
Tannin	Pistacia lentiscus L. (lentisk)	Anthelmintic activity	[34]
Camptothecin	Camptotheca acuminata	Anticancer and antiviral	[35]
Gingerols	Ginger (Zingiber officinale)	Antioxidant, antitumor and anti-inflammatory	[36]
Gossypol	Gossypium hirsutum	Biopharmaceutical applications	[37]
Cinchona officinalis	Cinchona officinalis L	Antimicrobial	[38]
Capsaicin	Green and red peppers	Anti-cancer	[39]
Saffron	*Crocus sativus* L	Coloring and flavoring food agent	[40]
Taxol	Taxus brevifolia	Anticancer	[41]
Vincristine and Vinblastine	Catharanthus roseus	Anticancer	[42]
Berberine	Coptis	Antibacterial	[43]

In addition to their use in medicine, secondary metabolites have numerous other applications, including: the production of dyes, the development of agrochemical insecticides, the provision of raw materials for industries, the development of perfumes and cosmetics, and the production of colouring and flavouring agents. In this article, we will go over some of the secondary metabolites more salient features.

3.1.1. Terpenes: function and its uses

Dumas coined the term terpene in 1866, and it was originally derived from the Latin word 'turpentine' (Balsamum terebinthinae), which refers to a liquid extract of pine trees. Terpenes are the most abundant natural product and show the greatest structural diversity. They can have either a linear hydrocarbon or a carbocyclic skeleton. Approximately 55,000 members belong to this group. The terpenes are converted into terpenoids through oxidation, hydrogenation, or dehydrogenation. The isoprene unit (C5H8), a 5-carbon molecule that forms the backbones of terpenes, was postulated by Wallach in 1887 [44]. Since fatty acids don't play a role in their production, they are chemically speaking non saponifiable lipids. They get their name from the fact that the isoprene molecule serves as their backbone. They are categorised according on how many isoprene units they have. Hemiterpenes, which only have one isoprene unit and five carbons, are the simplest class to understand. Isoprene is the most well-known hemiterpene; it is a volatile product released by photosynthetically active tissues [30]. Sessile plants can communicate with other species including nearby plants, pollinators, and enemies of herbivores via the air-bone infochemicals provided by the terpenoids' volatilty. Plant volatiles are essential for three major physiological processes: plant-plant communication, symbiotic-organism signalling, and pollinator attraction [45]. It has been reported that many terpenoidal compounds exhibit immunodmodulatory, chemotherapeutic, antiviral, antimicrobial and antifungal effects. They can be utilised in the storage of agricultural products as natural pesticides and protective agents [46].

3.1.2. Phenolic compounds: function and its uses

Phenolic chemicals are a type of secondary metabolite that is widely distributed throughout plants as well as foods and beverages that are derived from plants. They exhibit a wide variety of structures, some of which are quite simple (such as vanillin, gallic acid, and caffeic acid), while others, such as polyphenols consisting of stilbenes, flavonoids, and polymers generated from these diverse groups, are quite complex. For instance, just the flavonoid family has been recognized for the discovery of over 8,000 different compounds, and the number is ever growing [47]. The bitter taste from the fruit comes from phenolic chemicals, which react with salivary glycoprotein to produce an unpleasant taste. The colour of many different fruits and vegetables can also be altered by the addition of phenolics. It is widely accepted that phenolic compounds are responsible for the variety in flavor and colour found among various wine brands. Plants include a variety of phenolic compounds, including flavonoids, phenolic acids, stilbenes, lignans, and tannins [48]. The health benefits of this secondary metabolite have led to its rapid rise in popularity. They can be found in high concentrations across the entire species of plant and are made up of a hydroxyl group (-OH) connected to an aromatic ring. The flavonoids are the first class of phenols. Flavonoids are vacuolar pigments that are found in plant cells. Two phenyl rings and one heterocyclic ring are fused together to form its basic structural unit of C6 - C3 - C6. They are abundant in plants and play a significant role as secondary metabolites, most notably in the members of the family Rutaceae [31]. Experts encourage eating lots of fruits and vegetables because they contain phenolic chemicals that help prevent and treat disease. Phenolic chemicals, for instance, are commonly utilised as antioxidants and antimicrobials. The food and pharmaceutical industries can benefit from the phenolic compounds because of their antiallergenic, antiatherogenic, and antiinflammatory properties [49]. Considering phenolic compounds' antioxidant potential, they may be included in functional foods as all-natural additives. Antimicrobial phenolic chemicals, like those found in olive mill wastewater, have been used to increase the shelf life of baked products [50]. It is also reported in literature that products that include phenolic compounds may be useful in lowering the threat of cancer, cardiovascular disease, and neurological disorders [49].

Polyphenols possess multiple functions that also include metal chelating capacities. Polyphenols are also utilized for their anti-amyloidogenic properties as well and can directly prevent or modulate amyloid aggregation by inhibiting amyloid fibril formation in multiple amyloidogenic proteins such as Aβ, amylin, tau and α-synuclein. [50][51]

There are two categories that can be applied to phenolic acids: derivatives of benzoic acid, such as gallic acid, and derivatives of cinnamic acid, such as coumaric, caffeic, and ferulic acid. Gallic acid is an example of a derivative of benzoic acid. Caffeic acid is the most common phenolic acid, and it is found in several fruits and vegetables. It is typically esterified with quinic acid, like chlorogenic acid, the primary phenolic molecule in coffee. Ferulic acid, which is abundant in cereals and esterified to hemicelluloses, is another prevalent phenolic acid [51].

3.1.3. Alkaloids: function and its uses

The term "alkaloid" refers to the fact that the vast majority of alkaloids fall into the category of basic (alkaline) chemicals. More than 12,000 different alkaloid compounds have been discovered, making this category of secondary metabolites one of the most extensive on the planet. The group is characterised by a large variety of structural formulas, which originate from a variety of biosynthetic pathways and exhibit a wide range of pharmacological effects [25]. Alkaloids are a type of secondary metabolite with basic nitrogen atoms. Alkaloids also contain several similar chemicals with neutral and slightly acidic characteristics. This group may also contain oxygen, sulphur, and, in very rare instances, additional elements including chlorine, bromine, and phosphorus. These elements are in addition to carbon, hydrogen, and nitrogen. Alkaloids are produced as secondary metabolites by a wide range of species, including bacteria, fungi, and animals, but most notably by plants [52]. Although there isn't a universal system for categorising alkaloids, several researchers have attempted a classification based on characteristics including biosynthetic origin, the existence of a basic heterocyclic nucleus in the structure, pharmacological effects, and plant genus or species distribution. The biosynthetic origin of the alkaloids is one of the criteria that has been applied pretty often. There are three distinct types of alkaloids based on this criteria: (a) true alkaloids, (b) protoalkaloids, and (c) pseudoalkaloids [30]. Alkaloids are linked to a vast array of pharmacological actions. Even in minute quantities, many substances are lethal and hazardous. It would appear that defence mechanisms are connected to the function of alkaloids in both plants and animals. The presence of toxicity in an organism can be a useful tool in the fight against herbivores and other predators [25]. Alkaloids possess extraordinary physiological and toxicological features that are largely exerted on the central nervous system, with a predominance in a few of its levels. They can be utilised as medications for these reasons. The pharmacological and therapeutic significance of alkaloids provides a strong impetus to continue their chemical-biological investigation. This is one among the most significant secondary plant metabolites having medicinal value [30].

3.1.4. Flavonoids: function and its uses

A significant group of natural products are flavonoids; in specifically, they are a group of secondary plant metabolites with a polyphenolic structure that are prevalent in fruits, vegetables, and some drinks. They are divided into different categories such as flavones, flavanols, isoflavonoids, bifalvonoids and anthocyanidins. They have a variety of beneficial biochemical effects, as well as antioxidant properties, which are related with a wide range of disorders, including cancer, Alzheimer's disease, atherosclerosis, and others [53]. Flavonoids are present in nearly every plant organ and can be detected in the vast majority of plants. They are the most prevalent type of secondary plant metabolite, although their concentrations vary from plant to plant and even organ to organ depending on the conditions in which the plant is grown. Water and nutrient availability, sunlight, soil type, plant age, and other environmental factors all have an impact on flavonoid content. Nonetheless, plants within the same taxon have a tendency to produce a shared set of flavonoids, indicating that dominant genetic predispositions play a role in plant development [54]. Many flavonoids are pharmacologically active plant components that serve as active ingredients in medicinal plants. They are also beneficial to the plant itself because they are physiologically active compounds, stress-relieving agents, attractants, or feeding deterrents. They also have a significant impact on plant resistance, which is advantageous to all plants [55]. They have a wide range of pharmacological and health benefits for humans, such as antioxidative activity, the ability to get rid of free radicals, preventing coronary heart disease, protecting the liver, reducing inflammation, and fighting cancer. As a result, the pharmaceutical and healthcare companies are paying close attention to flavonoids. In particular, flavonoids are produced by plants in response to microbial infection, and they have been shown to be an effective antimicrobial agent in vitro against a wide variety of pathogenic microbes [54].

3.1.5. Lignins: function and its uses

Lignin, a naturally occurring phenolic polymer with a high molecular weight, intricate composition, and structure, is one of the essential parts of plant cell walls. Biosynthesis of lignin is one of the most important contributors to plant growth, as well as to the development of plant tissues and organs, resistance to lodging, and other responses to biotic and abiotic stressors. The metabolic route of phenylalanine/tyrosine in plant cells produces lignin, one of the most significant secondary metabolites. It ranks as the second-most prevalent biopolymer and contributes 30% of the biosphere's organic carbon. Three distinct processes make up the highly complicated network of lignin biosynthesis: (a) lignin monomer biosynthesis, (b) transport, and (c) polymerization [56]. The chemical structure of lignin is highly branching and amorphous, and it differs substantially depending on the biomass species and the isolation method used. It is a three-dimensional heterogeneous biopolymer that was produced by the radical polymerization of three different types of monoolignols, which include p-coumaryl, coniferyl, and sinapyl alcohols [57]. Because of the presence of phenolic and aliphatic hydroxyl groups in lignin structures, plant lignin is usually used as an energy source or to create new materials, such as lignin-based carbon fibres. Lignin is a low-cost and renewable resource. The three categories that can be used to categorise lignin according to plant species are softwood lignin, hardwood lignin, and grass lignin [56]. As far as lignin valorization and long-term sustainability are concerned, the production of biopolymers from lignin offers the most hope. Valorization of lignin has the potential to be converted into biopolymers like PHA, PHB, PU etc [58]. As the supply of lignin grows faster than the demand for it as a fuel and as interest in renewable chemicals grows, more and more attention is being paid to turning lignin into new chemicals and materials. This is due to the fact that lignin is the most abundant source of renewable aromatic compounds on Earth. Considering the importance of aromatic functionalities in numerous significant chemical sectors, lignin has been investigated in the perfume and flavouring industries as well as polymers, coatings, and resins [59].

3.1.6. Polysaccharides and its uses

Among all plant by-products, polysaccharides are perhaps the most widely distributed on a global scale that includes their synthesis in all other forms of life. Since they are renewable, it is simple to make them in enormous quantities. Polysaccharides can be found in every living thing, from mammals to plants to bacteria. Plant cells and the chitinous exoskeletons of crustaceans rely heavily on polysaccharides like cellulose, mannans, and chitins for structural support. They give shape to the cells or organisms where they are found. Plant cell walls are also made up of polysaccharides, the majority of which are classified as pectins. In general, these polysaccharides can be broken down into two classes: arabinogalactans and rhamnogalacturonans. They provide the plant cell with both strength and flexibility, and they also play a vital role as intercellular molecules, which are important because they allow the cells to glide freely and provide the plant structure with elasticity [60]. Polysaccharides are long chains of sugar molecules (monosaccharide residues) linked together by glycosidic linkages. Polysaccharides can range in molecular weight from the tens of thousands to the millions, and their structures often include linear or branched side chains. Polysaccharides have been demonstrated to have a wide range of pharmacological actions, including those that inhibit tumour growth, viral replication, reduce inflammation, protect against cardiovascular disease, and even inhibit mutations. Recently, significant progress has been made in utilising biomaterials based on polysaccharides for a wide range of applications, including regenerative medicine and tissue engineering [61].

4. Application of secondary metabolites derived polymers of plants

In this section, five applications of plant derived secondary metabolites are presented.

4.1. Healing wounds and dressing up wounds

Plant secondary metabolites (PSMs), which have the ability to speed up the healing process of wounds, are an emerging area of study. PSMs have been suggested to reduce inflammation, encourage cell growth, and aid in the healing of wounds. PSMs were incorporated into dressings using several processes for polymerization, including emulsification, homogenization, supercritical impregnation, gelation, film hydration, encapsulation, electrospinning and solution casting, as well as through use of topical applications [62]. Wounds on the skin are a common type of inflammatory illness, and for millennia, people have turned to plants and essential oils extracted from those plants as a treatment option. According to the findings of one of the studies, the essential oil of Origanum vulgare L. exhibits anti-inflammatory activity and promotes wound healing in a human keratinocytes cell culture [63]. Polysaccharides like cellulose, alginate, chitosan, hyaluronan, and chitin have been employed extensively in the preparation of wound healing materials because of their pharmamaceutical biomedical action, low toxicity and intrinsic biocompatibility [64, 65]. Hyaluronan, a key extracellular substance that possesses distinctive rheological, viscoelastic and hygroscopic, qualities, has been widely developed for the goals of tissue healing due to its physicochemical characteristics and special interacts to cells and extracellular matrix. Every stage of wound healing, including inflammation, granulation tissue development, reepithelialization, and remodelling, is thought to be mediated by hyaluronan, which also performs a number of roles in the conciliation of the tissue repair process. Hyaluronan derivatives have also been produced for tissue repair and wound healing, including cross-linked, esterified, and other chemically modified compounds [64]. A different study found that all-natural composite wound dressing films made by dispersing and encapsulating essential oils (e.g., chamomile blue, tea tree, eucalyptus, lemon oils, lemongrass, peppermint, elicriso italic, lavender and cinnamon) in sodium alginate matrices demonstrated impressive antifungal and antimicrobial properties and may be used as disposable wound dressings [66].

4.2. Active packaging films

As a result of its non-toxic nature, biodegradability, and biocompatibility, pectin is increasingly being used as a biopolymer in the production of active packaging films. An active packaging film is made out of a continuous thin matrix that is both biodegradable and edible. This matrix can be made from natural polymers, lipids and proteins and proteins, among other things [67]. There are a few of these natural polymers, such as pectins, that have the capacity to transport antimicrobial compounds. They also guarantee a continuous migration and encasing of these substances on the food item, which lengthens the shelf life of the food item and protects it from microbial contamination. These substances can either reduce the progression of microorganisms or directly inactivate them through physical contact [67]. Traditional food packaging has several limitations when it comes to extending the shelf life of goods and safeguarding customers from foodborne outbreaks, but it does protect food from environmental conditions and gives consumers information about the product it contains. Active packaging alters packing conditions to improve certain food product qualities or to increase shelf life, indicating a workable, cutting-edge approach regarding food processing and distribution. Instead of adding antimicrobials to the food matrix, active packaging releases them gradually from the package material into the food. The main elements of plant essential oils, such as cinnamaldehyde, have antibacterial qualities that are effective against food pathogens and can be released via active films to replace synthetic preservatives. The antimicrobial property of cinnamonaldehyde was demonstrated against a variety of bacteria, including *E. coli*, *L. monocytogens*, *S. enterica*, *S. aureus*. It has been observed that antimicrobial edible films made from renewable sources have been produced successfully. The enhanced bacterial inhibition offered by the same amount of cinnamaldehyde in smaller nanodroplets may significantly contribute to reducing the amount of preservatives needed to meet consumer demands [68]. Essential oils (EOs) are the most investigated chemicals for pectin functionalization. There is a wide range of bioactivities present, including antimicrobial, antiviral, antifungal, and insecticidal properties. The terpenoid and terpene components of EOs are largely responsible for their effectiveness as food preservatives. Essential oils (EOs) generated from citrus extracts, such as sesquiterpenes, monoterpenes, and its oxygenated derivatives, suppress the growth of harmful bacteria. Numerous studies have found that combining pectins with essential oils increases their antibacterial potency [67]. Other approaches, in addition to the utilisation of essential oils (EOs) for the functionilization of pectin, were also reported, such as (a) Pectin functionalization using nanoparticles, (b) Free fatty acid (FFA) functionalization of pectin, and (c) Utilizing phenolics and other naturally occurring bioactives to functionalize pectin [67].

4.3. Delivery of drugs and the regulation of their release

Pharmaceutical companies use cellulose and its derivatives for a variety of purposes, from excipients to transporters and protective agents to active ingredients themselves. One of these applications is oral drug delivery, where polysaccharide excipients are used to improve the bioavailability and solubility of the active pharmaceutical ingredients, achieve a specific release profile from the finished formulation, and improve the stability of the finished pharmaceutical products [64]. Natural polysaccharides like glycogen, starch, and cellulose are examples of natural polysaccharides that have the potential to eliminate a major concern in the process of selecting appropriate inexpensive polymers without sacrificing specific bioactivity or significantly reducing the likelihood of serious side effects. To boost their potential in bio-pharmaceutics, these molecules were designed onto biologically superior molecules using a variety of ways including atom transfer radical polymerization (ATRP), co-polymer grafting and chemical modification [69]. Hydroxylpropylmethyl cellulose, methyl cellulose, hydroxypropyl cellulose and hydroxyethyl cellulose are just some of the cellulose derivatives that have found use in the pharmaceutical industry because they offer unique responses or superior physicochemical qualities compared to cellulose itself. For instance, phthalated hydroxypropylmethyl cellulose was designed for controlled intestinal targeted drug release systems because to its good pH-dependent solubility, i.e. stability in an acidic environment (such as the stomach), but soluble in solutions that range from mildly acidic to slightly alkaline [64]. Other polysaccharides have also been developed for delivery of drugs or controlled release of drugs including chitosan, gellan gum, guar gum, pectin, dextran, xanthan gum, chitin and chondroitin.

4.4. Cancer therapeutics

Cancer is a multistep process that ultimately results in an unregulated and rapid division of cells. It is also one of the primary causes of death in the world. The cases that have been documented and the forecasts for the relatively near future are inconceivable. According to data provided by the Food and Drug Administration, forty percent of the molecules that have been given the go ahead are natural compounds [71, 72] or compounds inspired by natural chemicals; of these, seventy-four percent are utilised in anticancer therapy [73]. Naturally occurring secondary metabolites in plants are typically promising candidates for future medicinal research. Therefore, altering the chemical makeup of these more promising chemicals is one smart strategy to boost their anticancer efficacy and selectivity, enhance their absorption, distribution, metabolism, and excretion properties, and lessen their toxicity and side effects [73]. Capsaicinoids, and capsaicin in particular, are bioactive chemicals that exhibit properties that are of significant interest to researchers, notably for their uses in pharmacobiology, such as their current applications against cancer. Both capsaicin and its analogues have a long history of use in medicinal practises; however, in more recent times, capsaicin has been the subject of a great deal of research for its antioxidant, anti-obesity properties, analgesic, and anti-inflammatory, as well as, most recently, its anticancer activity against a wide variety of cancer types [74]. There is a wide variety of cytotoxic agents that have been discovered in plants; however, very few of these have been able to make it into clinical use after passing through the entire lengthy, selective, expensive, and bureaucratic process, beginning with their chemical identification and ending with their effectiveness in the therapeutic treatment of cancer such as Vincristine, Paclitaxel, Homoharringtonine [73].

4.5. Biopolymers derived from lignin

The refractory nature of lignin is the primary barrier to progress in the field of lignin bio-refinery (biopolymer formation). This persistent concern demonstrates that the issue is connected to the lignin itself, in addition to the processing technology [58]. It is possible to alter the nature and makeup of feedstock prior to its synthesis in order to make it an appropriate substrate for the synthesis of biopolymers. This can be accomplished by genetic engineering or the application of biotechnology. But because it is still in its early stages, investigation on the synthesis of biopolymers from genetically modified lignocellulosic materials is still required. To improve the usage and application of lignin in the production of biopolymers, two methods for controlling its biosynthesis have emerged. Altering the composition of lignin and bioengineering lignin for simpler depolymerization are the two main methods used in lignin bioengineering [58].

4.6. Tissue engineering

Materials made of polysaccharides offer favourable biocompatibility, a manageable host reaction, and the capacity to encourage cell adhesion, proliferation, and differentiation. Over the years, other tissue analogues have been made using these polymers, often without much or any fibre encapsulation. Tissue engineering (TE) encompasses a wide range of applications; but, in practise, the word is most closely connected with applications that repair or replace parts of or entire tissues such as bone, bladder, muscle, nerve and heart. The results of a substantial amount of research have been incorporated into many therapeutic approaches, most notably in the field of skin replacement. In addition to that, efforts have been done to restore the cartilage and bone tissues [75]. Chitin and chitosan (CS) based materials have been shown to improve osteogenesis both in vitro and in vivo; however, the application of these materials is restricted due to their inherent mechanical fragility and instability, as well as their inability to keep a predetermined shape. Therefore, researchers in the field of tissue engineering have mixed CS with a range of materials, such as hydroxyapatite (HAp), hyaluronic acid (HA), alginate, calcium phosphate, poly(methyl methacrylate), and poly(L-lactic acid) (PLLA), for the purpose of developing prospective applications in orthopaedics and cell-based TE applications [75]. The different functionlized products of plant and its applications have been shown in Table 3.

Table 3. Functionalization of plant polymer and their potential uses.

Polymer	Modification approaches	Applications	Reference
Pectin	Pectin integrated with essential oils	Antibacterial properties in food packaging	[76]
Pectin	Nanoparticles made from Zn, Au, Ag, Ti, Cu, integrated with pectin based films	Enhance the antimicrobial activity and mechanical stability	[67]
Tamarind Gum	Carboxymethylated, thiolated, graft-modified	Drug delivery	[77]
Cellulose	Cellulose-based antibacterial hydrogls loaded with plant extracts	Antibacterial related biomedical fields	[78]
Hydroxypropyl methylcellulose (HPMC)	HPMC incorporated with a natural red color compound by casting method (Zingiber officinale)	As color antioxidant food packaging	[79]
Inulin (INU)	INU derivatized with spermine	Feasible INU based nucleic acid based drugs (NABD) delivery system	[80]
Starch	Pomegranate peel as an antimicorbial agent as well as a reinforcing agent	Edible film and food grade packaging material	[81]
Zein	Incorporation of pomegranate peel, which are rich in polyphenols	Packaging material for himalayan cheese, prolonged shelf life of fresh cheese, antibacterial activity	[82]
Strach, citric pectin	Feijoa (acca sellowiana burret)	Stable antioxidant compounds with antimicrobial activity	[83]
Strach encapsulated HtCuONPs	Folic acid	Targeted drug delivery in breast cancer therapy	[84]

5. Plant biopolymers: An opportunity for transition towards circular economy introduction

As time goes on, plant-based resources become increasingly significant to a sustainable or circular economy. Our existing economic paradigm is mostly linear, with scarce resources like energy and minerals being used to produce consumables that are used up and discarded. Planned obsolescence is the deliberate shortening of a product's useful life span in order to hasten its replacement and increase sales at the outset of a new model. Inevitably, this cannot last forever due to the exhaustion of precious resources and the environmental catastrophe caused by GHG. Conversely, plant-based materials utilise sustainable resources in their production. At the end of their useful lives, these materials may break down into CO2, which plants can then use again or recycle into more materials [85]. Smarter waste management and the adoption of circular economic models are two key components in the push toward more sustainable development. Plant industrial wastes still include valuable compounds like secondary metabolites, which opens up a wide range of opportunities for their valorization [86]. There are numerous opportunities for the monetization of agricultural byproducts due to the presence of secondary metabolites in all plant tissues. As a matter of fact, only a small percentage of plant organs are plucked and ultimately consumed, leading to a great deal of waste across the agricultural industry's supply chain. Finding the bioactive compounds in these underutilised matrices is a critical first step in developing a market for them [86]. There can be no successful move toward a circular economy without the widespread use of plant-based materials. Even while the bioplastics market is expanding rapidly, it still makes up less than one percent of the world's plastic production. Plant polymers such as starch and cellulose are inexpensive and plentiful, making them ideal for several industrial applications. Biodegradable polyesters such as poly(lactic acid) (PLA) and poly(hydroxyalkanoates) (PHA) are renewable resources that can be degraded down by natural processes. As manufacturing prices continue to decrease, it is expected that both polymers will capture a larger proportion of the commodity plastics market. There is a growing need for biodegradable synthetic polyesters and plant-based commodity plastics, both of which are commercially available. Waste is reduced, greenhouse gas emissions are lowered, rural investment is encouraged, the volume of dangerous chemicals/pollutants is decreased, ecosystems and biodiversity are protected, and the transition to a circular economy is aided by the increased use of plant-based products [85]. There is a global movement to investigate potential routes for shifting from linear to CE business models, as identified by the European Environment Agency as a crucial goal to attain by 2050. In a linear economy, the raw materials that are extracted, processed, used up, and then thrown away as waste are the primary component of the economic development model. Recovering and maximising the value of trash under the principles of a circular economy enables resources to be recycled and reintroduced into the supply chain, which in turn makes it possible to generate economic growth from the reduction of environmental damage [87]. A recent analysis from the U.S. Department of Agriculture indicates that bio-based products are becoming increasingly significant to the growth and creation of jobs in the United States. This expansion is due in large part to the use of bio-fuels. For instance, the United States produced approximately 14.7 billion gallons of ethanol in 2015, which is a significant increase from the 175 million gallons produced in 1980. A whopping 1.26 billion gallons of biodiesel were produced in 2015, up significantly from 2010's 343 million gallons [85].

6. Concluding remarks and outlook

Since they are non-toxic, biocompatible, and biodegradable, polymers derived from plants have garnered a lot of attention as potential functional materials for innovative and extremely value-added applications. Some examples of these applications include those in the pharmaceutical, biomedical, and cosmetic industries. When compared to other classes of materials, polysaccharides are surprisingly adaptable. It has many potential uses in medicine, from bandages to the long-lasting scaffolds necessary for TE. Synthetic polymers are already the focus of extensive research with the hope of inspiring the development of innovative biomaterials. In biomedicine and biotechnology, these novel materials have numerous potential uses (including TE, medication delivery, wound dressings, and implants). Many synthetic polymers have limitations, though. For example, they typically lack the necessary mechanical qualities and aren't biocompatible. The healthcare and pharmaceutical sectors rely heavily on engineered biomaterials due to their novel and appealing qualities, such as high drug-loading efficiency, regulated drug delivery [88], the capacity to enable tissue engineering, protein transport, and antibacterial capabilities. It is possible to achieve innovative features for specific applications by altering polymer composites (drugs, biomolecules), synthesis processes, and biomaterials research with a solid understanding. This review aims to encourage direction towards sustainable green biomaterials out of cellulose, glycogen, and starch-based nanomaterials, conjugates, and polymers for their functional properties and biocompatibility, especially in the pharmaceutical and medical industries. When creating antibacterial coatings for medical devices, it is vital to understand how essential oils can be preserved or kept from losing their bioactivity while being contained within a thin film. Even though only a few systematic studies have been done on the topic, the results of those studies have shown that encapsulating essential oils may have antibacterial action. Despite this, there should be more research done in this area. Because of the complexity of the underlying physiological mechanism, wound healing can cause several anomalies. For this reason, it is vital to select a wound dressing that will aid in and direct the healing process. As a result of their biocompatibility, biodegradability, antibacterial activity, and ability to promote wound healing, chitosan and its derivatives have emerged as some of the most promising biopolymers for developing wound dressings in recent years. To speed up the wound-healing process, however, using active substances with antibacterial, antifungal, anti-infective, and anti-inflammatory characteristics is particularly promising. Due to toxicity and a lack of clinical research, these active natural compounds cannot be used in the clinic. It is therefore necessary to conduct more clinical research to reduce toxicity and inflammation and learn more about natural metabolites' role in wound healing.

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